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Self-Assembly of Amphiphilic OEG-Linked Glutamide Lipid

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1. General Procedures: 2

2. Synthesis: 3

3. The results of Gel Experiments: 14

4. Thermodynamic parameters of CT gel which formed from 3 in various solvents: 16

5. ^{1}H NMR and ^{13}C NMR spectra 18

6. The variable-concentration ^{1}H NMR spectra 25

7. The images of SEM, AFM and TEM. 31

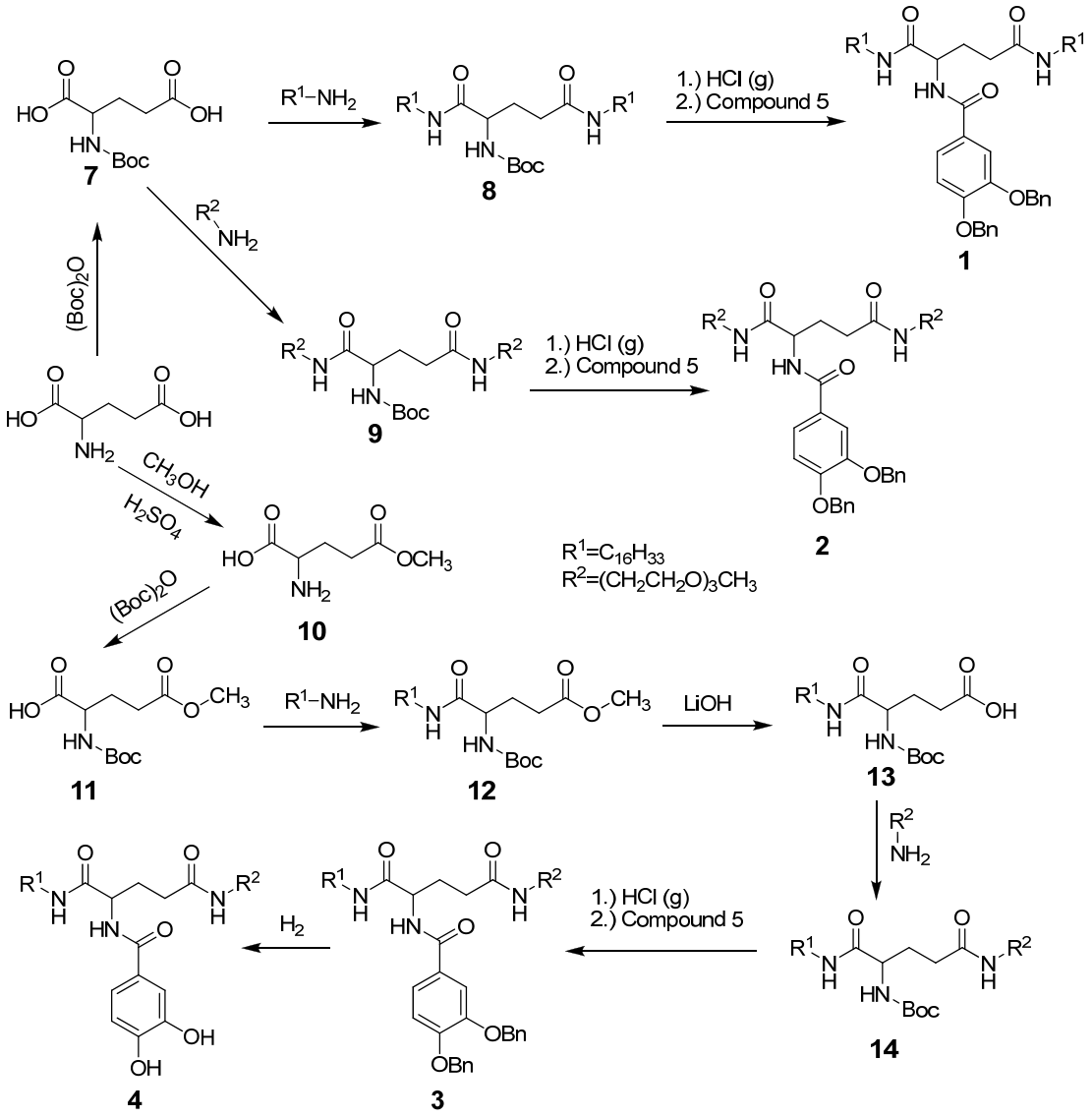
8. The FT-IR spectra of xerogels of 3. 34

9. The measurement of circular dichroism 35

1. General Procedures:

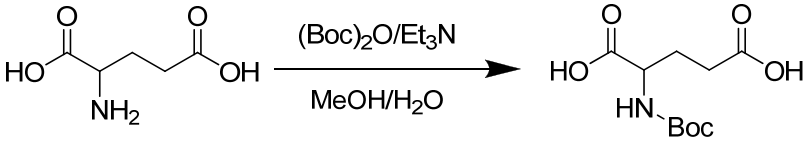
^{1}HNMR spectrum was recorded with a Bruker Avance 600 spectrometer in $CDCl_3$ or DMSO-d_6, and tetramethylsilane was used as an internal standard substance. The aging gel was cast on single-crystal silica plates, then vacuum-dried. The sample surface was coated with Pt, which were recorded on an Ultra 55 FE-SEM microscope, operating at accelerating voltages of 5-7 kV. For AFM observation, a diluted solution of gel was placed onto freshly cleaved mica and dried under vacuum for 12 h, which were recorded on a SPA300HV scanning probe microscope to get the AFM images. A small droplet of the diluted solution (5-10 μL) of gel was placed on a holey carbon film supported on a TEM copper grid and dried under vacuum for 1 day, then get the TEM images on a Libra 200FE transmission electron microscopy operating at the accelerating 200kV. The fully aging samples were cast on glass substrates and vacuum-dried for X-ray diffraction, which was performed on an X'Pert PRO X-ray diffractometer with $Cu_{K\alpha}$ radiation, operating at 40 kV, 40 mA. FT-IR spectra were recorded on a Spectrum one (Version BM) spectrophotometer with the resolution of 4 cm^{-1} at room temperature. Samples were first vacuum-dried and made into plates with KBr for FT-IR spectral measurements. UV/Vis spectra were recorded on UV5500PC spectrophotometer. All chemicals were purchased from commercial suppliers. Dichloromethane and tetrahydrofuran were distilled before used and other reagents were used without further purification.

2. Synthesis:



Scheme S1. The synthesis pathway of **1**, **2**, **3** and **4**

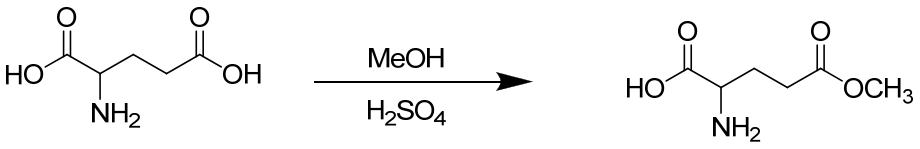
2.1 The synthesis procedures:



7

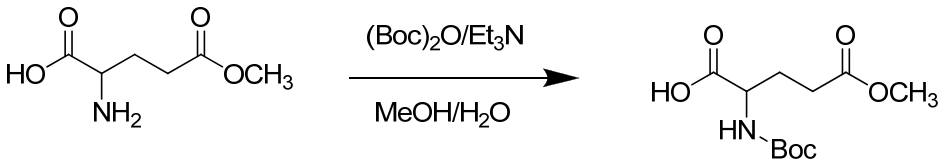
Compound 7: L-glutamic acid (12.02 g, 81.6mmol) was suspended in a mixture of MeOH:H_2O (3:2, 200 ml). Triethylamine (18 ml, 130 mmol) was slowly added and the mixture was stirred for 10 minutes, resulting in a clear solution. Di-tert-butyl

dicarbonate (21.25 g, 97.9 mmol) was added to the solution that was stirred for overnight. Then, the solvent was removed at 55 ºC under high vacuum. The obtained residue was dissolved in ethyl acetate (150 ml) and the solution was adjusted the pH to 8-9 with 1M HCl(aq)(100 ml). The aqueous layer was extracted with ethyl acetate (250 ml, 3x).The combined organic layers were washed with brine (150 ml, 3x) and, dried over anhydrous Na_2SO_4. Then, after filtration of the solution, the solvent was removed and get target product 18.52 g (75.0 mmol, Yield 92%). [1]



10

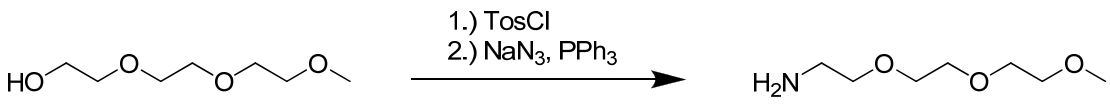
Compound 10: L-glutamic acid (5.03 g, 34.2 mmol) was suspended in MeOH (200 ml). Sulfuric acid (3 ml, 55.2 mmol) was slowly added and the mixture was stirred for 10 minutes, resulting in a clear solution. Keeping the temperature at 25 □ and stirred for 4-5 hours. Adjusting the pH to 8 with a mixture of MeOH:TEA (2:1,60 mL), Put in the refrigerator for overnight. Then, after filtration of the solution the solid recrystallization with MeOH(90%), drying to get compound 10 4.41 g.(yield 80.88%) .



11

Compound 11: Compound 10 (1.42 g, 8.9 mmol) was suspended in a mixture of MeOH:H_2O (6:1, 70 ml). Triethylamine (14 ml) was slowly added and the mixture was stirred for 10 minutes, resulting in a clear solution. Di-tert-butyl dicarbonate (2.34 g, 10.7 mmol) was added to the solution that was stirred for overnight. Then, the solvent was removed at 55 ºC under high vacuum. The obtained residue was dissolved in ethyl acetate (100 ml) and the solution was adjusted the pH to 8-9 with 1M

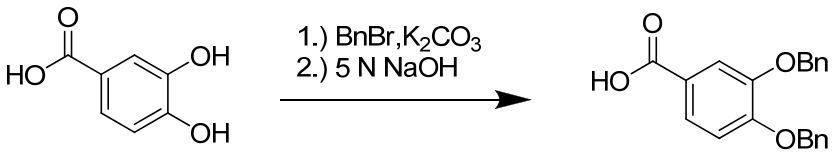
HCl(aq)(100 ml). The aqueous layer was extracted with ethyl acetate (150 ml, 3x).The combined organic layers were washed with brine (100 ml, 3x) and, dried over anhydrous Na_2SO_4. Then, after filtration of the solution, the solvent was removed and get target product 2.24 g (8.6 mmol, Yield 97%).



6

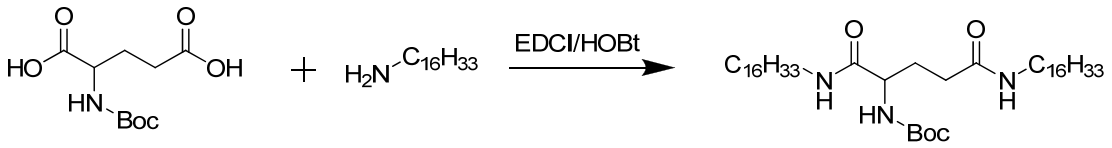
Compound 6: Triethylene glycol mono methyl ether (65.6 g, 400 mmol) and triethylamine (101 g, 1000 mmol) were dissolved in ethyl acetate (200 mL) and the solution was cooled to 0 °C. A solution of tosyl chloride (76.2 g, 400 mmol) in ethyl acetate (150 mL) was then added dropwise. The mixture was stirred for overnight at room temperature. The mixture was adjusted the pH to 8-9 with 1M HCl(aq), the aqueous layer was extracted with ethyl acetate (100 ml, 3x).The combined organic layers were washed with brine (100 ml, 3x) and, dried over anhydrous Na_2SO_4. Then, after filtration of the solution, the solvent was removed and get colorless oil 118 g. Then the 118 g colorless oil was dissolved in N,N-dimethylformamide (200 mL) and sodium azide (60.3 g, 930 mmol) was added. The flask was flushed with argon and the mixture stirred in a prewarmed oil bath at 67 °C. After 10 hours, the resulting mixture was diluted with water (80 mL) and stirred further 3 hours. The solution was poured in an Erlenmeyer flask containing ~100 mL ice. The cold mixture was extracted with diethyl ether (150 mL, 5 x) and the combined organic layers were washed with water (200 mL, 2x). The organic layer was then dried over Na_2SO_4, filtered and the solvent was removed at room temperature. The crude product was used in the next step without further purification. The crude azide was dissolved in diethyl ether (250 mL) and the solution cooled at 0 °C. Triphenyl phosphine (106.6 g, 410 mmol) was added and the mixture was stirred 2 hours at 0 °C and 2 hours at room temperature. The reaction was quenched with water (150 mL) and the mixture stirred vigorously for 4 hours. Toluene (150 mL)

was added and the mixture was stirred overnight. After decantation, the layers were separated and the aqueous layer was extracted once with toluene. After concentration of the aqueous layer, 35.4 g (217 mmol, 54.3%) of the free amine **Compound 6** was obtained which was used in the next step without further purification[2].



