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Conjugates of naphthalene and dipeptides confer molecular hydrogelators with high efficiency of hydrogelation and superhelical nanofibers

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Synthesis and characterization of compound 1-12:

Compounds **1**-**12** were synthesized by the previously reported method.[5] All compounds were made by the same method. The below shows the synthesis of compound **2** as an example: ***Synthesis of 2:*** After dicyclohexylcarbodiimide (DCC) (437 mg, 2.1 mmol) was added into 20 mL of chloroform solution of 2-(naphthalen-2-yloxy)acetic acid (404 mg, 2.0 mmol) and N-hydroxy succinimide (NHS) (230 mg, 2.0 mmol), the resulting mixture was stirred at room temperature for half an hour. Then, the precipitate was separated by filtration, and the filtrate was dried by rotary evaporation. The solid was used for the next reaction without further purification. Glycine (150 mg, 2.0 mmol) and $NaHCO_3$ (336 mg, 4.0 mmol) were dissolved in 20 mL of water, and the solid obtained earlier was dissolved in 30 mL of acetone and added to the aqueous solution of glycine. The resulting clear solution was stirred at room temperature overnight. After all the solvent was removed, the residue was re-dissolved in 40 mL of water. The insoluble part was removed, and the filtrate was acidified to pH~3. The solid was collected by filtration, washed by water (20 mL x 3), and dried in vacuum. The white powder was used to synthesize title product by repeating the same procedure except replacing the glycine to a D-alanine and the title product was obtained without further purification. Yield: 371 mg (56.2%). Purity: 94% (based on HPLC result). ^{1}H NMR: δ 1.10-1.16 (3H, d, $-CH_3$), 3.68-3.74 (2H, d, $-CH_2$-CO), 3.84-3.92 (1H, q, -CH-), 4.58 (2H, s, O-CH_2), 7.18-7.21 (1H, dd), 7.22-7.30 (2H, m), 7.37-7.41 (1H, t), 7.70-7.80 (3H, m), 7.63-7.65 (1H, d, NH) and 8.37-8.40 (1H, t, NH). EI-MS *m/z* 330.9 $[M+H]^+$. Calcd for $C_{16}H_{16}N_2O_5$: 330.1.

Characterization of 1: Yield: 325 mg (51.4%). Purity: 91% (based on HPLC result). ^{1}H NMR: δ 3.84-3.86 (2H, d, $-CH_2$-COOH), 3.88-3.90 (2H, d, $-CH_2$-), 4.70 (2H, s, O-CH-CO), 7.38-7.40 (1H, dd), 7.42-7.45 (2H, m), 7.56-7.60 (1H, t), 7.86-8.00 (3H, m), 8.34-8.38 (1H, t, NH) and 8.50-8.54 (1H, t, NH). EI-MS *m/z* 316.9 $[M+H]^+$. Calcd for $C_{16}H_{16}N_2O_5$: 316.1.

Characterization of 3: Yield: 365 mg (55.3%). Purity: 96% (based on HPLC result). ^{1}H NMR: δ 1.10-1.17 (3H, d, $-CH_3$), 3.68-3.74 (2H, d, $-CH_2$-CO), 3.86-3.94 (1H, q, -CH-), 4.58 (2H, s, O-CH_2), 7.18-7.21 (1H, dd), 7.22-7.30 (2H, m), 7.37-7.41 (1H, t), 7.70-7.80 (3H, m), 7.64-7.66 (1H, d, NH) and 8.38-8.40 (1H, t, NH). EI-MS *m/z* 330.9 $[M+H]^+$. Calcd for $C_{16}H_{16}N_2O_5$: 330.1.

Characterization of 4: Yield: 332 mg (48.0%). Purity: 88% (based on HPLC result). ^{1}H NMR: δ3.72-3.76 (2H, d, $-CH_2$-), 4.07-4.20 (2H, m, $-CH_2$-OH), 4.40-4.46 (1H, m, -CH-), 4.58 (2H, s, O-CH_2), 7.19-7.21 (1H, dd), 7.24-7.32 (2H, m), 7.38-7.43 (1H, t), 7.71-7.80 (3H, m), 7.63-7.65 (1H, d, NH) and 8.37-8.40 (1H, t, NH). EI-MS *m/z* 347.0 $[M+H]^+$. Calcd for $C_{16}H_{16}N_2O_5$: 346.1.

Characterization of 5: Yield: 438 mg (61.1%). Purity: 96% (based on HPLC result). ^{1}H NMR: δ

1.12-1.48 (6H, d, 2-CH_3), 2.45-2.52 (1H, m, -CH-$(CH_3)_2$), 3.74-3.80 (2H, d, -CH_2-), 4.34-4.38 (1H, m, -CH-COOH), 4.60 (2H, s, O-CH_2), 7.14-7.20 (1H, dd), 7.20-7.30 (2H, m), 7.35-7.40 (1H, t), 7.70-7.80 (3H, m), 7.60-7.62 (1H, d, NH) and 8.36-8.40 (1H, t, NH). EI-MS *m/z* 359.0 $[M+H]^+$. Calcd for $C_{16}H_{16}N_2O_5$: 358.2.

