

Click chemistry-assisted, Bischolesteryl appended, Isosorbide based, dual-responsive organogelators and their self-assemblies

R. Balamurugan, Y.-S. Zhang, S. Fitriyani and J.-H. Liu*

Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

DOI: 10.1039/b000000x

SEM and TEM measurements	S3
Synthesis & characterization of precursors and target molecules	S3-S8
Fig. S1. Representative TGA thermograms of BCIE (top) and BCIC₂ (bottom)	S9
Fig. S2. Molecular model (MM2 software) of the compounds.	S10
Fig. S3. Representative DSC analysis of the BCIE gels in different solvents.	S11
Fig. S4 Representative SEM images of BCIE in (a) toluene (2 μm), (b) MEK (50 μm), (c) DPE (10 μm), (d) pyridine (30 μm), (e) DMF (40 μm) and (f) benzene (50 μm).	S12
Fig. S5 Representative SEM images of BCIE in (a) xylene, (b) anisole, (c) BCIC ₂ in xylene, (d) BCIC ₄ in xylene, (e) BCIC ₄ in cyclohexane and (f) Gel-emulsions in styrene-water (90:10).	S13
Fig. S6 Representative SEM images of gel-emulsions consisting of (a) 40%, (b) 60% and (c) 80% water.	S14
Fig. S7 Representative TEM images of xerogels of (a) 1-hexanol, (b) 1-octanol, (c) cyclohexanone, (d) cyclohexane, (e) toluene and (f) BCIC ₄ in DMSO.	S15
Fig. S8 Representative TEM images of xerogels of BCIC ₂ and BCIC ₄ in xylene.	S16
Fig. S9. Circular dichroism (CD) spectra of BCIE gel in 1-hexanol and 1-octanol.	S17
Fig. S10 Real images of the effect of metal ions (Pd ²⁺ and Zn ²⁺) and pH (TFA/TEA) on BCIE gel in pyridine.	S18
Fig. S11 ¹ H-NMR spectra of BCIE gel in benzene-d ₆ (a) before and (b) after the addition	

of deuterated TFA and (c) along with TMS.	S19
Fig. S12 Representative SEM images of BCIE gel after treatment with TFA in (a) benzene, (b) 1-hexanol and (c) BCIE gel+TFA+TEA in 1-hexanol.	S20
Fig. S13 $^1\text{H-NMR}$ spectra of BCIE gel in pyridine- d_5 before and after the addition of Zn^{2+} .	S21
Fig. S14 $^1\text{H-NMR}$ spectra of BCIE gel in benzene- d_6 before and after the addition of Pd^{2+} and Zn^{2+} .	S21
Fig. S15 Representative SEM images of BCIE gel (a) Zn^{2+} in pyridine (b) Pd^{2+} in pyridine (c) Zn^{2+} in benzene and (d) Pd^{2+} in benzene.	S22
Fig. S16 Temperature-dependent $^1\text{H-NMR}$ spectra of BCIE/benzene- d_6 gel over the temperature range of 30 ~100 $^\circ\text{C}$.	S23
Fig. S17 Concentration-dependent $^1\text{H-NMR}$ spectra of BCIE/benzene- d_6 gel over the temperature range of 30 ~100 $^\circ\text{C}$.	S24
Fig. S18 Partial 2D-NMR spectrum of BCIE/benzene- d_6 gel.	S25
Fig. S19 XRD analysis of BCIE gels in 1-hexanol and 1-octanol.	S26
Fig. S20 FTIR spectra of BCIE as (a) solid, (b) CHCl_3 solution, (c) gel in 1-hexanol and (d) gel in 1-octanol.	S27
Fig. S21. Representative ATR analysis of the BCIE gels in different solvents.	S28
Fig. S22 Schematic representation of dropping ball method for the determination of T_{gel}	S29

SEM measurements

The gel prepared in a sample tube was frozen by liquid. The sample was evaporated by a vacuum pump under reduced pressure for 1 day at room temperature. The obtained sample was shielded with platinum. The accelerating voltage of the transmission electron microscope was 25 kV and the beam current was 10 μ A.

TEM measurements

A piece of the gel was placed in a carbon-coated copper grid. The sample was dried by a vacuum pump under reduced pressure for 1 day at room temperature. The accelerating voltage of the transmission electron microscope was 120 kV and the beam current was 65 A.

Synthesis of compound I

The 4-azidobenzoic acid (**I**) was prepared according to the reported procedure¹. First, the 4-aminobenzoic acid (50 mmoles) was dissolved in 10 mL of concentrated HCl, diluted with 20 mL of water and keep it cool in icebath. Then, sodium nitrite (50 mmoles) dissolved in 10 mL of water was added dropwise to the above solution and keeping the temperature between -5 to 0°C. After 45 min, the solution was filtered in the cold. To this solution, sodium azide (50 mmoles) dissolved in 10 mL of water were added dropwise, keeping the temperature below 0°C. Ethyl acetate was added during the reaction to prevent excessive foaming due to nitrogen evolution. Finally chloroform was added and the collected organic phase was concentrated to yield 4-azidobenzoic acid (**I**), which was recrystallised from ethanol/water.

FT-IR (KBr, $\nu_{\max}/\text{cm}^{-1}$) : 2100 ($-\text{N}_3$), 1684 ($-\text{C}=\text{O}$). ¹H-NMR (DMSO- d_6 , 500MHz, δ in ppm) : 13.0 (s, 1H, $-\text{COOH}$), 7.9 (d, 2H, Ar-H), 7.0 (d, 2H, Ar-H).

Reference: A. Hayashi, Y. Goto, M. Nakayama, H. Sato, T. Watanabe, S. Miyata, *Macromolecules* 25 (1992) 5094.

Synthesis of compounds IIb and IIc:

The synthesis of compound IIb and IIc were given in our previous report^{1b}. A solution of cholesteryl chloroformate (4.00 g, 8.91 mmol, 1 eq.) in dry dichloromethane (75 mL) was

added dropwise to a solution of ethane-1,2-diamine (7.22 mL, 133.59 mmol, 15 eq.) and dry triethylamine (1.24 mL, 8.91 mmol, 1 eq.) in dry dichloromethane (75 mL) at 0°C. This mixture was stirred at ambient temperature under a nitrogen atmosphere for 18 h. The resulting precipitate was filtrated, and the filtrate was washed four times with a brine solution. Next, the organic layer was dried over Na₂SO₄ and evaporated to obtain the desired white solid (76% yield, 3.2 g). The other compound of the same series (**IIc**) was prepared using a similar procedure, but 1,4-butanediamine was used rather than ethylenediamine.

