Electronic Supplementary Information (ESI)

Gelation behavior and supramolecular chirality of a BTA derivative in a deep eutectic solvent

Ying Zhang[a], Hejie Wang[a], Qintang Li[b] and Xiao Chen[a,*]

[a]*Key Laboratory of Colloid and Interface Chemistry, Shandong University, Ministry of Education, Jinan, 250100, China*

[b]*School of Materials and Chemical Engineering, Xuzhou University of Technology, Xuzhou, 221018, China*

***Corresponding author: Xiao Chen**

Address: Key Laboratory of Colloid and Interface Chemistry, Shandong University, Ministry of Education, Jinan, 250100, China

E–mail: xchen@sdu.edu.cn.

Tel.: +86–531–88365420.

1. Synthesis and characterization of compounds used in this study

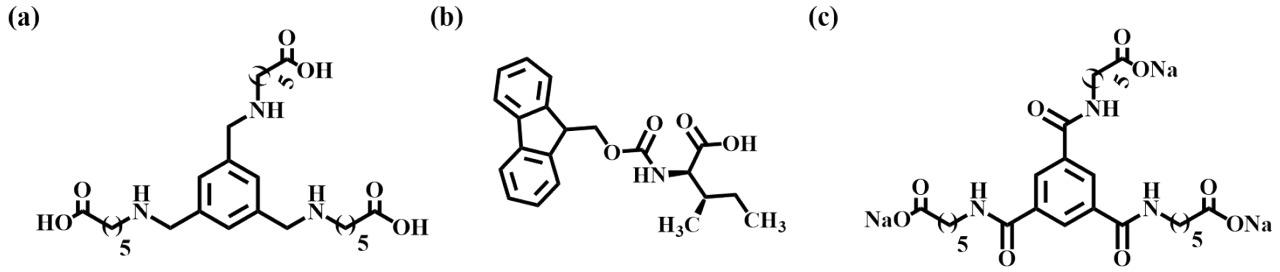

Fig. S1 The chemical structures of BTA-c (a), Fmoc-L-lsoleucine (b) and BTA3Na (c).

Compounds TP1~TP4. The appropriate amino acid ester hydrochloride (20 mmol) and triethylamine (26.7 mmol) were mixed and dissolved in anhydrous dichloromethane (DCM, 250 mL), which was then cooled to 0 °C. The 1,3,5-benzenetricarbonyl trichloride (6.7 mmol) in anhydrous dichloromethane (20 mL) was added dropwise to the mixture. After stirring for 24 h at room temperature, the reacted solution was washed twice respectively with the saturated $NaHCO_3$ solution and deionized water. The organic phase was collected and dried over anhydrous Mg_2SO_4. The solvent was then evaporated and dried under vacuum to obtain the dry white powder, which was finally purified by silica column chromatography. The yields of TP1~TP4 were 80%, 75%, 82%, and 69%, respectively.

Compound TP1: ^{1}H NMR (400 MHz, DMSO, 298 K): δ = 8.72 (t, 3H), 8.38 (s, 3H), 3.59 (s, 9H), 3.45 (dd, 6H), 2.40 (t, 6H), 1.89–1.69 (m, 6H). HRMS (TOF) m/z $[M+H]^+$: calcd. for $C_{24}H_{33}N_3O_9$, 508.2250; found, 508.2374.

Compound TP2: ^{1}H NMR (400 MHz, DMSO, 298 K): δ = 8.69 (s, 3H), 8.37 (s, 3H), 3.59 (s, 9H), 3.37–3.20 (m, 6H), 2.36 (s, 6H), 1.57 (d, 12H). HRMS (TOF) m/z $[M+H]^+$: calcd. for $C_{27}H_{39}N_3O_9$, 550.2720; found, 550.2870.

Compound TP3: ^{1}H NMR (400 MHz, DMSO, 298 K): δ = 8.67 (t, 3H), 8.37 (s, 3H), 3.58 (s, 9H), 3.28 (6H), 2.35 (t, 6H), 1.56 (m, 12H). HRMS (TOF) m/z $[M+H]^+$: calcd. for $C_{30}H_{45}N_3O_9$, 592.3189; found, 592.3387.

Compound TP4: ^{1}H NMR (400 MHz, DMSO, 298 K): δ = 8.65 (s,3H), 8.35 (s, 3H), 3.58 (d, 9H), 3.25 (dt, 6H), 2.30 (t, 6H), 1.64–1.29 (m, 18H), 1.06 (t, 1H). HRMS (TOF) m/z $[M+H]^+$: calcd. for $C_{33}H_{51}N_3O_9$, 634.3659; found, 634.3795.