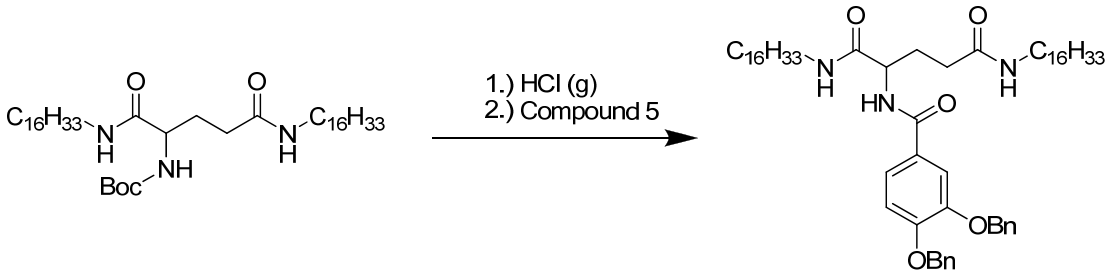
5

Compound 5: To a solution of 3,4-dihydroxybenzoic acid (1.54 g, 10 mmol) and benzyl bromide (7.9 g, 50 mmol) in DMF (30 mL) was added finely powdered K_2CO_3 (8.97 g, 65 mmol).The suspension was stirred vigorously for 20 h, poured into an ice/water mixture that was extracted with AcOEt (100 mL, 3x). The combined organic layers were extracted with sat.aq. NH_4Cl and brine, and dried (Na_2SO_4). After filtration, the solution was concentrated in vacuo and purified by flash chromatography (petroleum ether/AcOEt 8:1) to give 3,4-bisbenzyloxybenzoic acid benzyl ester as a colorless solid (3.13 g, 74%). The benzyl ester (3.01 g, 7.1 mmol) was dissolved in MeOH (80 mL), and aq. NaOH (5 M, 20 mL) was added. The mixture was refluxed for 4 h, and the solvent was removed under reduced pressure. The residue was dissolved in water (100 mL) and extracted with petroleum ether.
The aqueous phase was then acidified with aq. HCl (2 M), which led to precipitation of a solid. This mixture was extracted with AcOEt (100 mL,3x), and the combined organic layers were extracted with brine and dried (Na_2SO_4). After filtration, evaporation of the solvent gave the acid **5** (1.74 g, 74 %) as a colorless solid[3].^{1}H NMR (600 MHz, DMSO) δ 12.68 (s, 1H), 7.58 – 7.53 (m, 2H), 7.49 – 7.42 (m, 4H), 7.42 – 7.36 (m, 4H), 7.35 – 7.30 (m, 2H), 7.18 – 7.13 (m, 1H), 5.22 (s, 2H), 5.18 (s, 2H).



8

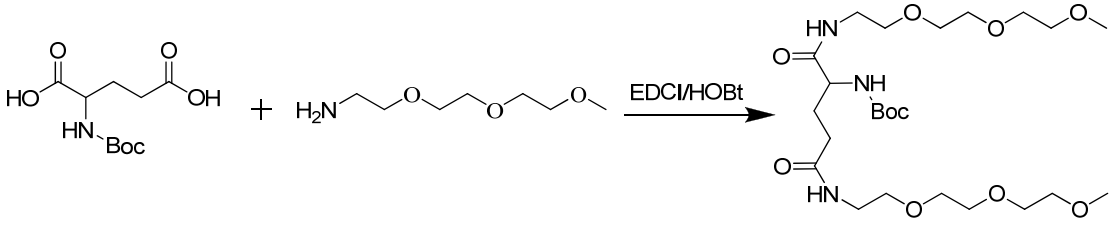
Compound 8: Compound 7 (2.27 g, 9.2 mmol) was dissolved in anhydrous THF (70 ml) and EDCI(3.51 g, 18.4 mmol)、HOBT(2.48 g, 18.4 mmol)、DMAP(1.78 g, 13.8 mmol)、DIPEA(3.37 g, 27.6 mmol) were added in order, then 1-hexa decanamine (3.94 g, 16.5 mmol) was added to the solution. The mixture was stirred for 30 min and heated at 40 °C for 24 hours. 1M HCl (aq) (50 ml) was poured into the mixture and the product was extracted with DCM (100 ml, 3x). The combined organic layers were washed with water (100 ml), 3N $NaHCO_3$ (aq) (50 ml), water (100 ml) and, brine (100 ml). The mixture was purified by column chromatography (PE:EA=2:1) and get compound 8 (4.43 g, 77.3%) as a colorless solid. ^1H NMR (600 MHz, $CDCl_3$) δ 6.68 (s, 1H), 6.08 (s, 1H), 5.74 (s, 1H), 4.09 (s, 1H), 3.23 (s, 4H), 2.41 – 2.20 (m, 2H), 1.96 (dd, *J* = 52.5, 46.0 Hz, 2H), 1.59 – 1.17 (m, 65H), 0.93 – 0.80 (m, 6H).



1

Compound 1: Compound 8 (4.05 g, 5.8 mmol) was dissolved in anhydrous DCM (30 mL). HCl (g) is introduced into the solution and stirred for 50 min, Testing of raw materials reacted complete by TLC, and the solvent was removed under reduced pressure, and get a white solid (3.51 g). The white solid (1.19 g, 2 mmol) was dissolved in anhydrous DCM (60 mL), and EDCI(0.76 g, 4 mmol)、HOBT(0.54 g, 4 mmol)、DMAP(0.25 g, 2 mmol) were added in order. Stirring to completely dissolved, then compound 5 was added to the solution and DIPEA(2.15 g, 18 mmol) were added slowly, the mixture was stirred for 30 hours. DCM(150 mL) was added into the

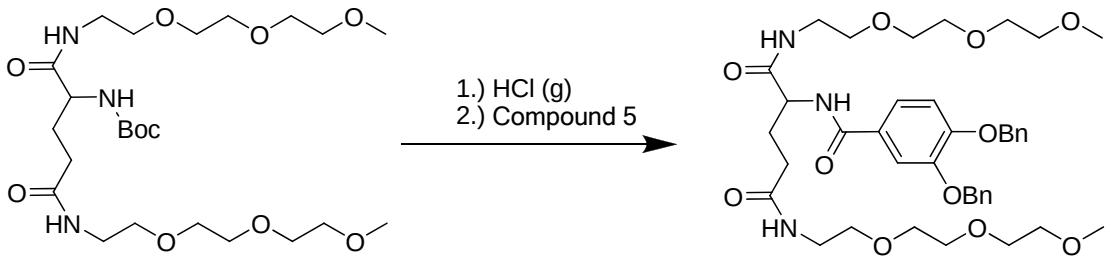
mixture for dilution, then 1M HCl (aq) (50 ml) was poured into the mixture and the product was extracted with DCM (100 ml, 3x). The combined organic layers were washed with water (100 ml), 3N $NaHCO_3$ (aq) (50 ml), water (100 ml) and, brine (100 ml), dried over anhydrous Na_2SO_4. The mixture was purified by column chromatography and get compound 1 (1.27 g, 72.6%) as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (d, *J* = 6.4 Hz, 1H), 7.61 (t, *J* = 6.8 Hz, 1H), 7.50 – 7.41 (m, 5H), 7.39 – 7.34 (m, 4H), 7.30 (dd, *J* = 15.1, 7.8 Hz, 2H), 6.95 (d, *J* = 8.4 Hz, 1H), 6.88 (t, *J* = 5.6 Hz, 1H), 5.94 (t, *J* = 5.5 Hz, 1H), 5.21 (d, *J* = 3.8 Hz, 4H), 4.50 (dd, *J* = 12.0, 6.7 Hz, 1H), 3.27 – 3.18 (m, 4H), 2.54 (ddd, *J* = 15.5, 8.4, 4.4 Hz, 1H), 2.33 (ddd, *J* = 15.4, 7.1, 4.4 Hz, 1H), 2.21 – 2.09 (m, 2H), 1.53 – 1.42 (m, 4H), 1.34 – 1.12 (m, 52H), 0.88 (dd, *J* = 8.9, 5.2 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.36, 171.25, 167.05, 151.84, 148.72, 136.89, 136.68, 128.56, 128.50, 127.94, 127.91, 127.47, 127.14, 126.63, 120.82, 113.66, 71.12, 70.92, 53.46, 39.91, 39.67, 33.10, 31.93, 29.71, 29.67, 29.62, 29.58, 29.56, 29.53, 29.51, 29.37, 29.31, 29.28, 28.49, 26.96, 26.91, 22.70, 14.13.



9

Compound 9： Compound 7 (4.20 g, 17 mmol) was dissolved in anhydrous DCM (130 ml) and EDCI(9.74 g, 51 mmol)、HOBT(6.89 g, 51 mmol)、DMAP(2.07 g, 17 mmol)、DIPEA(10.97 g, 85 mmol) were added in order, then Compound 6 (5.54 g, 34 mmol) was added to the solution. The mixture was stirred at room temperature for 36 hours. 1M HCl (aq) (50 ml) was poured into the mixture and the product was extracted with DCM (150 ml, 3x). The combined organic layers were washed with water (100 ml), 3N $NaHCO_3$ (aq) (50 ml), water (100 ml) and, brine (100 ml). The mixture was purified by column chromatography and get compound 9 (6.74 g, 73.7%) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.13 (d, *J* = 41.6 Hz, 1H), 6.74 (d, *J*

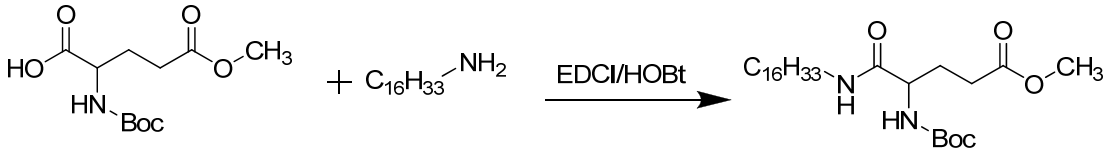
= 69.6 Hz, 1H), 5.70 (d, *J* = 7.1 Hz, 1H), 4.06 (d, *J* = 5.2 Hz, 1H), 3.76 – 3.25 (m, 30H), 2.30 – 2.12 (m, 2H), 2.04 – 1.83 (m, 2H), 1.39 (d, *J* = 39.8 Hz, 9H).



2

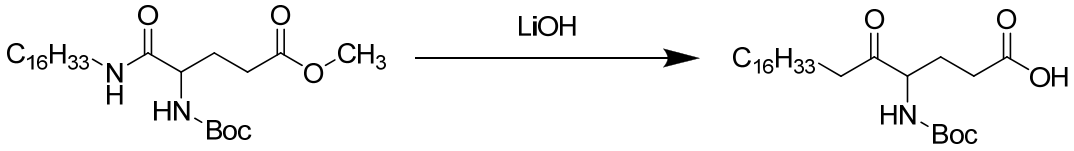
Compound 2: Compound 9 (5.20 g, 9.7 mmol) was dissolved in anhydrous DCM (35 mL). HCl (g) is introduced into the solution and stirred for 50 min, Testing of raw materials reacted complete by TLC, and the solvent was removed under reduced pressure, and get oily product (4.09 g). The oily product (2.23 g, 4.72 mmol) was dissolved in anhydrous DCM (50 mL), and EDCI(1.35 g, 7.08 mmol)、HOBT(0.96 g, 7.08 mmol)、DMAP(0.58 g, 4.72 mmol) were added in order. Stirring to completely dissolved, then compound 5 was added to the solution and DIPEA(3.04 g, 23.6 mmol) were added slowly, the mixture was stirred for 30 hours. DCM(100 mL) was added into the mixture for dilution, then 1M HCl (aq) (50 ml) was poured into the mixture and the product was extracted with DCM (100 ml, 3x). The combined organic layers were washed with water (100 ml), 3N $NaHCO_3$ (aq) (50 ml), water (100 ml) and, brine (100 ml), dried over anhydrous Na_2SO_4. The mixture was purified by column chromatography and get oily compound 10 (1.80 g, 78.9%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (d, *J* = 6.5 Hz, 1H), 7.64 – 7.59 (m, 1H), 7.48 (d, *J* = 7.4 Hz, 2H), 7.46 – 7.41 (m, 3H), 7.36 (td, *J* = 7.5, 3.9 Hz, 4H), 7.31 (t, *J* = 7.2 Hz, 2H), 7.16 (dt, *J* = 18.2, 5.6 Hz, 1H), 6.94 (dd, *J* = 8.2, 3.9 Hz, 1H), 6.84 – 6.75 (m, 1H), 5.21 (t, *J* = 5.9 Hz, 4H), 4.60 – 4.50 (m, 1H), 3.64 – 3.27 (m, 30H), 2.52 – 2.43 (m, 1H), 2.38 – 2.29 (m, 1H), 2.25 – 2.12 (m, 2H). 13C NMR (151 MHz, CDCl3) δ 173.53, 172.59, 171.60, 166.84, 151.75, 148.68, 136.94, 136.70, 128.56, 128.52, 127.95, 127.91, 127.45, 127.16, 126.71, 120.86, 113.80, 113.64, 71.85, 71.12, 70.92, 70.50, 70.41, 70.36,

70.25, 70.15, 69.61, 69.57, 58.99, 58.97, 53.84, 39.43, 39.33, 32.57, 27.97.



12

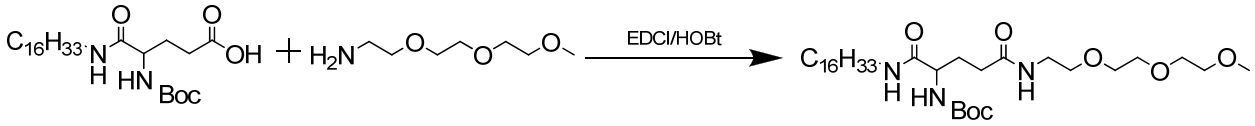
Compound 12： Compound 11 (518 mg, 2 mmol) was dissolved in anhydrous DCM (30 ml) and EDCI(764 mg, 4 mmol)、HOBT(540 mg, 4 mmol)、DMAP(129 mg, 1 mmol)、DIPEA(833 mg, 7 mmol) were added in order, then 1-hexa decanamine (478 mg, 2 mmol) was added to the solution. The mixture was stirred at room temperature for 24 hours. 1M HCl (aq) (15 ml) was poured into the mixture and the product was extracted with DCM (50 ml, 3x). The combined organic layers were washed with water (50 ml), 3N $NaHCO_3$ (aq) (15 ml), water (50 ml) and, brine (50 ml). The mixture was purified by column chromatography and get compound 12 (870 mg, 89.9%) as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.30 (s, 1H), 5.31 (d, *J* = 7.8 Hz, 1H), 4.11 (s, 1H), 3.69 (s, 3H), 3.24 (dd, *J* = 13.2, 6.7 Hz, 2H), 2.50 (dt, *J* = 16.6, 7.3 Hz, 1H), 2.42 – 2.34 (m, 1H), 2.12 (td, *J* = 13.4, 7.1 Hz, 1H), 1.91 (tt, *J* = 17.3, 8.7 Hz, 1H), 1.53 – 1.40 (m, 11H), 1.35 – 1.15 (m, 26H), 0.88 (t, *J* = 7.0 Hz, 3H).