IIb: FT-IR (KBr, $\nu_{\max}/\text{cm}^{-1}$) : 3335 (NH stretching), 1714 (C=O), 1253 (COC). ¹H-NMR (CDCl₃, 500MHz, δ in ppm) : 5.37 (s, 1H, C=CH in cholesteryl), 4.96 (s, 1H, -NH-C(=O)O-Chol), 4.50 (t, 1H, Cholesteryl CH-O-C=O), 3.22 (2H, t, CH₂-NH-C=O), 2.82 (2H, t, NH₂-CH₂-), 1.01 (s, 3H, CH₃ in Cholesteryl), 0.92 (d, 3H, CH₃ in Cholesteryl), 0.87 (s, 3H, CH₃ in Cholesteryl), 0.68 (s, 3H, CH₃ in Cholesteryl), 1.33 (t, 2H, CH₂ in Cholesteryl), 1.53 (t, 2H, CH₂ in Cholesteryl). ¹³C NMR (125.7 MHz, CDCl₃, δ in ppm): δ = 156.41 (C=O), 139.87, 122.46, 74.34, 56.72, 56.18, 50.06, 43.74 (CH₂ in ethylenediamine), 42.33, 41.83 (CH₂ in ethylenediamine), 39.77, 39.53, 38.59, 37.02, 36.58, 36.20, 35.79, 31.90, 31.90, 28.22, 28.19, 28.00, 23.84, 21.05, 18.71, 14.29, 12.01.

IIc: Yield 76%; FT-IR (KBr, $\nu_{\max}/\text{cm}^{-1}$) : 3330 (NH stretching), 1717 (C=O), 1250 (COC). ¹H-NMR (CDCl₃, 500MHz, δ in ppm) : 5.39 (s, 1H, C=CH in cholesteryl), 4.94 (s, 1H, -NH-C(=O)O-Chol), 4.51 (t, 1H, Cholesteryl CH-O-C=O), 3.24 (2H, t, CH₂-NH-C=O), 2.80 (2H, t, NH₂-CH₂-), 1.50-0.66 (m, all protons in cholesteryl group are similar as in compound **4a**). ¹³C NMR (125.7 MHz, CDCl₃, δ in ppm): δ = 156.21 (C=O), 139.83, 122.65, 75.26, 56.70, 56.16, 50.03, 43.32 (CH₂ in ethylenediamine), 42.33, 40.83 (CH₂ in ethylenediamine), 39.75, 39.51, 38.57, 37.00, 36.58, 36.19, 35.79, 31.89, 31.90, 28.21, 28.19, 28.00, 24.28, 19.31, 14.31, 11.80.

Reference: 1(a) H.-S Jang, Y. Lee, T. Kim, J.-S. Park and J. S. Choi, *Bull. Korean Chem. Soc.* 2012, **33**, 1353; (b) R. Balamurugan, W. K. Ming, C. C. Chien and J. H. Liu, *Soft Matter*, 2014, **10**, 8963-8970

Synthesis of III:

The compound III was synthesized according to the reported procedure^{1,2}.

In a 250 ml round bottom flask, isosorbide (2 g, 13.68 mmol) was dissolved in 20 ml of DMF. To this solution NaH (1.64 g, 68.4 mmol) and propargyl bromide (7.7 mL, 68 mmol) were added. The reaction mixture was stirred at room temperature overnight. Then the solvent was removed and the residue was extracted in ethyl acetate (2 x 100 ml) and washed with water, brine solution and then the organic layer was dried with MgSO₄ and concentrated to get crude compound. Thus above obtained crude compound was purified by column chromatography on silica gel, eluting with the mixture of ethylacetate and hexane (2:1) yielded compound III as pale yellow viscous oil (53%).

FT-IR (KBr, $\nu_{\max}/\text{cm}^{-1}$) : 3280 ($\equiv\text{CH}$) and 2110 ($\text{C}\equiv\text{C}$); ¹H-NMR (DMSO-d₆, 500MHz, δ in ppm) : 2.50 (d, 2H, $-\text{C}\equiv\text{CH}$), 4.20-4.40 (m, 4H, $-\text{O}-\text{CH}_2-\text{C}-$), 4.70 (m, 2H, $-\text{O}-\text{CH}-$), 4.50 (d, 2H, $-\text{O}-\text{CH}-\text{CH}-\text{O}-$), 3.90-4.10 (d, 4H, $-\text{O}-\text{CH}_2-$ in the ring); ¹³C NMR (500 MHz, DMSO-d₆, δ , ppm): 84.9, 82.65, 80.21, 79.64, 78.48, 77.32, 72.36, 70.17, 56.52

1. S. Beghdadi, I. A. Miladi, H. B. Romdhane, J. Bernard and E. Drockenmuller, *Biomacromolecules* 2012, **13**, 4138–4145.
2. C. Besset, J.-P. Pascault, E. Fleury, E. Drockenmuller and J. Bernard *Biomacromolecules* 2010, **11**, 2797–2803.

Synthesis of IVa:

The 4-azidobenzoic acid (**1**) (5g, 30.65 mmol) was placed in double neck round bottom flasks with nitrogen inlets and dissolved in dry chloroform. Next, a small amount of 4-(dimethylamino)pyridine (DMAP; 1.87g, 15.32mmol) dissolved in chloroform was slowly added to these solutions with constant stirring under a nitrogen atmosphere. Then, cholesterol (11.85 g, 30.65 mmol) that was dissolved in chloroform was added dropwise to the solutions through a funnel followed by the addition of N,N'-dicyclohexylcarbodiimide (7.588 g, 36.78 mmol) . After this addition, the reaction mixture was stirred at room temperature for 48 h. Next, the contents of the flasks were extracted with excess chloroform and washed with aqueous sodium bicarbonate, a brine solution and water. This procedure was used to obtain the organic phase, which was dried over anhydrous magnesium sulfate and then concentrated. The resulting crude product was purified from ethanol to obtain a pure final compound (yield 82%).

IVa: FT-IR (KBr, $\nu_{\max}/\text{cm}^{-1}$) : 1724 ($\text{C}=\text{O}$), 2106 ($-\text{N}_3$), 1253 (COC). ¹H-NMR (CDCl₃, 500MHz, δ in ppm) : 8.0 (s, 2H, $\text{HAr}-\text{C}(=\text{O})-$), 7.6 (2H, d, ArH), 5.26 (s, 2H, $\text{C}=\text{CH}$ in cholesteryl), 4.61 (t, 2H, Cholesteryl $\text{CH}-\text{O}-\text{C}=\text{O}$), 1.03 (m, 6H, CH_3 in Cholesteryl), 0.93 (d, 6H, CH_3 in Cholesteryl), 0.84 (m, 6H, CH_3 in Cholesteryl), 0.67 (m, 6H, CH_3 in Cholesteryl), 1.30 (t, 4H, CH_2 in

Cholesteryl), 1.52 (t, 4H, CH₂ in Cholesteryl). ¹³C NMR (125.7 MHz, CDCl₃, δ in ppm): δ= 166.4, 148.2, 140.60, 130.12, 122.80, 73.69, 56.5, 51.2, 42.3, 39.90, 37.12, 31.88, 28.23, 26.00, 23.24, 21.12, 18.86, 12.10.