Compounds BTA1~BTA4. The obtained BTA ester derivatives (TP1~TP4) (2 mmol) were respectively mixed with 5 equivalents of NaOH aqueous solution in 10 mL CH_3OH at 0 °C, which was then stirred at room temperature for 4 h. At the end of reaction, drops of acetic acid were added until a white precipitate was formed. It was then filtered and washed with ultrapure H_2O, and the resulted white solid was dried under vacuum. The yields of BTA1 ~BTA4 were 70%, 68%, 71%, and 70%, respectively.

Compound BTA1: 1H NMR (400 MHz, DMSO) δ 12.25 (s, 3H), 8.88 (t, 3H), 8.54 (s, 3H), 3.48(t, 6H), 2.46 (t, 6H), 1.93 (m, 6H). HRMS (TOF) m/z $[M+H]^+$, calcd for $C_{21}H_{27}N_3O_9$, 466.4590; found, 466.4480.

Compound BTA2: 1H NMR (400 MHz, DMSO) δ 12.11 (s, 3H), 8.77 (t, 3H), 8.46 (s, 3H), 3.29 (t, 6H), 2.25 (t, 6H), 1.55 (s, 12H). HRMS (TOF) m/z $[M+H]^+$, calcd for $C_{24}H_{33}N_3O_9$, 508.5400; found, 508.5467.

Compound BTA3: 1H NMR (400 MHz, DMSO) δ 12.08 (s, 3H), 8.86 (t, 3H), 8.52 (s, 3H), 3.42 (t, 6H), 2.36 (t, 6H), 1.79–1.62 (m, 9H), 1.47 (dd, 6H), 1.39 (s, 3H). HRMS (TOF) m/z $[M+H]^+$, calcd for $C_{27}H_{39}N_3O_9$, 550.6210; found, 550.6200.

Compound BTA4: 1H NMR (400 MHz, DMSO) δ 11.78 (s, 3H), 8.75 (t, 3H), 8.45 (s, 3H), 3.42 (t, 6H), 2.36 (t, 6H), 1.65–1.42 (m, 12H), 1.33–1.29 (m, 12H). HRMS (TOF) m/z $[M+H]^+$, calcd for $C_{30}H_{45}N_3O_9$, 592.3156; found, 592.3078.

Compound BTA3Na. The BTA3 (5 mmol) was added to the ethanol solution (15 mL) of sodium

ethoxide (5 mmol), which was sealed and stirred at 60 °C for 6 h to promote the carboxylic group to be completely neutralized by sodium ethoxide. After the reaction, the product was filtered, washed with ethanol for three times, and dried under vacuum. The yield of BTA3Na was 65%.

Compound BTA3Na: 1H NMR (400 MHz, DMSO) δ 8.75 (s, 3H), 8.65 (t, 3H), 3.26 (t, 6H), 2.45 (t, 6H) 1.58–1.44 (m, 12H), 1.33 (m, 6H). HRMS (TOF) m/z $[M+H]^+$, calcd for $C_{27}H_{36}N_3Na_3O_6$, 615.2145; found, 615.2167.

Compound BTA-c. A solution of 1,3,5-tris(bromomethyl)benzene (5 mmol) in dimethyl formamide (20 mL) was added to a suspension of the methyl 6-aminohexanoate hydrochloride (16.5 mmol) and K_2CO_3 (30 mmol) in dimethyl formamide (30 mL). The reaction sample was refluxed at 80 °C for 24 h. Then, it was filtered and evaporated by heating. The residue was dissolved in dichloromethane and washed with HCl (10 mM) and deionized water twice. The organic phase was collected and dried over anhydrous Mg_2SO_4. The solvent was evaporated and dried under vacuum to obtain the solid, which was then hydrolyzed in sodium hydroxide aqueous solution for 4 h at room temperature. Afterwards, drops of acetic acid were added until a brown precipitate was formed. The resulted solid was dried under vacuum with a yield of 60%.

Compound BTA-c: 1H NMR (400 MHz, DMSO) δ 11.85 (s, 3H), 7.25 (s, 3H), 4.09 (m, 3H), 3.76 (d, 6H) 2.53 (m, 6H), 2.21 (m, 6H), 1.54 (m, 6H), 1.38–1.33 (m, 12H). HRMS (TOF) m/z $[M+H]^+$, calcd for $C_{27}H_{36}N_3Na_3O_6$, 508.6720; found, 508.6678.

2. DSC measurement for BTA3 gel in Ch-Ph DES

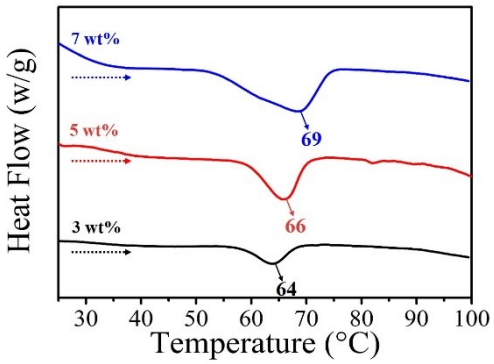

Fig. S2 DSC curves for 3, 5 and 7 wt% BTA3 gel samples in Ch-Ph. The arrows direction indicated the direction of heat flow.