13

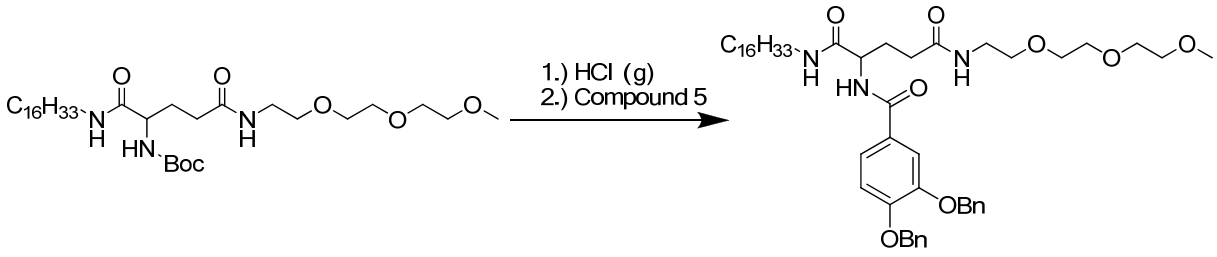
Compound 13： Under a ice water condition, Compound 12 (2.43 g, 5 mmol) was dissolved in THF (30 mL) and MeOH (30 mL) mixed solvent and Lithium Hydroxide Monohydrate aqueous solution (0.5 g/10 mL) was added, keep this condition stirring for 1 hour and then moved to room temperature stirred overnight. Testing of raw materials reacted complete by TLC, and the solvent was removed under reduced pressure, The aqueous phase was then acidified with aq. HCl (1 M), extracted with DCM (100 mL,3x), and the combined organic layers were extracted with brine and

dried (Na_2SO_4). The mixture was purified by column chromatography and get compound 13 (2.13 mg, 96.8%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.91 (s, 1H), 5.51 (d, *J* = 8.7 Hz, 1H), 4.30 (d, *J* = 6.8 Hz, 1H), 3.24 (dd, *J* = 13.1, 6.6 Hz, 2H), 2.51 (ddd, *J* = 16.4, 8.1, 4.9 Hz, 1H), 2.36 (d, *J* = 16.2 Hz, 1H), 2.05 (s, 1H), 1.91 (d, *J* = 7.3 Hz, 1H), 1.60 – 1.37 (m, 12H), 1.35 – 1.17 (m, 25H), 0.88 (t, *J* = 7.0 Hz, 3H).



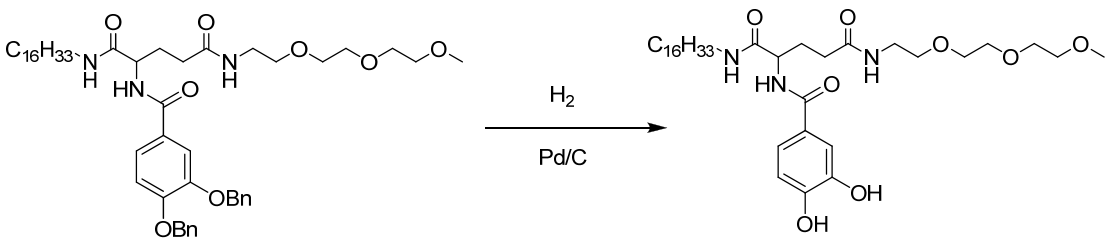
14

Compound 14： Compound 4 (103 mg, 0.63 mmol) was dissolved in anhydrous DCM (20 ml) and EDCI(240 mg, 1.26 mmol)、HOBT(170 mg, 1.26 mmol)、DMAP(75 mg, 0.63 mmol)、DIPEA(224 mg, 1.89 mmol) were added in order, then Compound 13 (300 mg, 0.63 mmol) was added to the solution. The mixture was stirred at room temperature for 24 hours. DCM (50 mL) was added, then 1M HCl (aq) (15 ml) was poured into the mixture and the product was extracted with DCM (50 ml, 3x). The combined organic layers were washed with water (50 ml), 3N $NaHCO_3$ (aq) (15 ml), water (50 ml) and, brine (50 ml). The mixture was purified by column chromatography and get compound 14 (330 mg, 84.6%) as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.69 (s, 1H), 6.52 (s, 1H), 5.70 (d, *J* = 7.2 Hz, 1H), 4.05 (dd, *J* = 14.2, 7.1 Hz, 1H), 3.69 – 3.27 (m, 15H), 3.21 – 3.11 (m, 2H), 2.36 – 2.18 (m, 2H), 2.01 – 1.87 (m, 2H), 1.47 – 1.30 (m, 11H), 1.29 – 1.12 (m, 26H), 0.81 (t, *J* = 7.0 Hz, 3H).



3

Compound 3: Compound 14 (1.20 g, 1.9 mmol) was dissolved in anhydrous DCM (25 mL). HCl (g) is introduced into the solution and stirred for 40 min, Testing of raw materials reacted complete by TLC, and the solvent was removed under reduced pressure, and get oily product (1.03 g). The oily product (0.60 g, 1.08 mmol) was dissolved in anhydrous DCM (50 mL), and EDCI(0.41 g, 2.16 mmol)、HOBT(0.29 g, 2.16 mmol)、DMAP(0.14 g, 1.08 mmol) were added in order. Stirring to completely dissolved, then compound 5 was added to the solution and DIPEA(1.25 g, 9.72 mmol) were added slowly, the mixture was stirred for 36 hours. DCM(150 mL) was added into the mixture for dilution, then 1M HCl (aq) (50 ml) was poured into the mixture and the product was extracted with DCM (150 ml, 3x). The combined organic layers were washed with water (100 ml), 3N $NaHCO_3$ (aq) (50 ml), water (100 ml) and, brine (100 ml), dried over anhydrous Na_2SO_4. The mixture was purified by column chromatography and get white solid **3** (0.72 g, 76.6%).^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13 (d, *J* = 6.5 Hz, 1H), 7.61 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.52 – 7.41 (m, 5H), 7.36 (tt, *J* = 11.5, 5.7 Hz, 4H), 7.31 (t, *J* = 7.3 Hz, 2H), 6.97 (d, *J* = 18.0 Hz, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 6.73 (s, 1H), 5.21 (d, *J* = 1.8 Hz, 4H), 4.54 (dd, *J* = 11.8, 7.2 Hz, 1H), 3.70 – 3.29 (m, 15H), 3.23 (dd, *J* = 13.6, 6.6 Hz, 2H), 2.61 – 2.49 (m, 1H), 2.41 – 2.30 (m, 1H), 2.24 – 2.08 (m, 2H), 1.48 (dd, *J* = 14.0, 7.0 Hz, 2H), 1.33 – 1.19 (m, 26H), 0.88 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.64, 172.79, 171.34, 159.55, 155.32, 151.80, 150.02, 136.92, 136.70, 128.56, 128.52, 127.97, 127.95, 127.91, 127.46, 127.15, 126.70, 120.84, 113.75, 113.63, 72.72, 71.89, 71.13, 70.92, 70.86, 70.48, 70.38, 70.08, 69.56, 68.49, 58.98, 39.63, 39.42, 32.77, 32.38, 31.94, 30.12, 29.72, 29.68, 29.63, 29.57, 29.52, 29.38, 29.30, 26.93, 22.71, 21.56, 14.14.



4

Compound 4: Compound 3 (100 mg, 0.12 mmol) was dissolved in MeOH (15 mL) and DCM (3 mL) mixed solution, Pt/C(10%)(10 mg) was added and the flask was flushed with H_2 and the mixture stirred for overnight. Then, after filtration of the solution, the solvent was removed and purified by column chromatography to get compound 4 (680 mg, 99.7%) as a colorless solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.84 (s, 1H), 7.86 (dd, *J* = 18.0, 7.2 Hz, 1H), 7.78 (s, 1H), 7.43 (d, *J* = 1.7 Hz, 2H), 7.24 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.11 (dt, *J* = 10.9, 5.2 Hz, 1H), 6.80 (t, *J* = 9.2 Hz, 1H), 4.61 (dd, *J* = 13.2, 7.3 Hz, 1H), 3.63 – 3.29 (m, 15H), 3.23 – 3.12 (m, 2H), 2.49 – 2.29 (m, 2H), 2.22 – 2.09 (m, 2H), 1.43 (dt, *J* = 19.3, 9.5 Hz, 2H), 1.32 – 1.18 (m, 26H), 0.88 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.68, 172.11, 168.00, 148.72, 144.32, 125.01, 120.22, 115.10, 114.75, 71.76, 70.35, 70.21, 69.98, 69.87, 69.49, 58.83, 58.79, 53.78, 39.85, 39.43, 32.64, 31.92, 29.72, 29.67, 29.61, 29.36, 29.35, 28.48, 26.99, 22.68, 14.11.

3. The results of Gel Experiments:

Table S1 Gelation Behaviours of different compound in the Presence of Various Organic Solvents

solvent \ Compound	1	2	3	4
PE	I	I	I	I
$CHCl_3$	P	S	P	S
CH_2Cl_2	I	S	S	S
Toluene	S	S	G(10 mg/mL)	S
EtOAc	I	S	G(5 mg/mL)	S
THF	P	S	S	S
MeCN	I	S	G(1 mg/mL)	G(5 mg/mL)
EtOH	I	S	G(15 mg/mL)	S
MeOH	I	S	G(15 mg/mL)	S
Acetone	I	S	G(15 mg/mL)	S
DMSO	I	S	S	S
DMF	I	S	S	S
MMA	I	S	G(5 mg/mL)	S
PhOMe	I	S	G(15 mg/mL)	S
Cyclohexanone	I	S	G(-10□)	S

I:insoluble P:precipitate S:solution G:gel

Table S2 The gelation results of **compound 3** in the acetonitrile and water mixed solution.

solvent \ compound	3
acetonitrile/water （100，V/V）	G
acetonitrile/water （95:5，V/V）	G
acetonitrile/water （90:10，V%）	G
acetonitrile/water （85:15，V%）	G
acetonitrile/water （80:20，V%）	G
acetonitrile/water （70:30，V%）	G
acetonitrile/water （60:40，V%）	I

I:insoluble G:gel

Table S3 The gelation results of different concentration of **compound 3** dissolved in different solvents

solvent \ concentration（mg/mL）	1.3	2.5	5.5	7.5	10.5
EA	S/G	S/G	G	S/P	S/P
Toluene	S/G	G	G	G	G
MeCN	G	G	G	I/G	I/G
MeCN /H_2O（9:1，V/V）	S/G(10℃)	S/G(5℃)	G	G	G
MeCN /H_2O（8:2，V/V）	S/G(5℃)	G	G	G	G
MMA	S/G	S/G	G	G	G

I:insoluble P:precipitate S:solution G:gel

4. Thermodynamic parameters of CT gel which formed from 3 in various solvents:

Table S4 The different solution temperature of Gels

Solvent / Temperature/K / Concentration/mM	EA	Toluene	CH_3CN	MMA	MeCN /H_2O (9:1,V/V)	MeCN /H_2O (8:2,V/V)
1.3	298	268	303	283	278	303
3	313	301	323	298	303	313
4.8	318	308	329	308	308	317
6.6	323	318	335	318	313	322
7.8	324	322	341	322	324	334
9	325	328	345	333	338	345
10.8	326	331	349	335	344	348
12.6	327	333	352	338	350	356

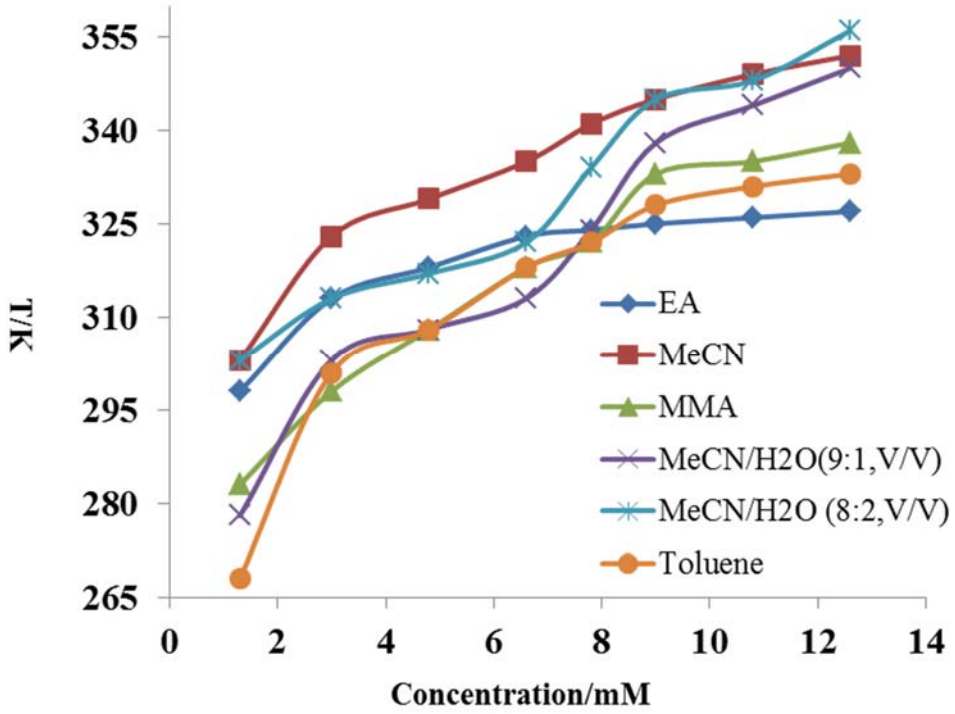


Figure S1: The different solution temperature of Gels

The thermoreversible melting of a two component gel can be expressed as:

Gel ⇌ liquid

For one component gel, the equilibrium constant can be expressed as:

C = [Gelator] / [Gel]

Assuming unit activity of the gel and taking the concentration of the solution to be equal to the dissolved concentration of the gelator, the equilibrium constant can be expressed as: C = [Gelator].[4-9]

The Gibbs free energy change during gel melting can be expressed as: $\Delta G^{o}=\Delta H^{o}-T\Delta S^{o}=-\Delta RT\ln C$ Hence, $\ln C=-\Delta H^{o}/R(1/T)+\Delta S^{o}/R$

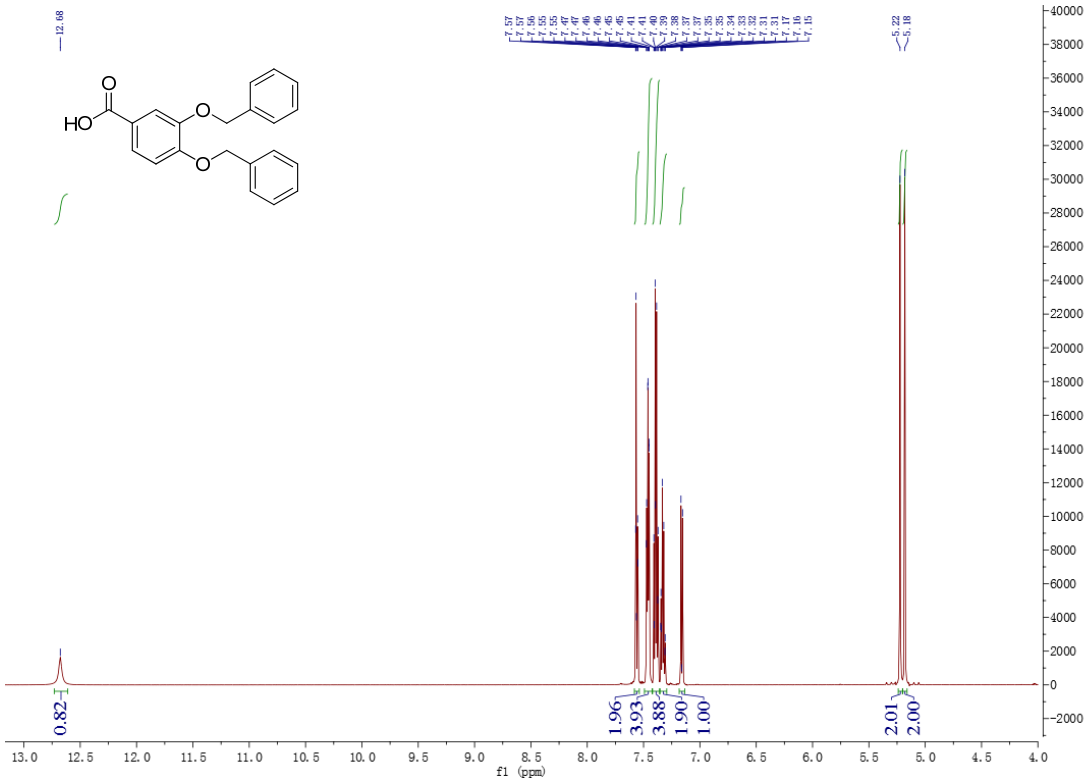
The gel melting temperature (T_{gel}) increases with the concentration of the "solutes". A plot of lnK vs 1/T allowed us to calculate the thermodynamic parameters.

Table S5 Thermodynamic parameters of gel in various solvents

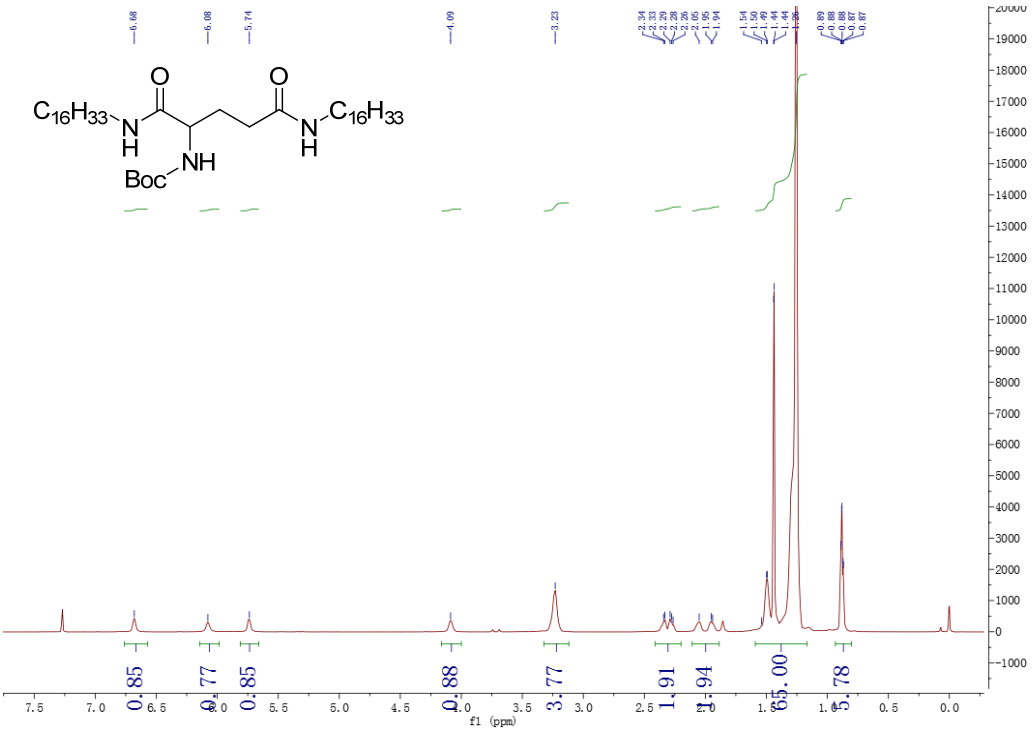
solvent	ΔH^{o}（kJ/mol）	ΔS^{o}（J/mol）	ΔG^{o}（kJ/mol）
EA	56.81	135.54	16.42
Toluene	25.32	38.36	13.89
MeCN	40.70	79.08	17.14
MeCN /H_2O（9:1,V/V）	24.91	34.37	14.67
MeCN /H_2O（8:2,V/V）	36.64	66.72	16.75
MMA	32.74	61.12	14.52

5. ^{1}H NMR and ^{13}C NMR spectra

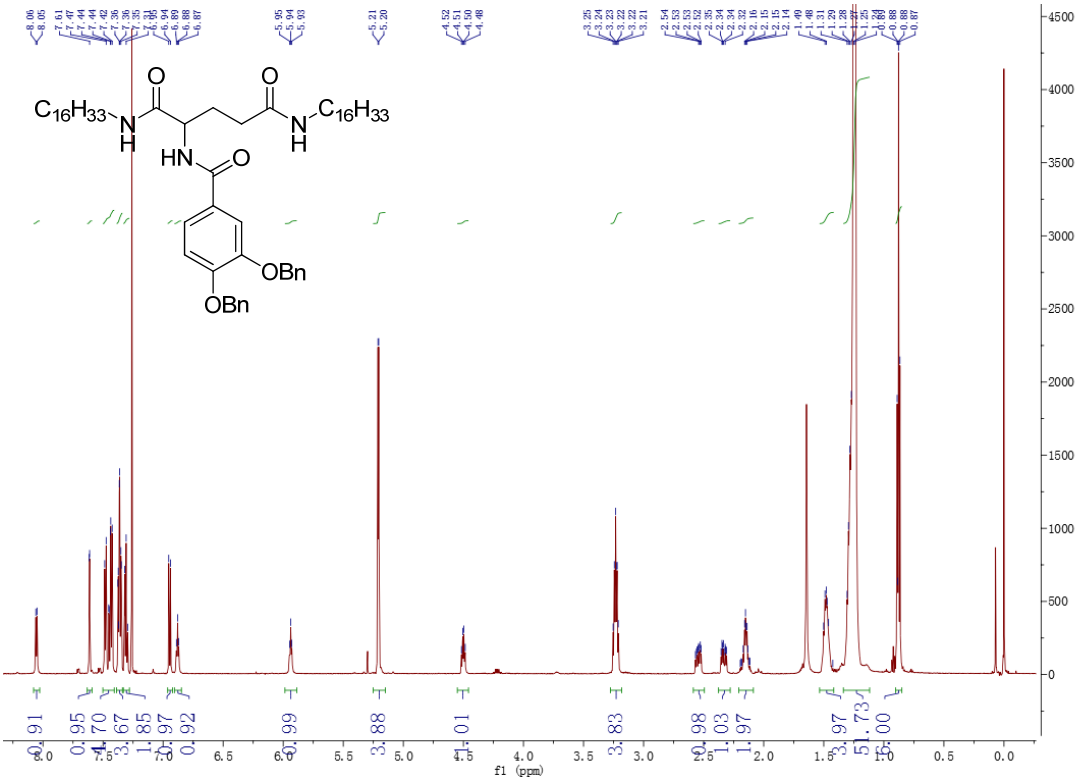
^{1}H NMR (600 MHz, DMSO) of compound **5**:



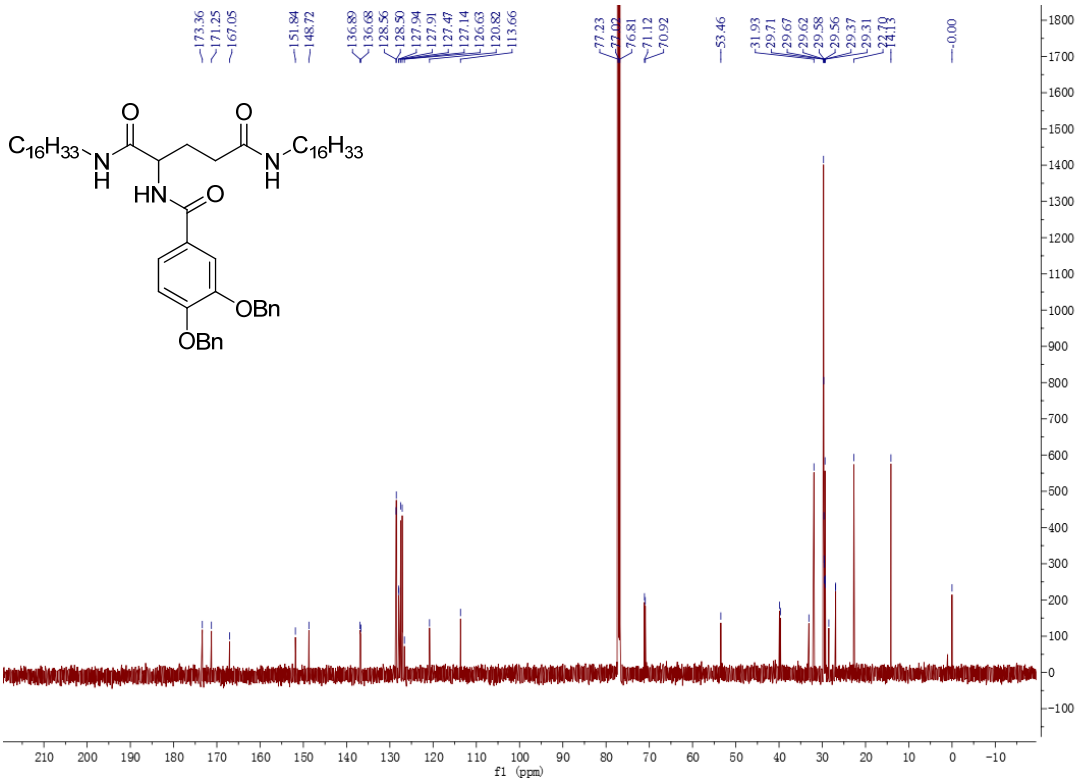
^{1}H NMR (600 MHz, $CDCl_3$) of compound 8:



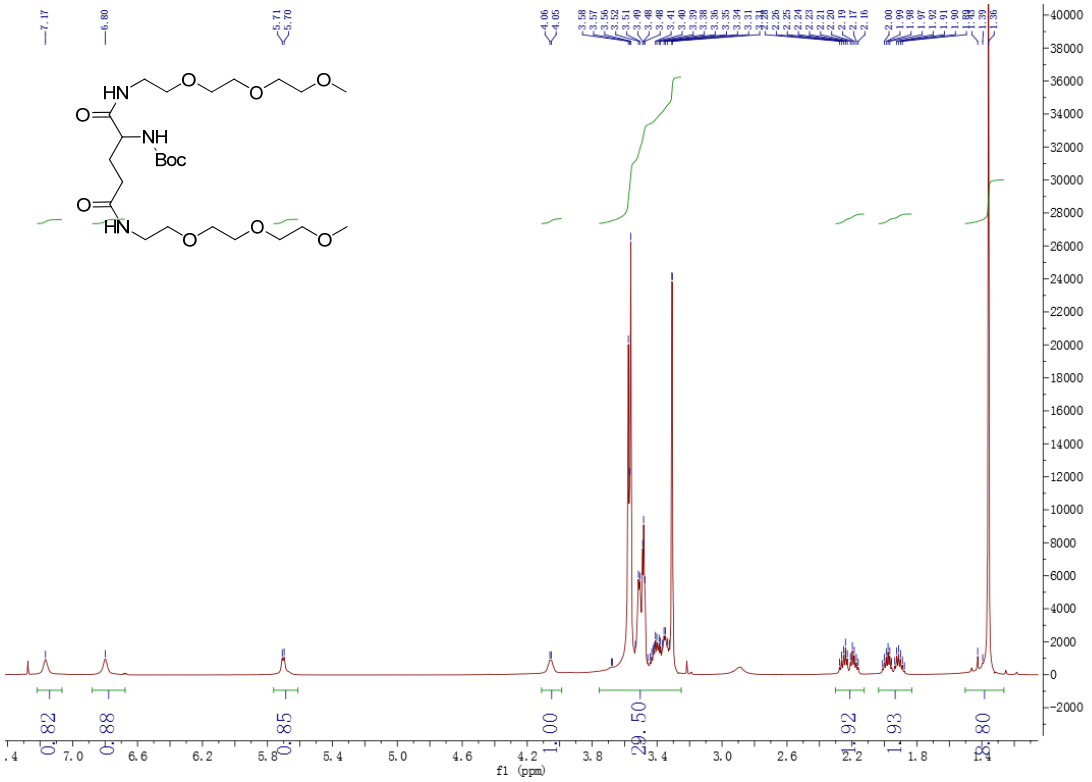
^{1}H NMR (600 MHz, $CDCl_3$) of compound 1:



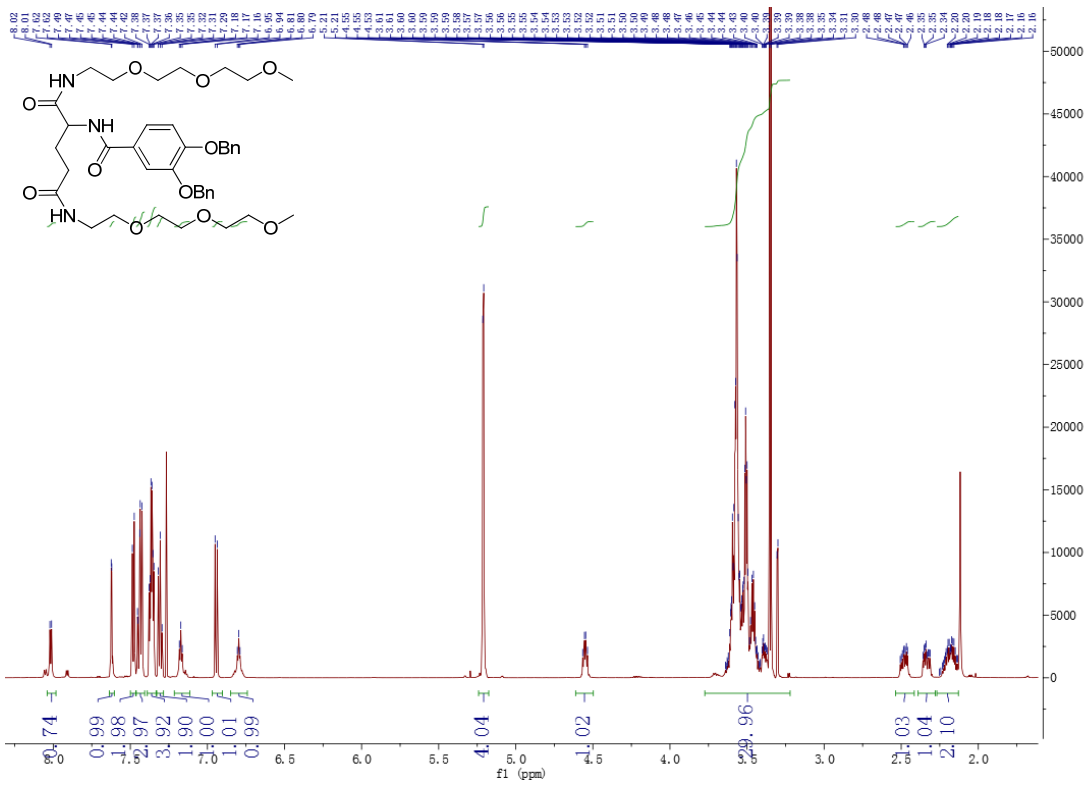
^{13}C NMR (151 MHz, $CDCl_3$) of compound 1:



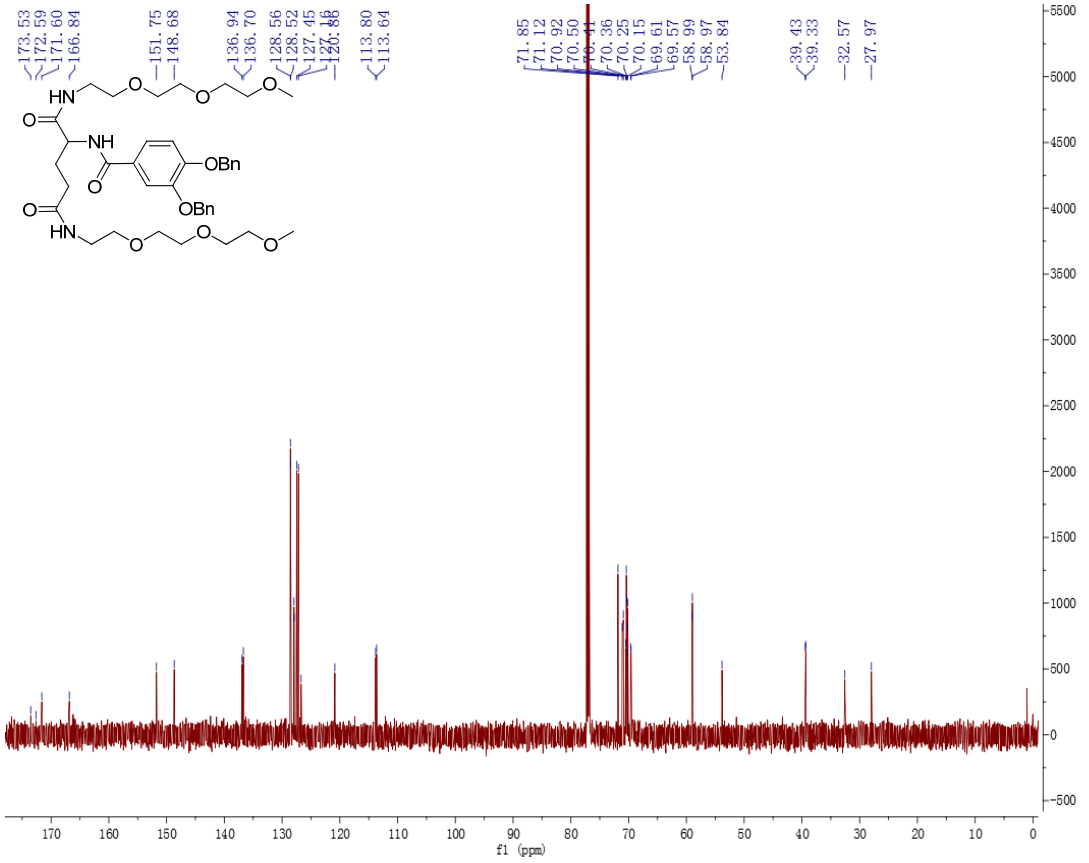
^{1}H NMR (600 MHz, $CDCl_3$) of compound 9:



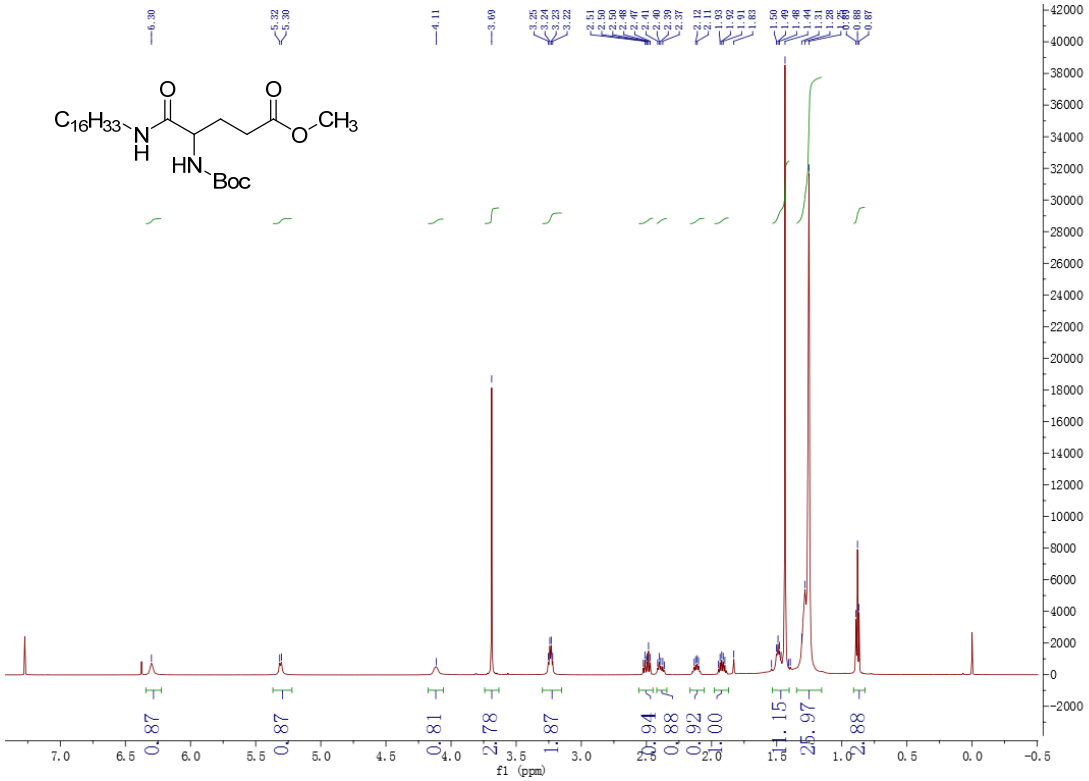
^{1}H NMR (600 MHz, $CDCl_3$) of compound 2:



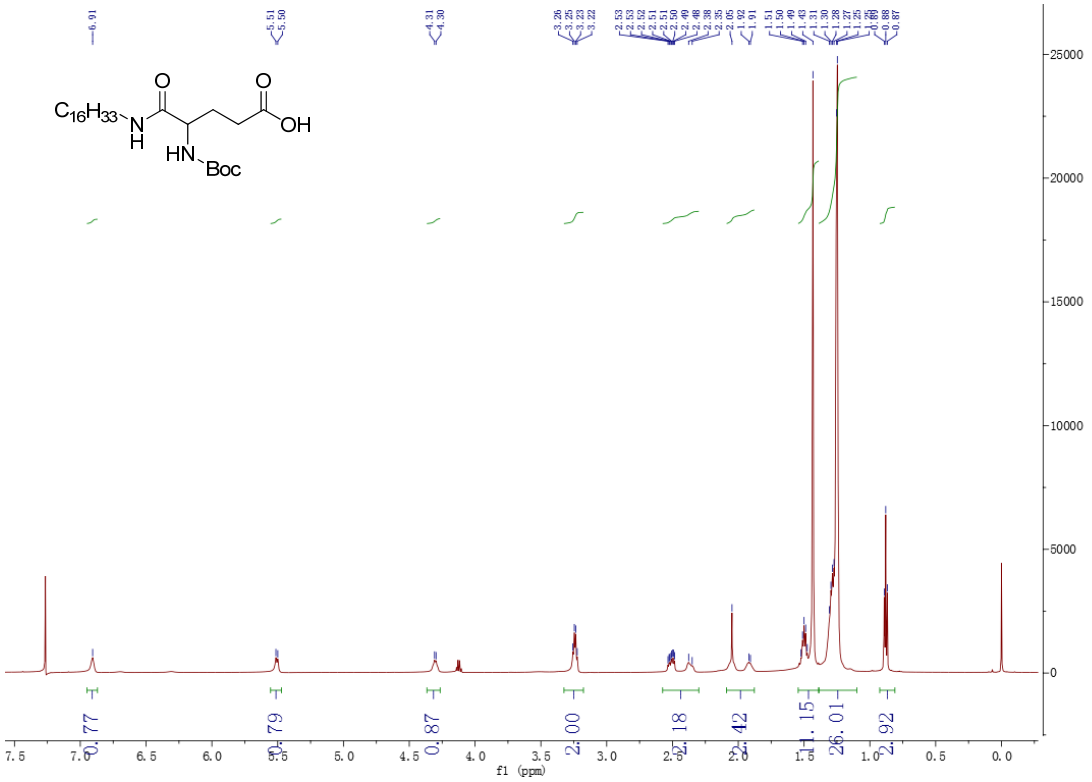
^{13}C NMR (151 MHz, $CDCl_3$) of compound 2:



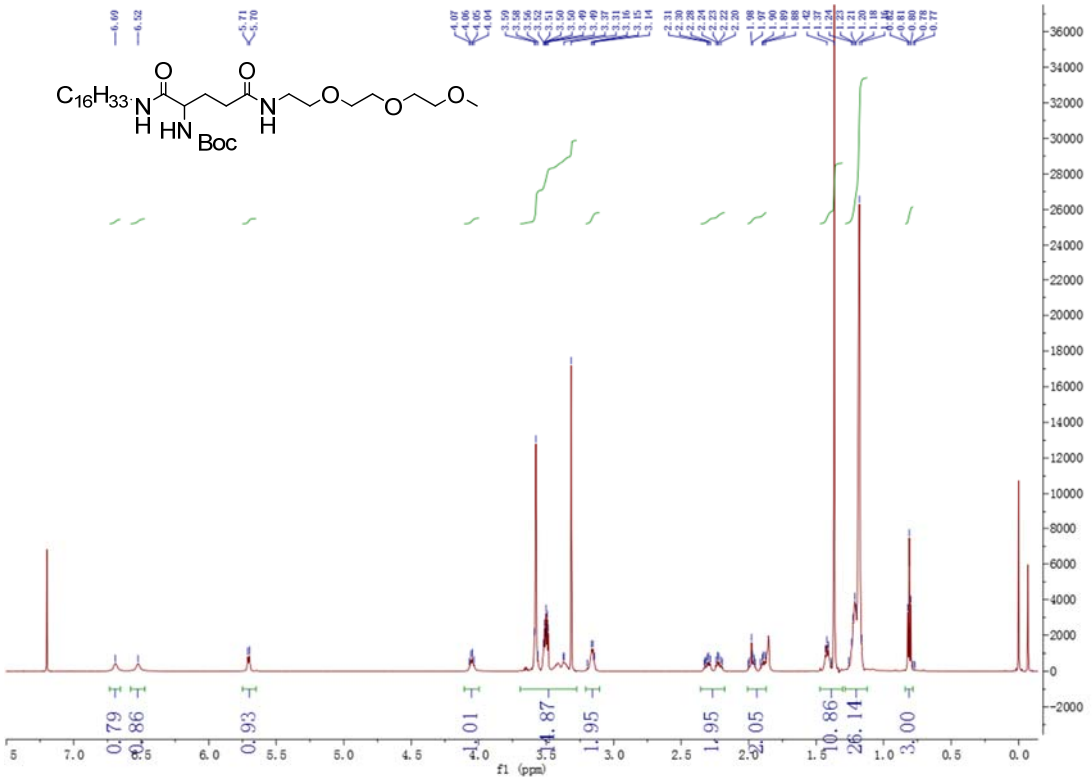
^{1}H NMR (600 MHz, $CDCl_3$) of compound 12:



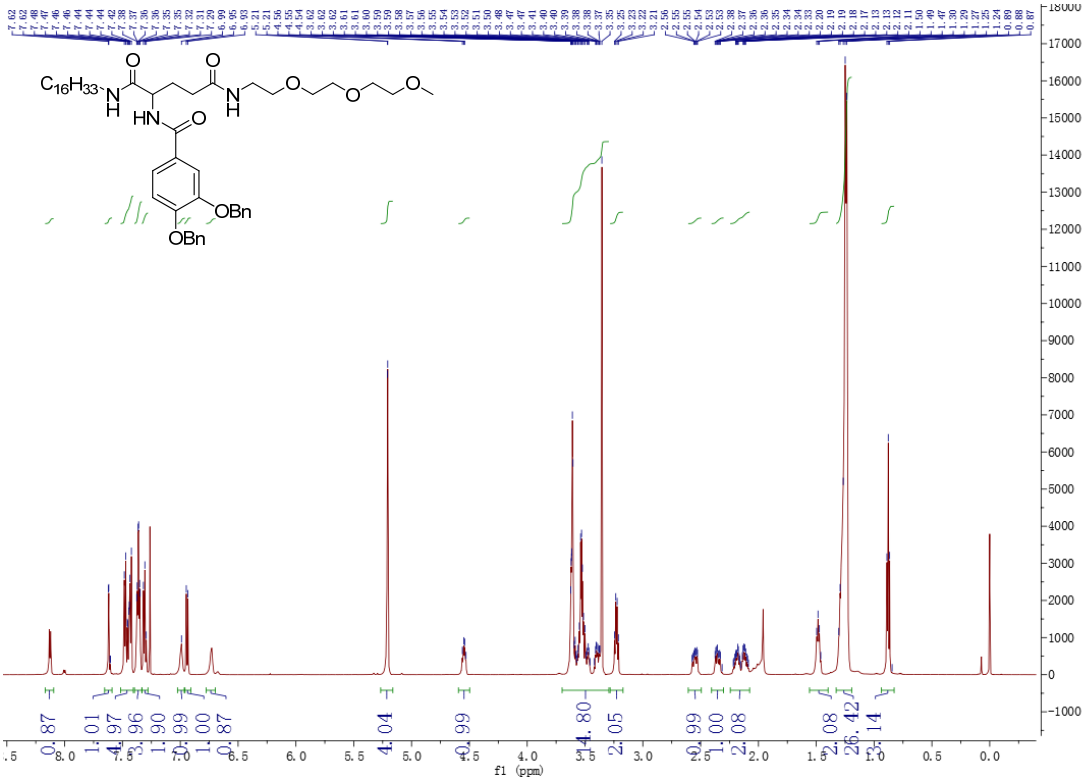
^{1}H NMR (600 MHz, $CDCl_3$) of compound 13:



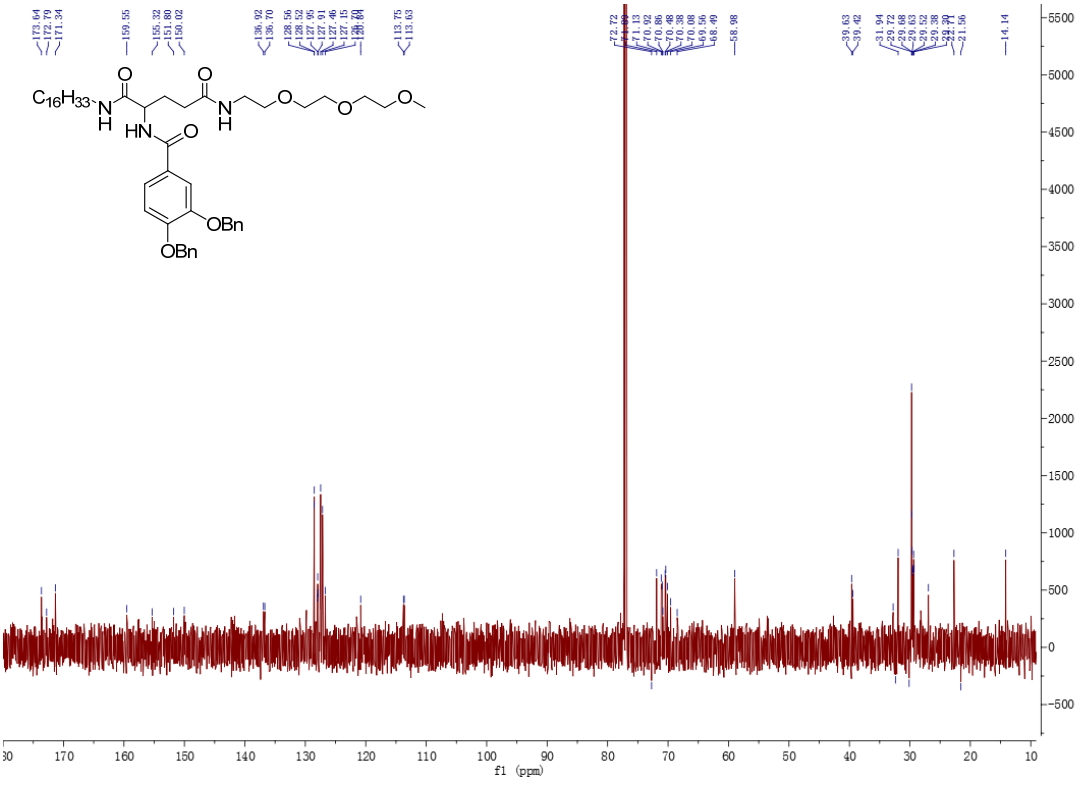
^{1}H NMR (600 MHz, $CDCl_3$) of compound 14:



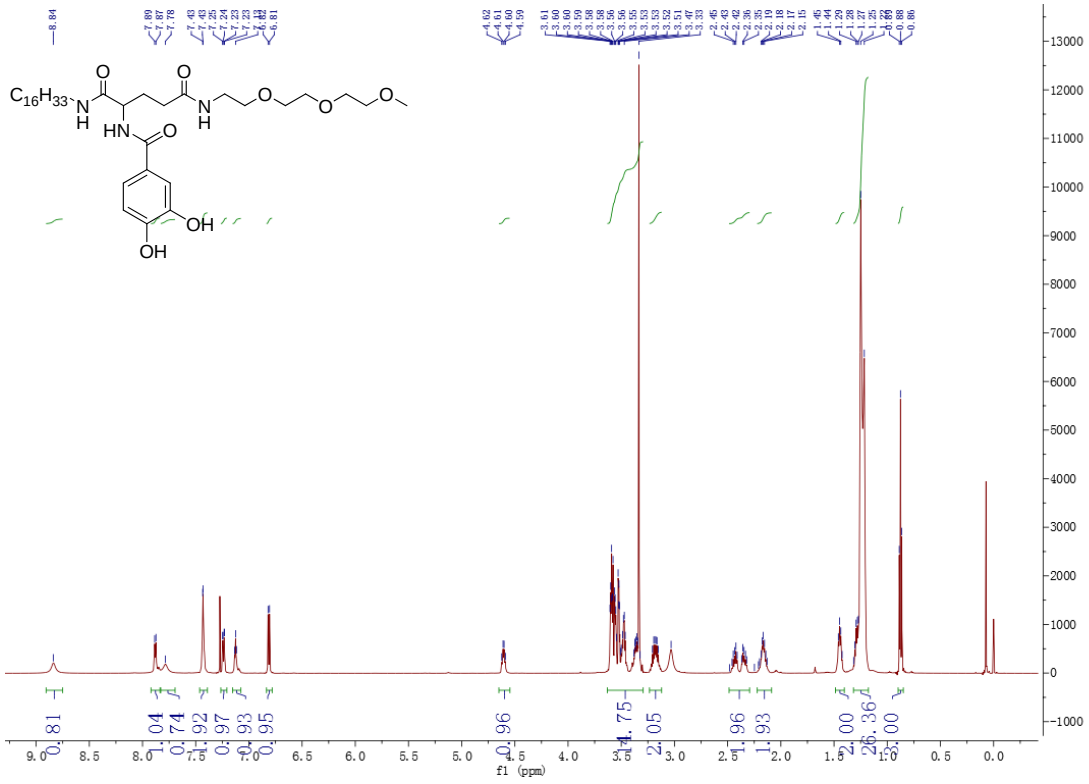
^{1}H NMR (600 MHz, $CDCl_3$) of compound 3:



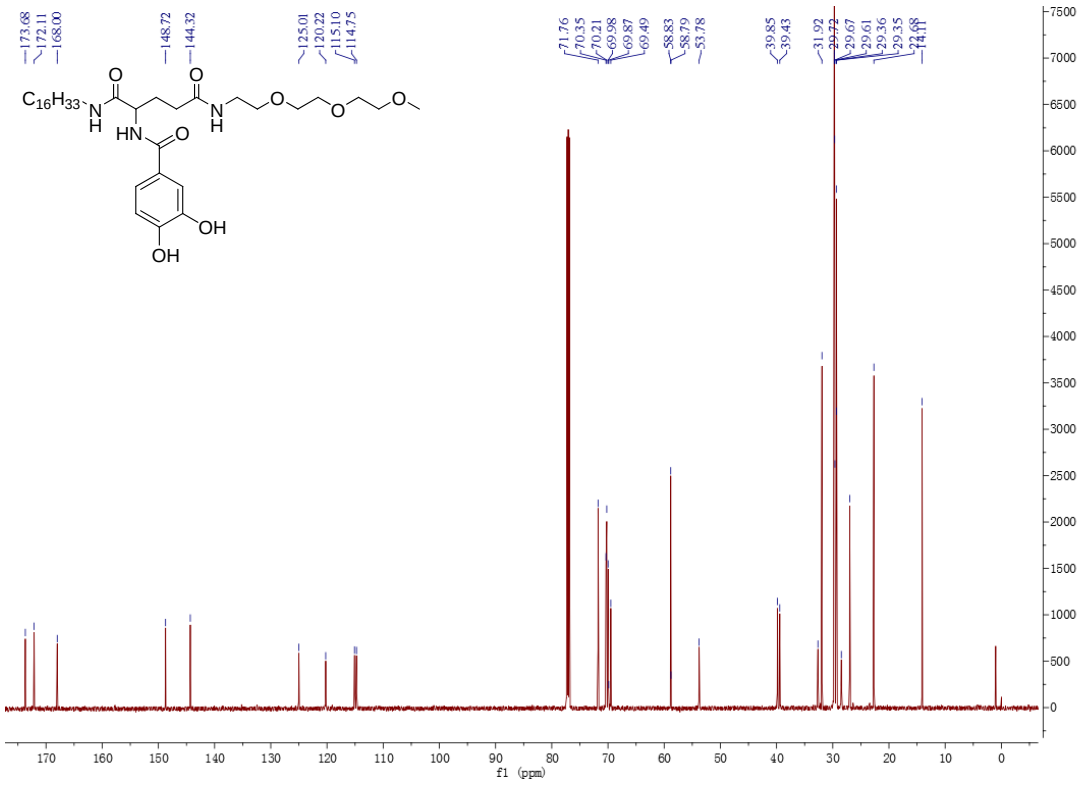
^{13}C NMR (151 MHz, $CDCl_3$) of compound 3:



^{1}H NMR (600 MHz, $CDCl_3$) of compound 4:



^{13}C NMR (151 MHz, $CDCl_3$) of compound 4:



6. The variable-concentration ^{1}H NMR spectra

6.1 The variable-concentration ^{1}H NMR spectra of **1** :

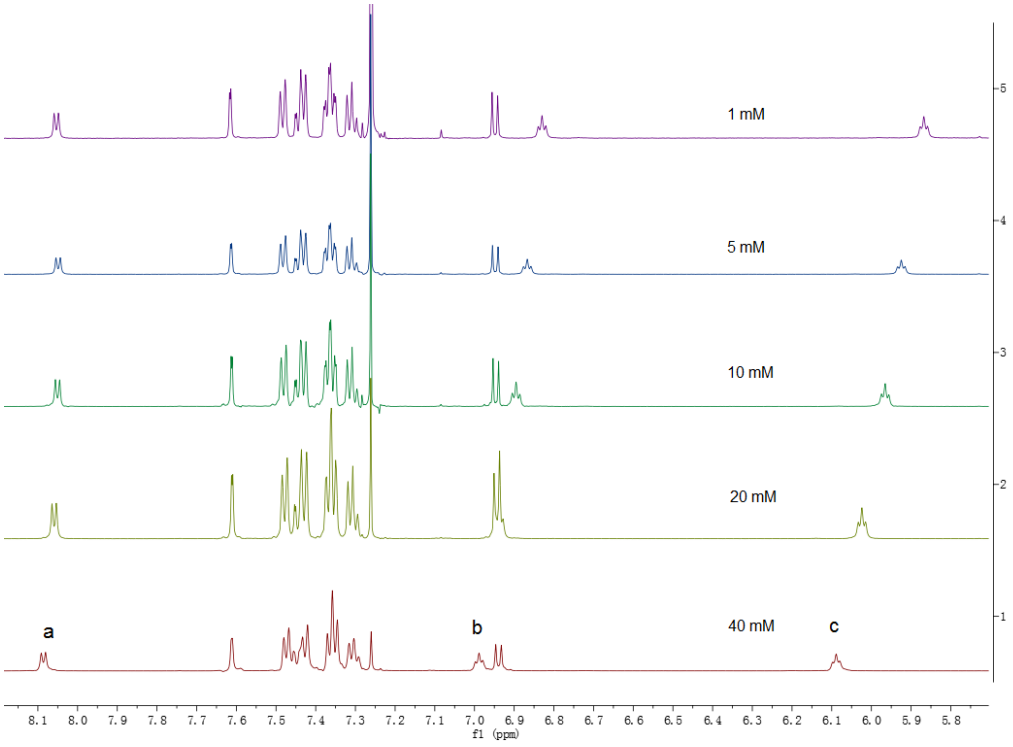


Table S6 The hydrogen chemical shift of **compound 1** in different concentration