Synthesis of IV b and IVc:

The compounds IVb and IVc were synthesized according to the reported procedure^{1a-f}. For example, IVb was synthesized as follows. First, the 4-azidobenzoic acid (**I**) (2.415g, 14.80 mmol) was added to a solution of compound IIb (7g, 14.80 mmol), 4-(dimethylamino)pyridine (0.90 g, 7.4 mmol) and N,N'-dicyclohexylcarbodiimide (3.66 g, 17.76 mmol) in dry dichloromethane. This solution was stirred for 48 h at room temperature. Next, the contents of the flask were washed with water followed by a brine solution. Then, the organic layer was collected, dried over magnesium sulfate and concentrated under reduced pressure. The resulting crude product was purified using column chromatography (*n*-hexane:EtOAc 1:1.5) to obtain the pure compound as a pale yellow solid (yield 76%). Similarly the other compound (IVc) also synthesized by using the above procedure, but with the respective amine compound (IIc) rather than IIb.

IVb: FT-IR (KBr, $\nu_{\max}/\text{cm}^{-1}$) : 3330 (NH stretching), 1715 (C=O), 2100 (-N₃), 1253 (COC). ¹H-NMR (CDCl₃, 500MHz, δ in ppm) :8.3 (s, 2H, Ar-C(=O)-NH) 8.1 (4H, d, ArH), 7.8 (4H, d, ArH), 6.8 (2H, NH-C(=O)-O-), 5.36 (s, 2H, C=CH in cholesteryl), 4.48 (t, 2H, Cholesteryl CH-O-C=O), 3.24 (4H, t, CH₂-NH-C=O), 1.03 (m, 6H, CH₃ in Cholesteryl), 0.93 (d, 6H, CH₃ in Cholesteryl), 0.84 (m, 6H, CH₃ in Cholesteryl), 0.67 (m, 6H, CH₃ in Cholesteryl), 1.30 (t, 4H, CH₂ in Cholesteryl), 1.52 (t, 4H, CH₂ in Cholesteryl). ¹³C NMR (125.7 MHz, CDCl₃, δ in ppm): δ= 167.6, 156.21, 148.0, 140.44, 139.80, 130.61, 122.85, 122.45, 76.75, 40.49, 39.75, 56.72, 56.18, 50.06, 42.33, 39.77, 38.59, 37.02, 36.58, 36.20, 35.79, 31.89, 28.21, 28.17, 27.80, 23.84, 21.15, 18.43, 14.31, 12.00.

IVc: Yield 66%; FT-IR (KBr, $\nu_{\max}/\text{cm}^{-1}$) : 3332 (NH stretching), 1710 (C=O), 2110 (-N₃), 1256 (COC). ¹H-NMR (CDCl₃, 500MHz, δ in ppm) :8.3 (s, 2H, Ar-C(=O)-NH) 8.1 (4H, d, ArH), 7.9 (4H, d, ArH), 6.7 (2H, NH-C(=O)-O-), 5.30 (s, 2H, C=CH in cholesteryl), 4.52 (t, 2H, Cholesteryl CH-O-C=O), 3.20 (4H, t, CH₂-NH-C=O), 1.14 (m, 6H, CH₃ in Cholesteryl), 0.97 (d, 6H, CH₃ in Cholesteryl), 0.86 (m, 6H, CH₃ in Cholesteryl), 0.66 (m, 6H, CH₃ in Cholesteryl), 1.32

(t, 4H, CH₂ in Cholesteryl), 1.49 (t, 4H, CH₂ in Cholesteryl). ¹³C NMR (125.7 MHz, CDCl₃, δ in ppm): δ= 166.9, 156.20, 147.6, 140.41, 139.81, 130.57, 122.77, 122.40, 76.63, 40.50, 39.69, 56.70, 56.10, 50.18, 42.28, 39.74, 38.54, 37.18, 36.40, 36.27, 35.78, 31.71, 28.20, 28.10, 27.81, 23.80, 21.31, 18.32, 14.29, 11.90.

1. (a) M. Fritzsche, S.-S. Jester, S. Hoger, C. Klaus, N. Dingenouts, P. Linder, M. Drechsler and S. Rosenfeldt, *Macromolecules*, 2010, **43**, 8379. (b) S. Höger, S. Rosselli, A. –D. Ramminger, T. Wagner and G. Lieser, *Chem. Eur. J.* 2003, **9**, 3481; (c) S. Höger, A. –D. Ramminger, S. Rosselli, T. Wagner, B. Silier, S. Wiegand, W. Häußler, G. Lieser and V. Scheumann, *Angew. Chem.* 2001, **113**, 3233; (d) F. Aparicio, E. Matesanz and L. Sanchez, *Chem. Commun.*, 2012, 48, 5757; (e) A. Dawn, N. Fujita, S. Haraguchi, K. Sada and S. Shinkai, *Chem. Commun.*, 2009, 2100; (f) S. Ghosh, X. Li, V. Stepanenko and F. Würthner, *Chem. Eur. J.*, 2008, **14**, 11343.

Synthesis of BCIE, BCIC₂ and BCIC₄:

All the compounds (BCIE, BCIC₂ and BCIC₄) were synthesized according to the reported procedures. For example, synthesis of BCIE is as follows: To a solution of compound IVa (3g, 5.6415 mmol) and compound III (0.597g, 2.6864 mmol) in dry THF (50 mL) was added N,N,N',N''-pentamethyldiethylenetriamine (PMDETA, 1.396g, 8.059mmol) in a 250 mL round bottom flask fitted with magnetic stirrer and argon inlet. Then the solution was purged with argon for 15 min. After that copper (I) iodide (1.023g, 5.372 mmol) was added to the reaction mixture. The mixture was degassed with argon and then it was stirred at 60°C for 24 hr under argon atmosphere. At the end of the reaction time, the reaction mixture was cooled to room temperature, and the solvent was evaporated under reduced pressure. Thus obtained crude residue was further purified by column chromatography on silica gel with 3% methanol in Chloroform yielded a yellow colored solid (72%). Similarly the other compounds in this series such as BCIC₂ and BCIC₄ were synthesized by following the above same procedure in which compound IVa was replaced by IVb and IVc respectively.