Characterization of 6*:* Yield: 388 mg (52.1%). Purity: 91% (based on HPLC result). ^{1}H NMR: δ 1.10-1.35 (6H, d, 2-CH_3), 1.65-1.85 (3H, m, -CH_2CH), 3.72-3.78 (2H, d, -CH_2-CO), 4.32-4.36 (1H, m, -CH-COOH), 4.62 (2H, s, O-CH_2), 7.16-7.20 (1H, dd), 7.20-7.32 (2H, m), 7.35-7.40 (1H, t), 7.74-7.81 (3H, m), 7.60-7.64 (1H, d, NH) and 8.32-8.36 (1H, t, NH). EI-MS *m/z* 373.1 $[M+H]^+$. Calcd for $C_{16}H_{16}N_2O_5$: 372.2.

Characterization of 7: Yield: 280 mg (46.7%). Purity: 92% (based on HPLC result). ^{1}H NMR: δ 3.83 (2H, s, C-CH_2-CO), 3.95-3.98 (2H, t, -CH_2-), 4.44-4.47 (2H, m, -CH_2-COOH), 7.61-7.66 (3H, m), 7.96 (1H, s), 7.98-8.05 (3H, m), 8.24-8.26 (1H, d, NH) and 8.50-8.54 (1H, t, NH). EI-MS *m/z* 301.0 $[M+H]^+$. Calcd for $C_{16}H_{16}N_2O_5$: 300.1.

Characterization of 8: Yield: 330 mg (52.5%). Purity: 94% (based on HPLC result). ^{1}H NMR: δ 1.12-1.16 (3H, d, CH_3), 3.85 (2H, s, C-CH_2-CO), 3.98-4.02 (2H, t, -CH_2-), 4.44-4.47 (1H, m, -CH-), 7.60-7.66 (3H, m), 7.94 (1H, s), 7.99-8.05 (3H, m), 8.23-8.26 (1H, d, NH) and 8.50-8.54 (1H, t, NH). EI-MS *m/z* 315.0 $[M+H]^+$. Calcd for $C_{16}H_{16}N_2O_5$: 314.1.

Characterization of 9: Yield: 284 mg (43.0%). Purity: 88% (based on HPLC result). ^{1}H NMR: δ 1.40-1.43 (2H, d, -CH_2-OH), 3.82 (2H, s, C-CH_2-CO), 3.97-3.99 (2H, t, -CH_2-), 4.35-4.40 (1H, m, -CH), 7.60-7.68 (3H, m), 7.94 (1H, s), 7.99-8.05 (3H, m), 8.35-8.37 (1H, d, NH) and 8.49-8.53 (1H, t, NH). EI-MS *m/z* 331.1 $[M+H]^+$. Calcd for $C_{16}H_{16}N_2O_5$: 330.1.

Characterization of 10: Yield: 242 mg (42.3%). Purity: 91% (based on HPLC result). ^{1}H NMR: δ 3.88-3.92 (2H, d, -CH_2-CONH), 4.06-4.09 (2H, d, -CH_2-COOH), 7.70-7.73 (2H, q), 8.07-8.15 (4H, m), 8.35-8.39 (1H, m), 8.61 (1H, s, NH), and 9.04-9.08 (1H, t, NH). EI-MS *m/z* 287.0 $[M+H]^+$. Calcd for $C_{16}H_{16}N_2O_5$: 286.1.

Characterization of 11: Yield: 305 mg (50.8%). Purity: 93% (based on HPLC result). ^{1}H NMR: δ 1.38-1.41 (3H, d, -CH_3), 4.02-4.13 (2H, m, -CH_2-), 4.31-4.41 (1H, q, -CH-), 7.70-7.72 (2H, m), 8.05-8.15 (4H, m), 8.34-8.40 (1H, m), 8.60 (1H, s, NH), and 8.96-9.00 (1H, t, NH). EI-MS *m/z* 301.0 $[M+H]^+$. Calcd for $C_{16}H_{16}N_2O_5$: 300.1.

Characterization of 12: Yield: 278 mg (44.0%). Purity: 87% (based on HPLC result). ^{1}H NMR: δ 3.72-3.77 and 3.80-3.86 (2H, dd, -CH_2-), 4.05-4.18 (2H, m, -CH_2-OH), 4.40-4.46 (1H, m, -CH-), 7.69-7.75 (2H, m), 8.04-8.15 (4H, m), 8.19-8.22 (1H, d), 8.60 (1H, s, NH) and 8.98-9.02 (1H, t, NH). EI-MS *m/z* 317.1 $[M+H]^+$. Calcd for $C_{16}H_{16}N_2O_5$: 316.1.