Entry	40 mM	20 mM	10 mM	5 mM	1 mM
a	**8.086**	**8.0585**	**8.0505**	**8.049**	**8.0535**
1	7.610	7.609	7.610	7.612	7.614
2	7.480	7.484	7.487	7.488	7.489
3	7.468	7.472	7.475	7.476	7.477
4	7.453	7.454	7.458	7.452	7.452
5	7.433	7.436	7.436	7.438	7.438
6	7.421	7.423	7.424	7.425	7.425
7	7.370	7.374	7.377	7.375	7.375
8	7.358	7.361	7.362	7.362	7.363

9	7.346	7.350	7.349	7.350	7.350
10	7.316	7.319	7.320	7.321	7.321
11	7.304	7.307	7.308	7.309	7.309
12	7.292	7.294	7.296	7.297	7.297
b	**6.989**	**6.928**	**6.895**	**6.867**	**6.830**
13	6.940	6.944	6.946	6.948	6.949
c	**6.089**	**6.024**	**5.965**	**5.925**	**5.868**

6.2 The variable-concentration ^{1}H NMR spectra of **2** :

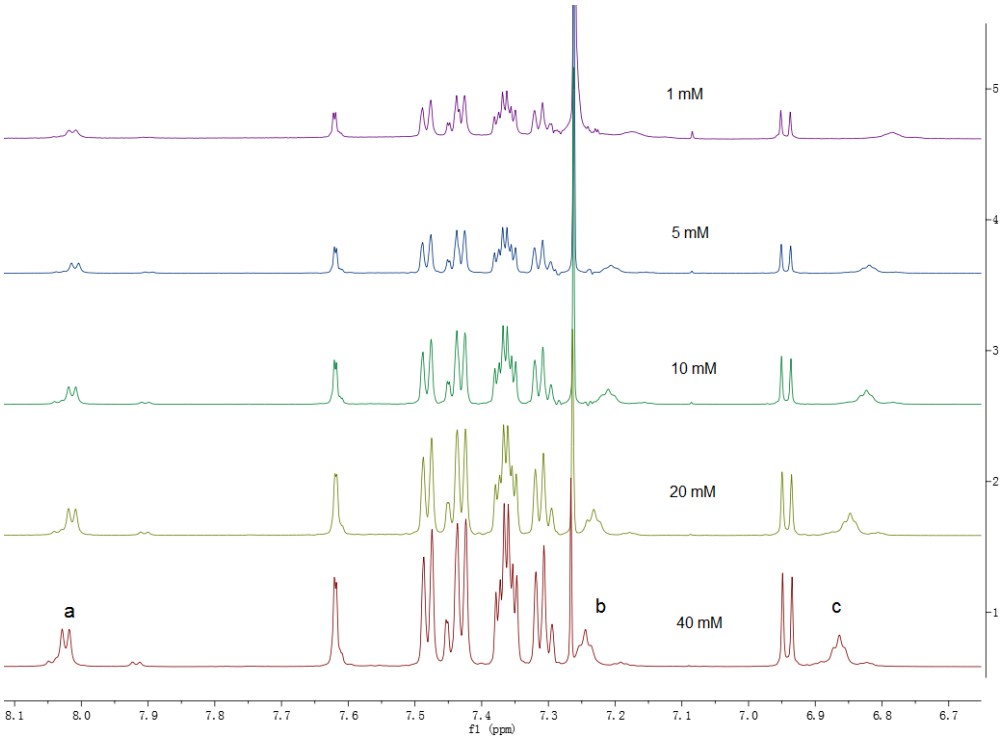


Table S7 The hydrogen chemical shift of **compound 2** in different concentration

δ C / Entry	40 mM	20 mM	10 mM	5 mM	1 mM
a	**8.0235**	**8.014**	**8.0135**	**8.0095**	**8.013**
1	7.6195	7.6185	7.6195	7.6195	7.6205
2	7.487	7.487	7.488	7.489	7.489
3	7.474	7.475	7.476	7.476	7.476
4	7.453	7.499	7.451	7.451	7.451
5	7.436	7.437	7.437	7.437	7.437
6	7.424	7.424	7.425	7.425	7.426
7	7.366	7.367	7.368	7.368	7.369
8	7.360	7.361	7.362	7.362	7.362
9	7.319	7.319	7.320	7.321	7.321
10	7.307	7.307	7.308	7.309	7.309

11	7.295	7.295	7.296	7.297	7.295
b	**7.244**	**7.232**	**7.210**	**7.206**	**7.176**
12	6.942	6.943	6.944	6.944	6.944
c	**6.864**	**6.848**	**6.823**	**6.819**	**6.785**

6.3 The variable-concentration ^{1}H NMR spectra of **3** :

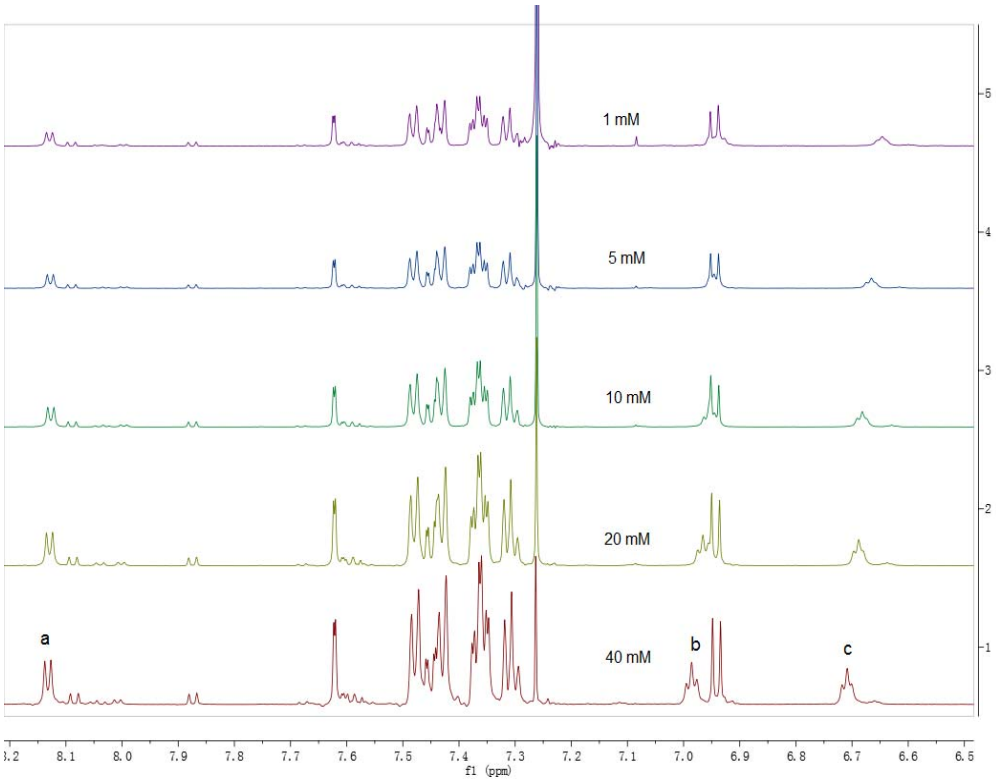


Table S8 The hydrogen chemical shift of **compound 3** in different concentration

δ / C / Entry	40 mM	20 mM	10 mM	5 mM	1 mM
a	**8.1325**	**8.1295**	**8.127**	**8.125**	**8.129**
1	7.6215	7.6215	7.622	7.622	7.622
2	7.484	7.486	7.487	7.487	7.488
3	7.472	7.473	7.475	7.475	7.475
4	7.459	7.458	7.457	7.457	7.457
5	7.435	7.436	7.438	7.440	7.439
6	7.423	7.424	7.425	7.425	7.425
7	7.362	7.363	7.364	7.365	7.365
8	7.318	7.320	7.321	7.321	7.322
9	7.306	7.308	7.308	7.309	7.309
10	7.293	7.296	7.296	7.297	7.296

b	**6.996**	**6.966**	**6.951**	**6.938**	**6.927**
12	6.941	6.943	6.944	4.940	6.940
c	**6.709**	**6.688**	**6.682**	**6.666**	**6.646**

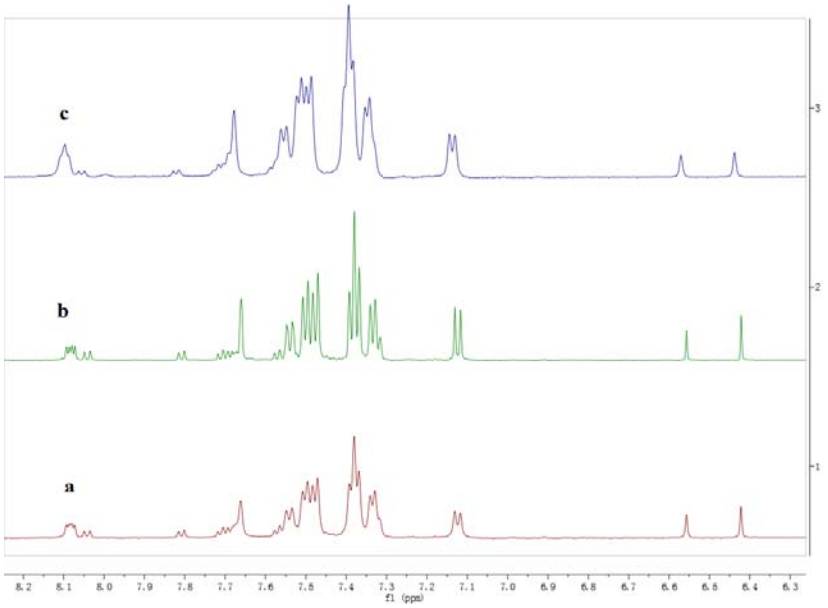


Figure S2: The ^{1}H NMR spectra of **3** in MeOD: a) gel (after 3h); b) gel/solution; c) solution.

7. The images of SEM, AFM and TEM.

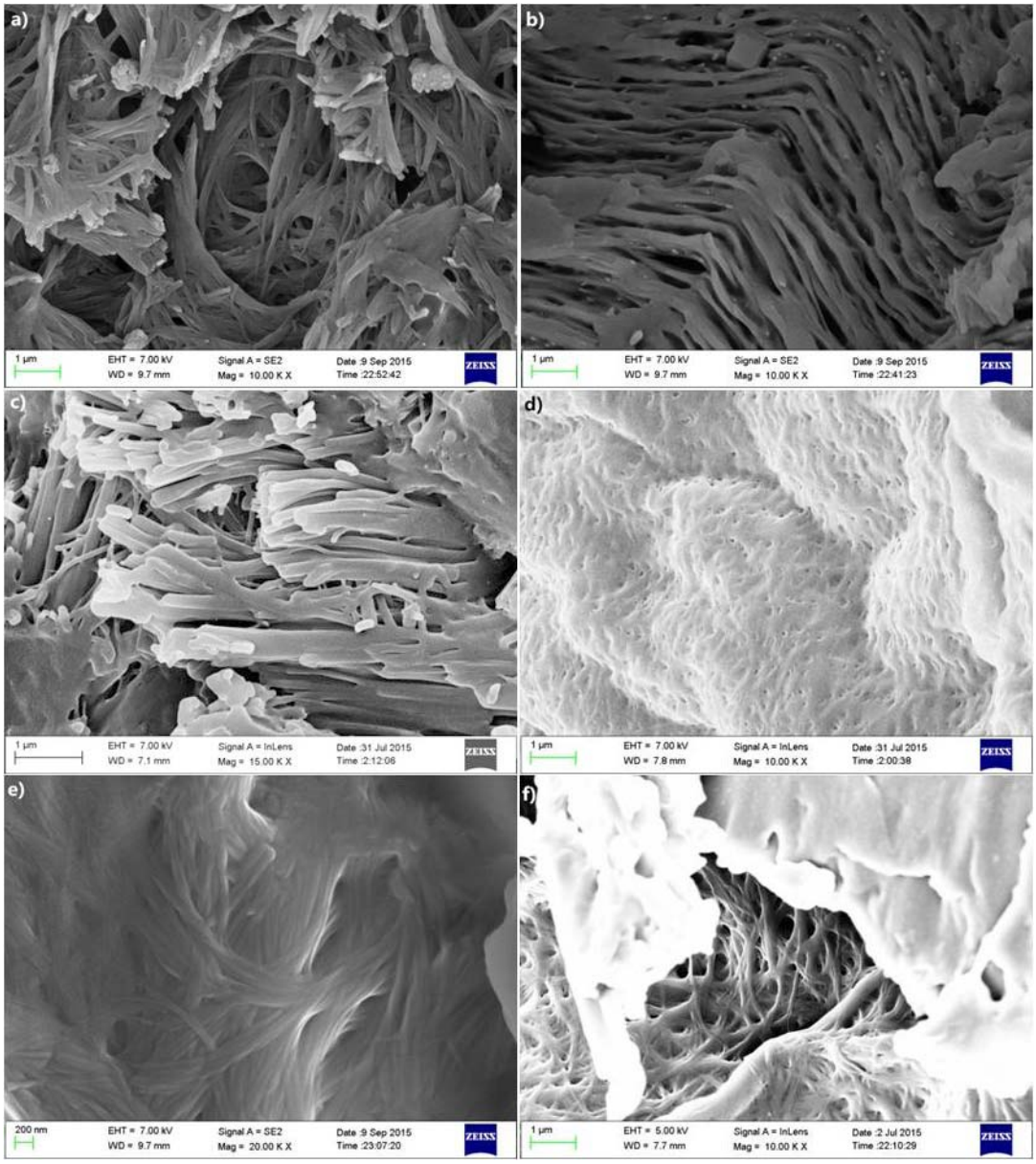


Figure S3: The SEM images of xerogels which formed in: a) toluene, b) ethyl acetate, c) acetone, d) ethanol, e) MMA, f) acetonitrile.