BCIE: Yield 72%; FT-IR (KBr, ν_{\max} /cm⁻¹) : Disappearance of peak at 3214 cm⁻¹ and 2095cm⁻¹ for ≡C-H and N₃ respectively revealed the formation of product. 1710 (C=O), 1528, 1610 (C-C in Ar), 1256 (COC). ¹H-NMR (CDCl₃, 500MHz, δ in ppm) :8.21-8.09 (m, 6H, ArH, C=CH in triazole), 7.82-7.84 (m, 4H, ArH), 5.44 (s, 2H, C=CH in cholesteryl), 4.63-4.90 (m, 8H, -O-

CH₂-and-O-CH-), 3.65-4.25 (m, 6H, isosorbide ring protons), 0.70-2.49 (m, 45H, in Cholesteryl). ¹³C NMR (125.7 MHz, CDCl₃, δ in ppm): δ= 166.1, 144.40, 140.70, 139.97, 130.61, 129.9, 122.53, 119.10, 92.7, 84.4, 73.69, 63.0, 56.2, 50.6, 42.7, 39.73, 37.41, 36.16, 32.18, 28.23, 28.15, 27.83, 23.86, 21.27, 18.39, 14.29, 11.80; HRMS (MALDI-TOF), m/z calculated 1285.81; found:1285.80

BCIC₂: Yield 44%; FT-IR (KBr, ν_{max}/cm⁻¹) : 3334 (NH stretching),1714 (C=O), 1532, 1614 (C-C in Ar), 1258 (COC). ¹H-NMR (CDCl₃, 500MHz, δ in ppm) :8.45 (s, 2H, Ar-C(=O)-NH) 8.1 (4H, d, ArH), 7.9 (4H, d, ArH), 6.8 (2H, NH-C(=O)-O-), 5.30 (s, 2H, C=CH in cholesteryl), 4.80 (6H, -O-CH₂-), 4.50 (t, 2H, Cholesteryl CH-O-C=O), 3.3 (4H, t, CH₂-NH-C=O), 1.14 (m, 6H, CH₃ in Cholesteryl), 0.97 (d, 6H, CH₃ in Cholesteryl), 0.86 (m, 6H, CH₃ in Cholesteryl), 0.66 (m, 6H, CH₃ in Cholesteryl), 1.32 (t, 4H, CH₂ in Cholesteryl), 1.49 (t, 4H, CH₂ in Cholesteryl). ¹³C NMR (125.7 MHz, CDCl₃, δ in ppm): δ= 167.6, 156.26, 144.5, 140.78, 139.79, 136.8, 134.2, 128.11, 122.81, 121.42, 120.5, 93.8, 91.8, 84.5, 72.0, 66.69, 63.0, 56.5, 50.8, 44.2, 42.6, 40.47, 39.73, 37.11, 36.61, 36.21, 35.77, 31.88, 28.23, 28.15, 27.83, 23.86, 21.27, 18.39, 14.29, 11.80.

BCIC₄: Yield 51%; FT-IR (KBr, ν_{max}/cm⁻¹): 3331 (NH stretching),1718 (C=O), 1528, 1617 (C-C in Ar), 1260 (COC). ¹H-NMR (CDCl₃, 500MHz, δ in ppm) :8.48 (s, 2H, Ar-C(=O)-NH) 8.14 (4H, d, ArH), 7.96 (4H, d, ArH), 6.78 (2H, NH-C(=O)-O-), 5.28 (s, 2H, C=CH in cholesteryl), 4.81 (6H, -O-CH₂-), 4.47 (t, 2H, Cholesteryl CH-O-C=O), 3.28 (4H, t, CH₂-NH-C=O), 1.14 (m, 6H, CH₃ in Cholesteryl), 0.97 (d, 6H, CH₃ in Cholesteryl), 0.86 (m, 6H, CH₃ in Cholesteryl), 0.66 (m, 6H, CH₃ in Cholesteryl), 1.28 (t, 4H, CH₂ in Cholesteryl), 1.50 (t, 4H, CH₂ in Cholesteryl). ¹³C NMR (125.7 MHz, CDCl₃, δ in ppm): δ= 167.2, 156.44, 144.0, 140.33, 140.13, 136.3, 134.1, 128.0, 122.62, 121.39, 119.8, 94.0, 91.6, 84.2, 72.0, 66.69, 63.0, 56.3, 50.8, 44.2, 42.6, 40.38, 39.64, 37.11, 36.32, 36.17, 35.43, 31.88, 28.23, 28.15, 27.77, 23.79, 21.28, 18.41, 14.31, 12.10.

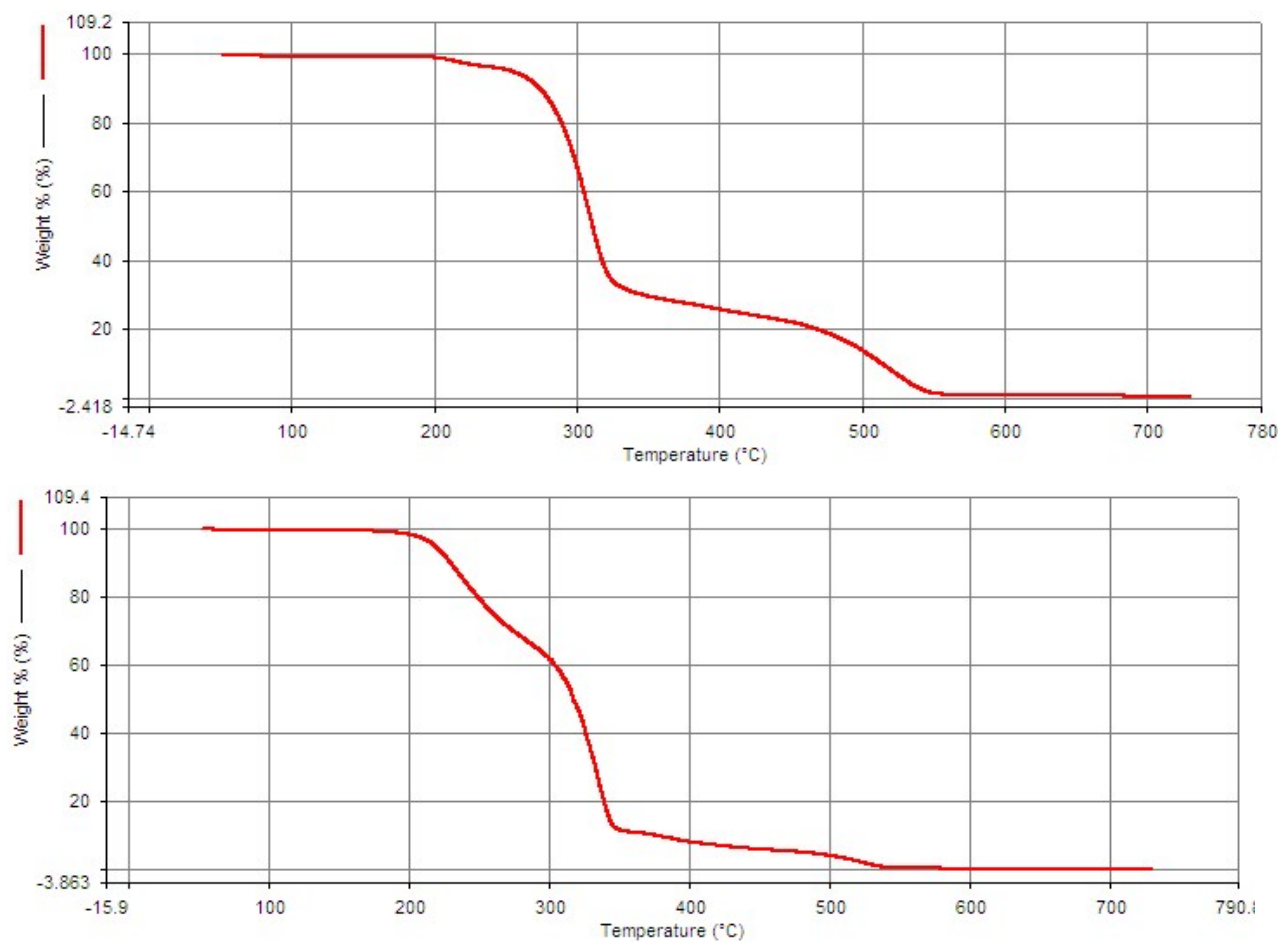


Fig. S1. Representative TGA thermograms of compound **BCIE** (top) and **BCIC₂** (bottom)