3. Rheological measurements for BTA3Na gel in Ch-Ph DES

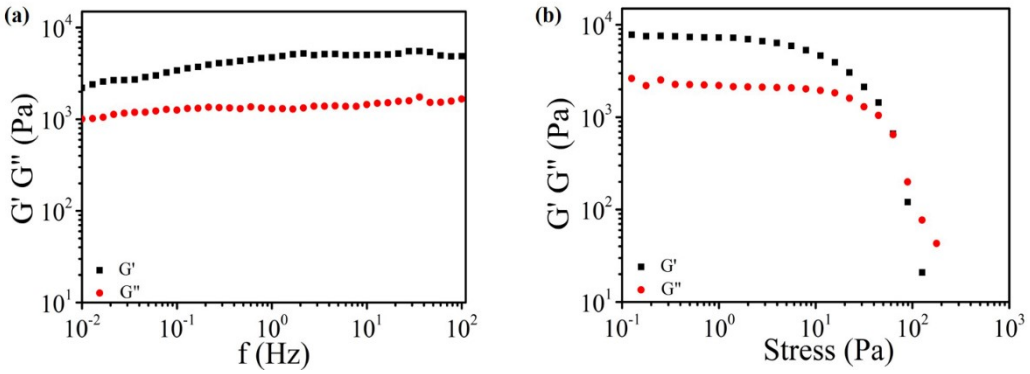

Fig. S3 Frequency (a) and stress sweep (b) results for the gel formed from BTA3Na at 3 wt% in Ch-Ph.

4. FTIR measurement for DES and eutectogel

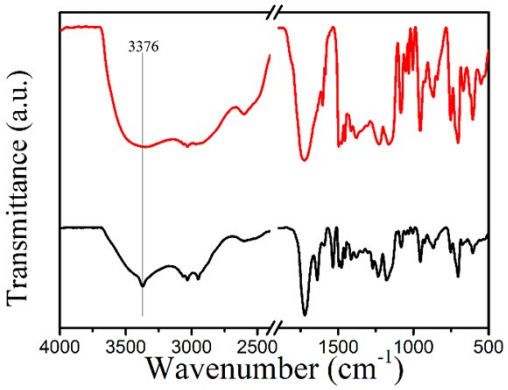

Fig. S4 The FT-IR spectra of Ch-Ph solvent (red line) and a eutectogel sample (black line).

5. The spectra of LD and CD

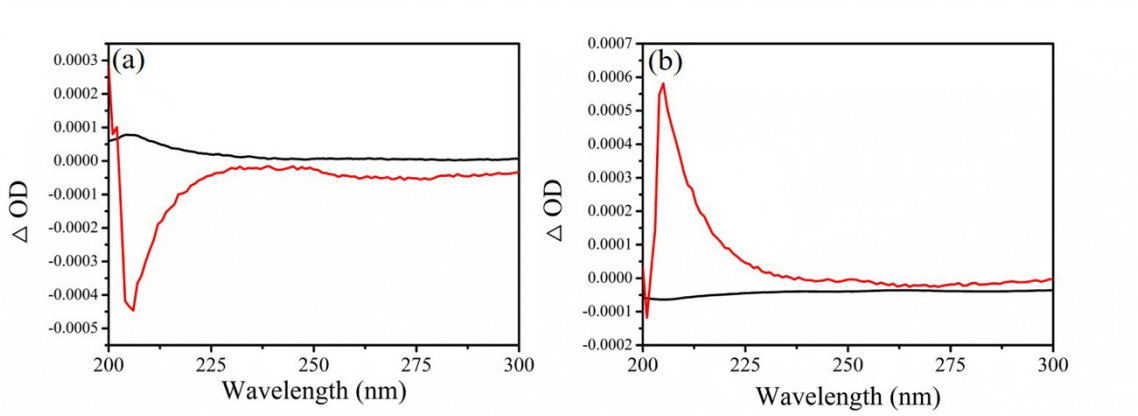

Fig. S5 The CD (red line) and LD (black line) spectra of xerogels at 5% BTA3 in Ch-Ph, which were unified as the same unit (Δ OD). The value of CD was defined as [ellipticity/32980]/absorbance[1].

6. Comparison of BTA3 solubilities in organic solvents

Table S1. Solubility results of BTA3 in several organic solvents.

Entry	Solvent	State
1	Ethylene glycol	S
2	Methanol	S
3	Acetylene	P
4	DMF	P
5	Acetone	P
6	Dichloromethane	P
7	Toluene	P
8	Cyclohexane	P

Notation: S-solution, P-precipitate.

REFERENCES

1 Y. T. Sang, P. F. Duan and M. H. Liu, *Chem. Commun.*, 2018, **54**, 4025-4028.