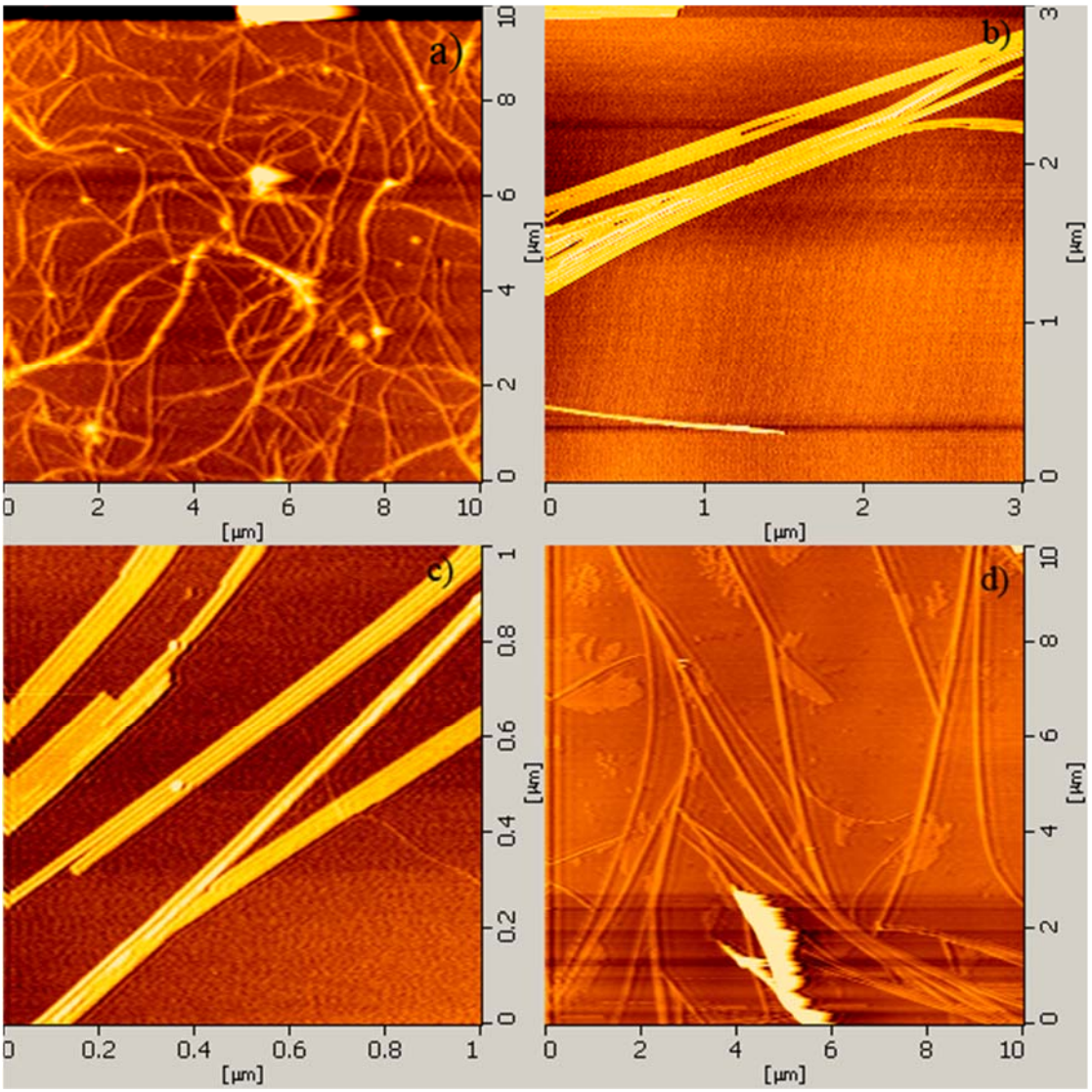


Figure S4: The AFM images of xerogels which formed in: a) toluene, b) acetonitrile, c) acetonitrile /water (8:2, v/v), d) acetonitrile /water (7:3, v/v)

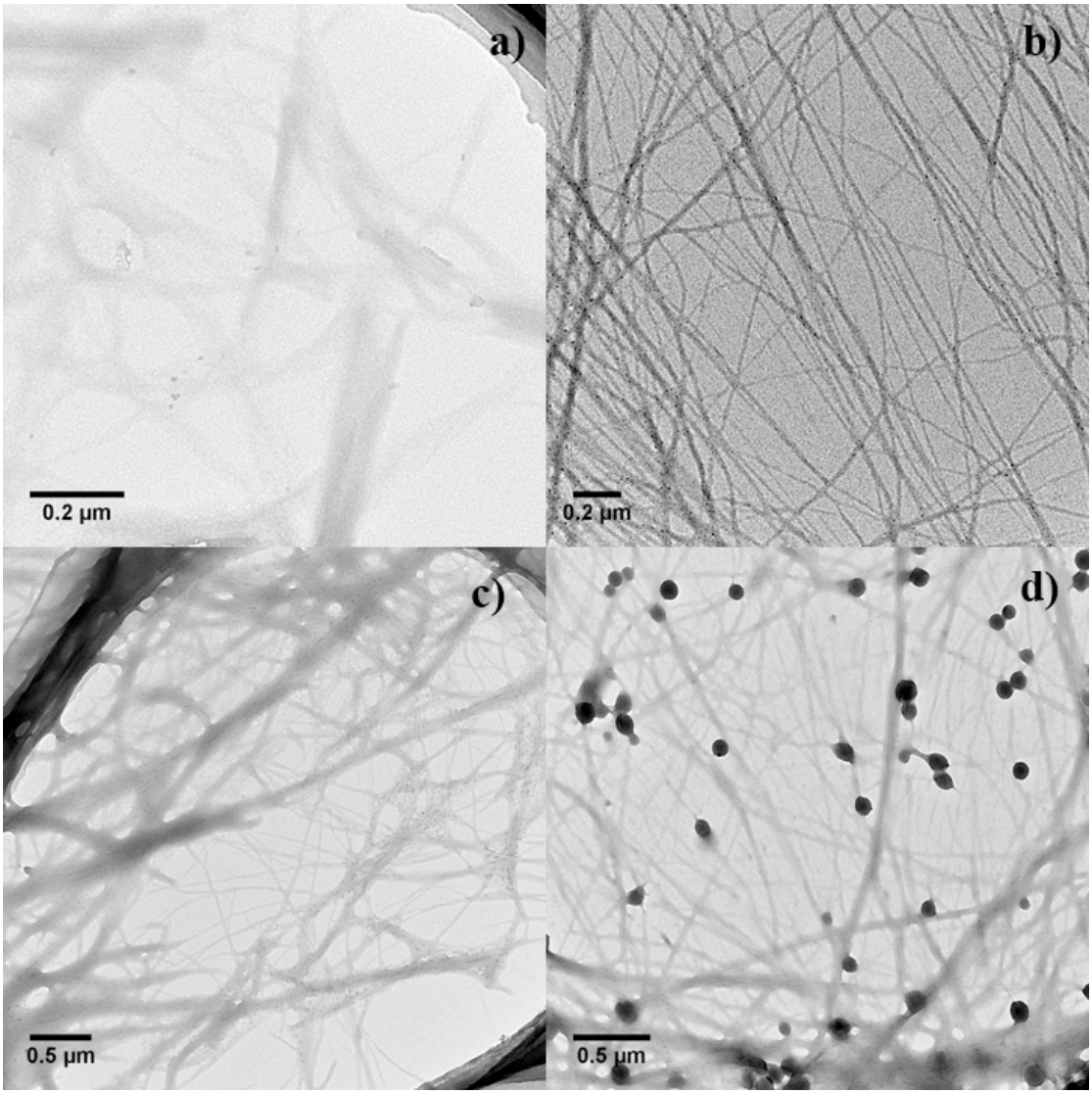


Figure S5: The TEM images of xerogels which formed in: a) toluene, b) acetonitrile, c) acetonitrile /water (8:2, v/v), d) acetonitrile /water (7:3, v/v)

8. The FT-IR spectra of xerogels of 3.

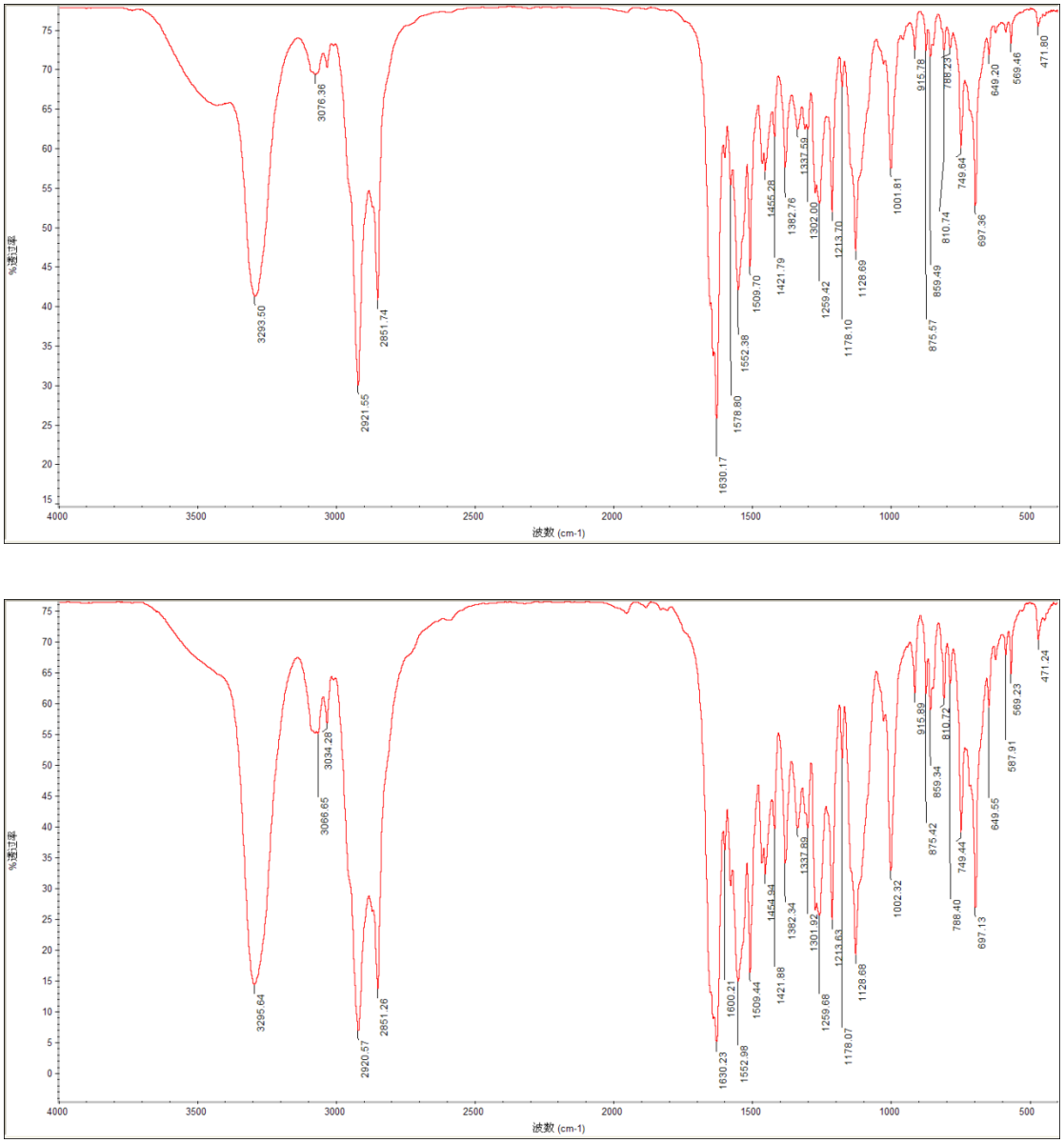


Figure S6. The FT-IR spectra of the xerogels of **3** formed in toluene (upper) and CH_3CN (down).

9. The measurement of circular dichroism

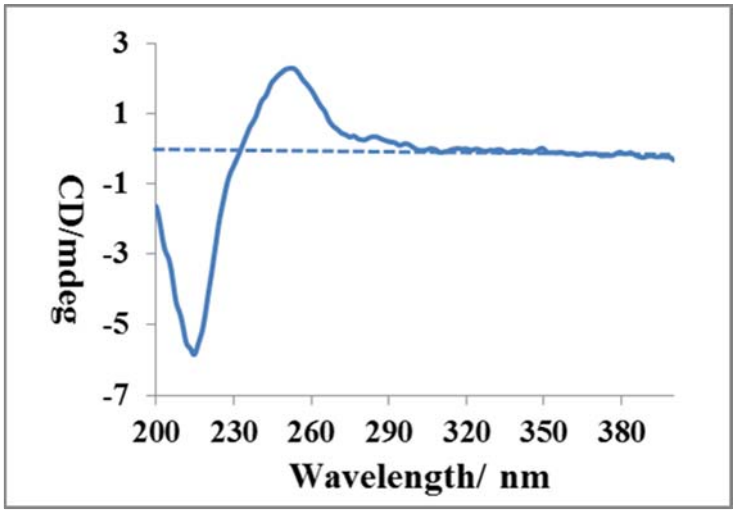


Figure S7: The CD spectra of compound **3** in MeOH (5 mg/mL)

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