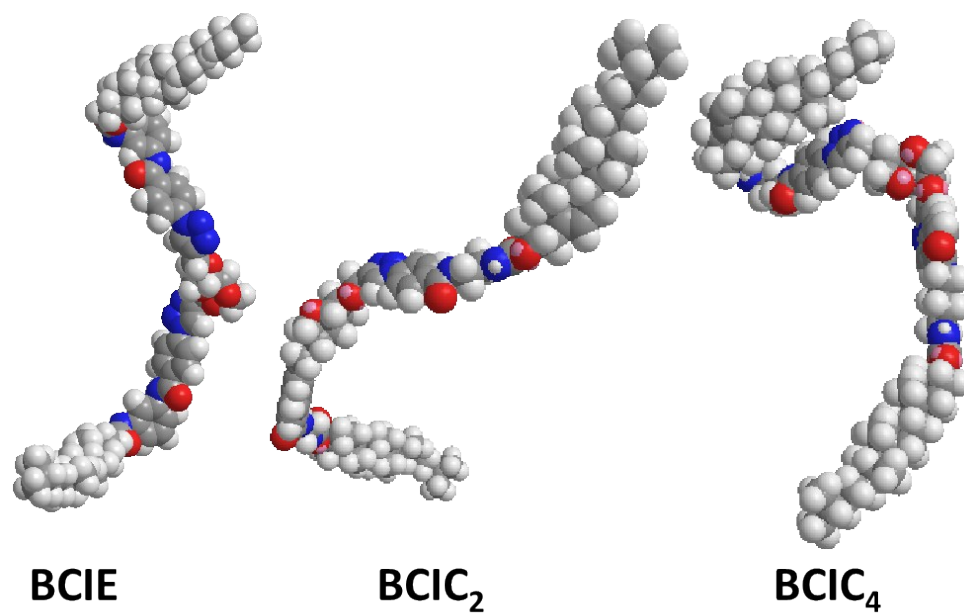


Fig.S2. Molecular model (MM2 software) of the compounds

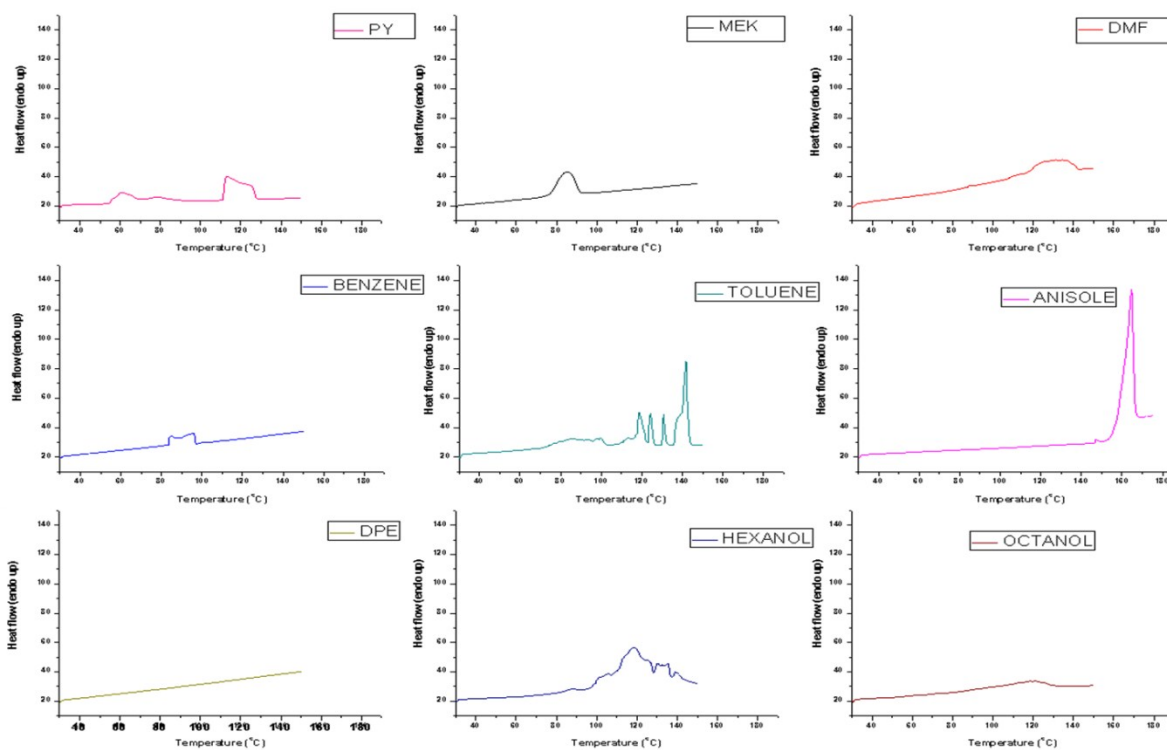


Fig.S3. Representative DSC analysis of the BCIE gels in different solvents

Table S1 T_{gel} of the gelator BCIE in different solvents determined from DSC analysis (n.d.=cannot be determined by DSC; by dropping ball method it was observed 126°C; all the Tgel values are in accordance with the dropping ball method).

