A versatile supramolecular hydrogel of nitrilotriacetic acid (NTA) for binding metal ions and magnetorheological response

Supporting Information

Materials and instruments

2-(Naphthalen-6-yl) acetic acid, N,N'-Dicylcohexylcarbodiimide (DCC), N-hydroxysuccinimide (NHS), L-phenylalanine, nitrilotriacetic acid (NTA) were purchased from Aldrich Co. and used without further purification. ^{1}H NMR spectra was obtained on Varian Unity Inova 400 and TEM on Morgagni 268 transmission electron microscope.

Synthesis and characterization:

Synthesis of 4: 2-(Naphthalen-6-yl)acetic acid (372 mg, 2 mmol) and NHS (230 mg, 2 mmol) were dissolved in 20 mL of chloroform, and DCC (432 mg, 2.1 mmol) was added. After the mixture was stirred at room temperature for 5 h, the resulting solid was filtered off, and the filtrate was rotary evaporation. The crude product **2** was used without purification.

L-Phenylalanine (330 mg, 2 mmol) and Na_2CO_3 (424 mg, 4 mmol) were dissolved in 8 mL of water, the solution of the crude product **2** (dissolved in 20 mL acetone) was added, and the resulting reaction mixture was stirred at room temperature overnight. The reaction mixture was rotary evaporation, and then 20 mL of water was added. The filtrate was acidified to pH=3 and the resulting product was obtained by filtration, and then further purified by flash column with chloroform-methanol as the eluent (100:1—20:1). Compound **4** (white powder) was collected with 60% yield (400 mg). ^{1}H NMR (DMSO): 7.1-7.9 (m, 12H), 4.5 (broad t, 1H), 3.5-3.7 (m, 2H), 2.8-3.2 (m, 2H).

Synthesis of 6: Compound **4** (333 mg, 1 mmol) and NHS (115 mg, 1 mmol) were dissolved in chloroform (10 mL). DCC (216 mg, 1.05 mmol) was added, and the reaction mixture was stirred at room temperature for 5 h. After filtered off, the filtrate was rotary evaporation and the crude product **5** was used without purification.

L-Phenylalanine (165 mg, 1 mmol) and Na_2CO_3 (212 mg, 2 mmol) were dissolved in 4 mL of water, the solution of crude product of **4** dissolved in 10 mL of acetone was added, and the resulting reaction mixture was stirred at room temperature overnight. The reaction mixture was rotary evaporation, and then 10 mL of water was added. The filtrate was acidified to pH=3, and the resulting product was obtained by filtration, and then purified by flash chromatography with chloroform-methanol as the eluent (100:1—20:1). Compound **6** (white powder) was collected with 58% yield (278 mg).

^{1}H NMR (DMSO): 7.1-7.9 (m, 17H), 4.4-4.6 (m, 2H), 3.5 (dd, 2H), 2.6-3.0 (m, 4H).

Synthesis of 9: Compound **6** (240 mg, 0.5 mmol) and NHS (57.5 mg, 0.5 mmol) were dissolved in chloroform (6 mL). DCC (107 mg, 0.52 mmol) was added, and the reaction mixture was stirred at room temperature for 5 h. After filtered off, the filtrate was rotary evaporation and the crude product **7** was used without purification.

Nitrilotriacetic acid (131 mg, 0.5 mmol) and Na_2CO_3 (106 mg, 1 mmol) were dissolved in 2 mL of water; the solution of crude product **6** dissolved in 6 mL of acetone was added. And the resulting reaction mixture was stirred at room temperature overnight. The reaction mixture was rotary evaporation, and then 10 mL of water was added. The filtrate was acidified to pH=2 and the resulting product was obtained by filtration, and then purified by flash chromatography with chloroform-methanol as the eluent (8:1-2:1(1%AcOH)). ^{1}H NMR (DMSO): 7.1-7.9 (m, 17H), 4.4-4.6 (m, 2H), 3.4-3.6 (m, 6H), 2.8-3.0 (m, 4H), 2.7 (t, 2H), 1.4-1.6 (m, 2H), 1.2-1.4 (m, 4H). obsvd. $(M-1)^-$ =723.55.

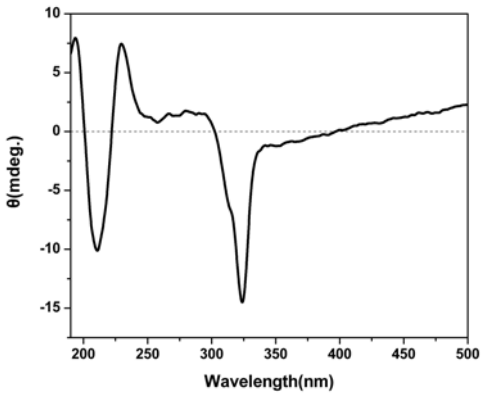

Fig. 1. The circular dichroism spectra of gel I.

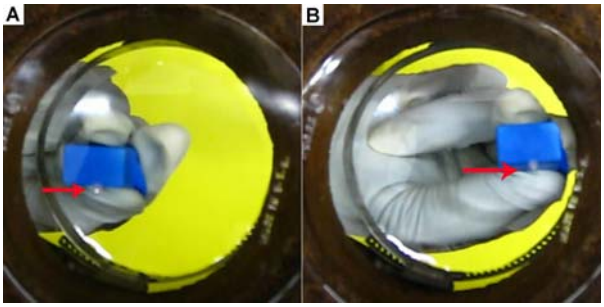

Fig. 2. Photographs showing the movement of a sphere of gel IV on the surface of $CHCl_3$ upon magnetic attraction.

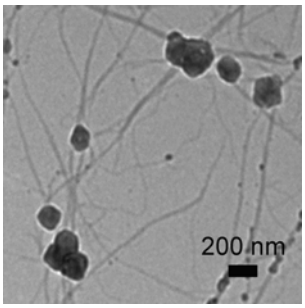

Fig 3. Higher magnified TEM image of Fig. 3D.

Table 1. Gelation properties of NTA based hydrogel

Gel	Volume of 0.9 wt% of **9**	Metal ions	pH
I	0.4 mL	---	5
III	0.4 mL	15 μl of 0.5M $Cu^{2+}_{(aq.)}$	9
V	0.4 mL	10 μl of 0.5M $Ni^{2+}_{(aq.)}$	9
IV	0.4 mL	30 μl of 0.5M $Ho^{3+}_{(aq.)}$	9
IX	0.4 mL	2 mg of raney nickel	8