Compound	solvent	Boiling point (°C)	T_{gel} (°C)	
			Dropping Ball method (naked eye)	DSC analysis
BCIE	Pyridine	115	61	60
BCIE	MEK	79	87	85
BCIE	DMF	153	130	130
BCIE	Benzene	80	84	85
BCIE	Toluene	110	102	100
BCIE	Anisole	153	150	148
BCIE	DPE	121	108	n.d.
BCIE	1-Hexanol	155-159	112	110
BCIE	1-Octanol	195	121	120

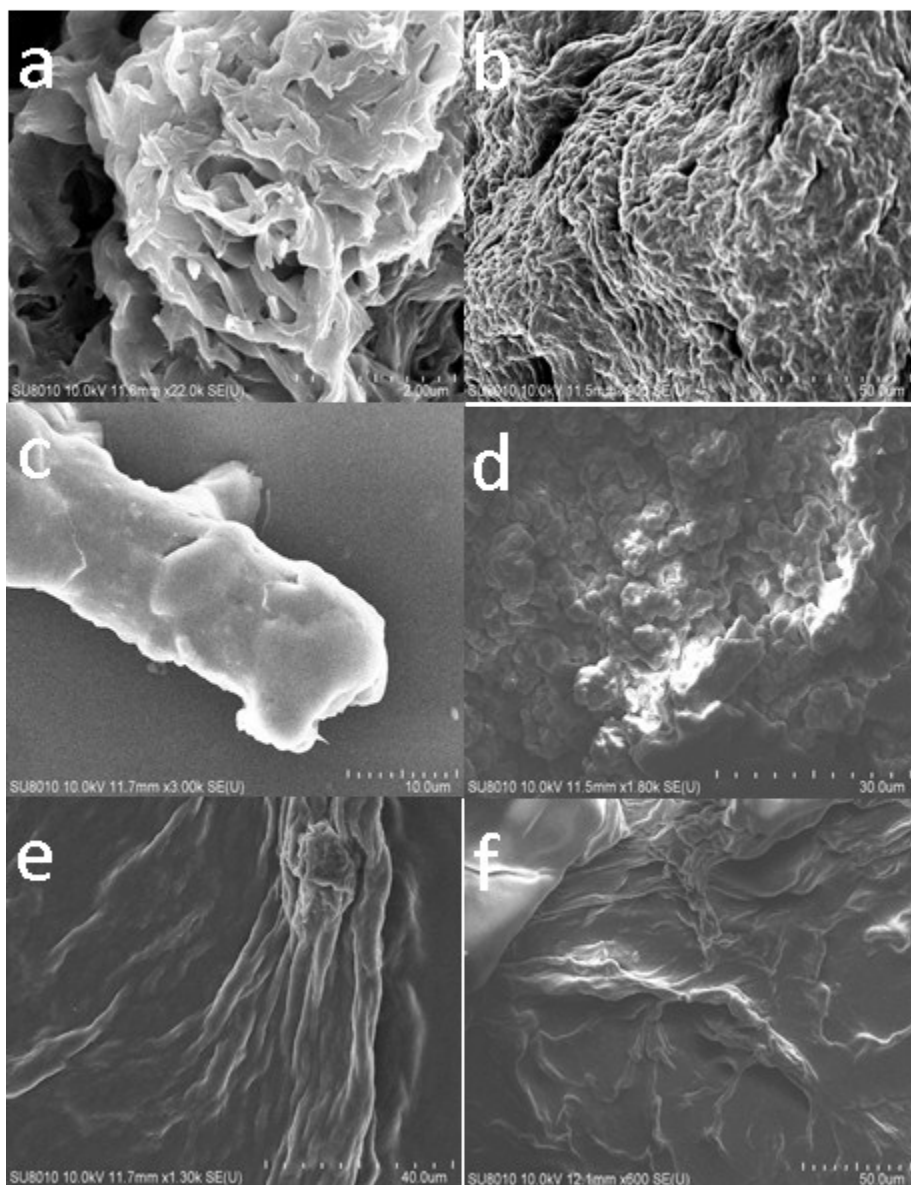


Fig.S4 Representative SEM images of BCIE in (a) toluene (2 μ m), (b) MEK (50 μ m), (c) DPE (10 μ m); (d) pyridine (30 μ m); (e) DMF (40 μ m) and (f) benzene (50 μ m).

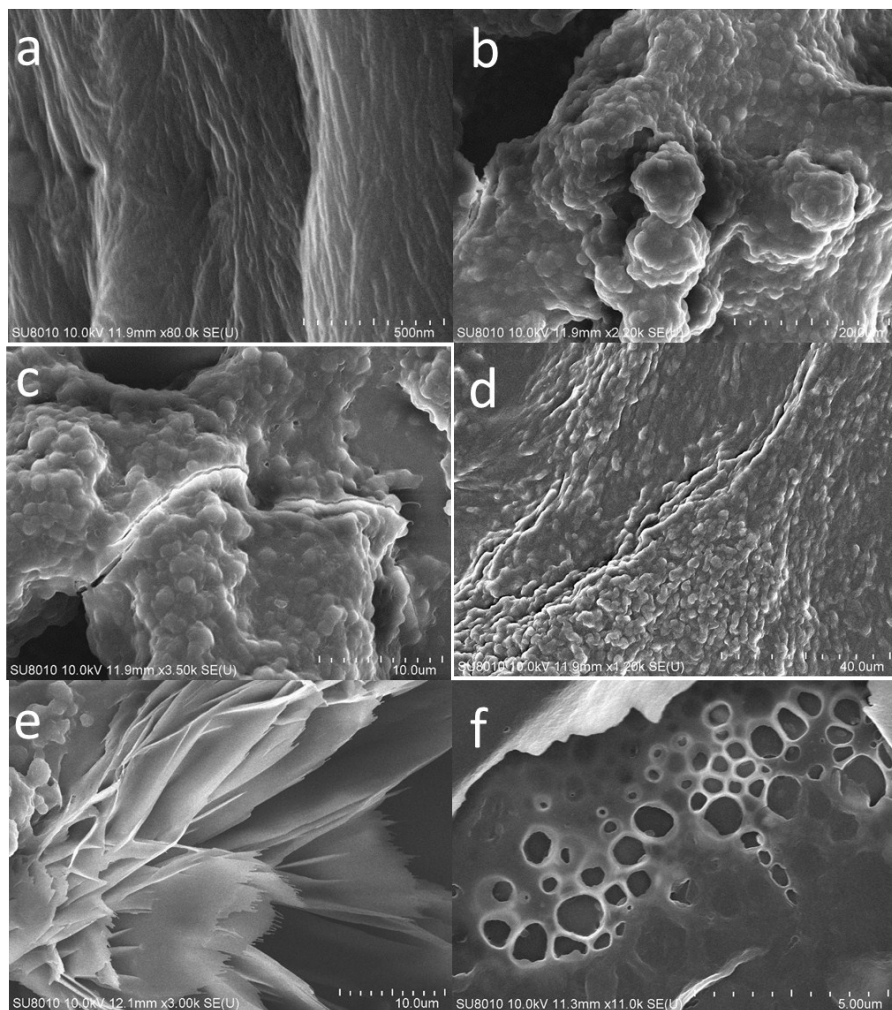


Fig.S5 Representative SEM images of BCIE in (a) xylene (500 nm), (b) anisole (20 μ m), (c) BCIC₂ in xylene (10 μ m); (d) BCIC₄ in xylene (40 μ m); (e) BCIC₄ in cyclohexane (10 μ m) and (f) Gel-emulsions in styrene-water (90:10) (5 μ m).

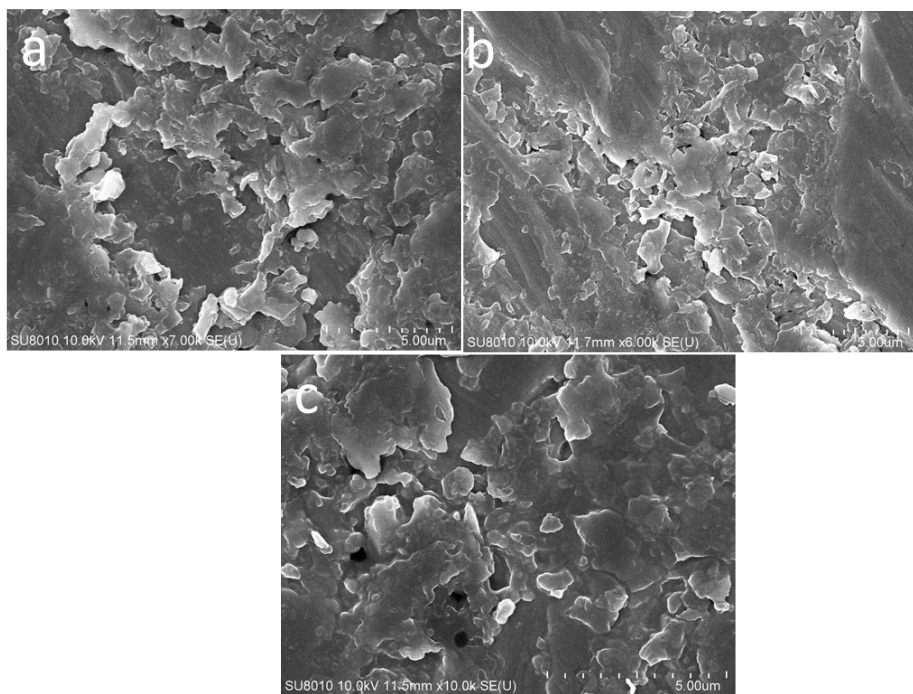


Fig.S6 Representative SEM images of gel-emulsions consist of (a) 40%, (b) 60% and (c) 80% of water

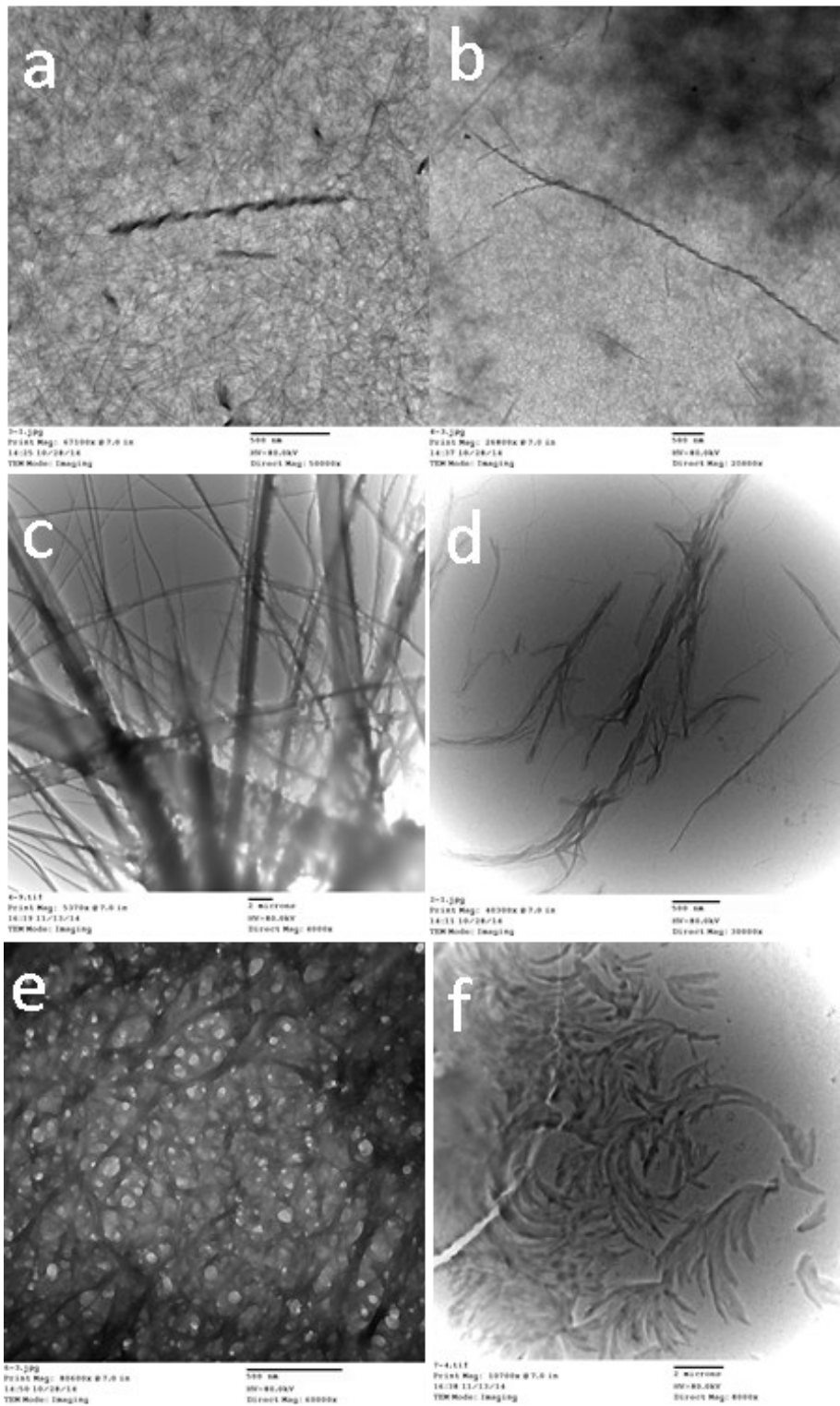


Fig.S7 Representative TEM images of xerogel of (a) 1-hexanol, (500nm), (b) 1-octanol (500nm), (c) cyclohexanone (2µm), (d) cyclohexane (500nm), (e) toluene (500 nm); (f) BCIC4 in DMSO (2µm).

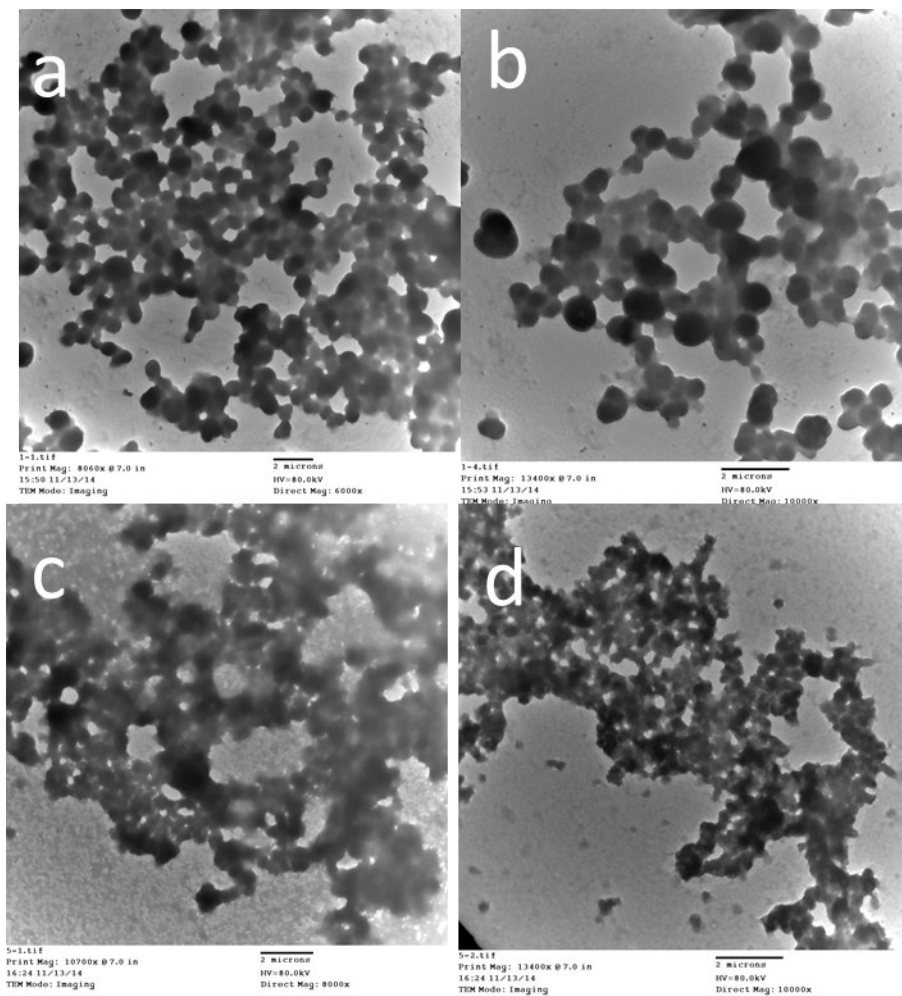


Fig.S8 Representative TEM images of xerogel of BCIC₂ (up) and BCIC₄ in xylene (down)

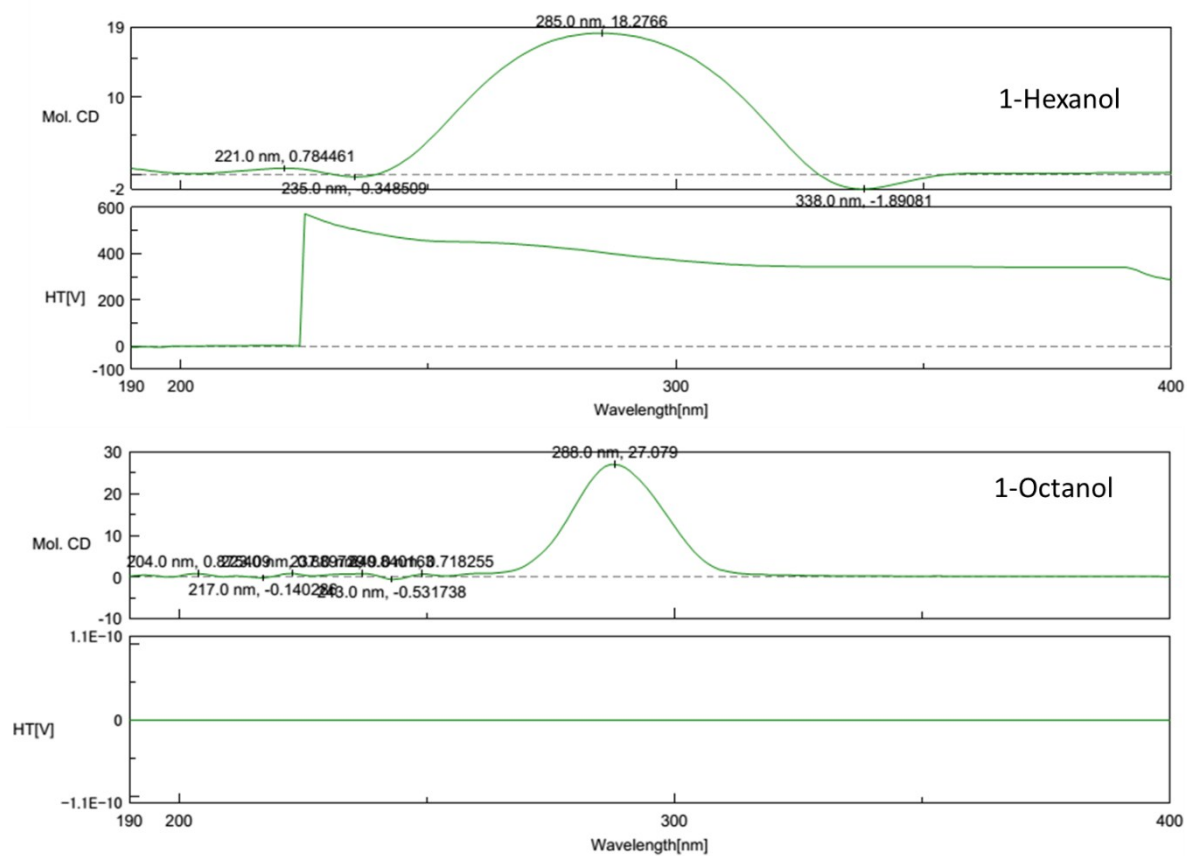


Fig. S9. Circular Dichroism (CD) spectra of BCIE gel in 1-Hexanol and 1-Octanol

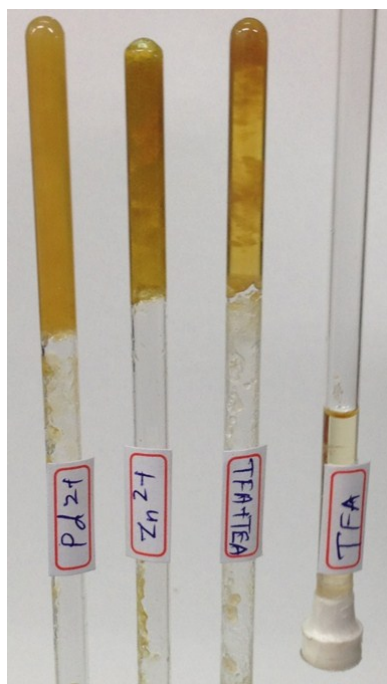


Fig.S10 Real images of effect of metal ions (Pd^{2+} and Zn^{2+}) and pH (TFA/TEA) on **BCIE** gel in pyridine

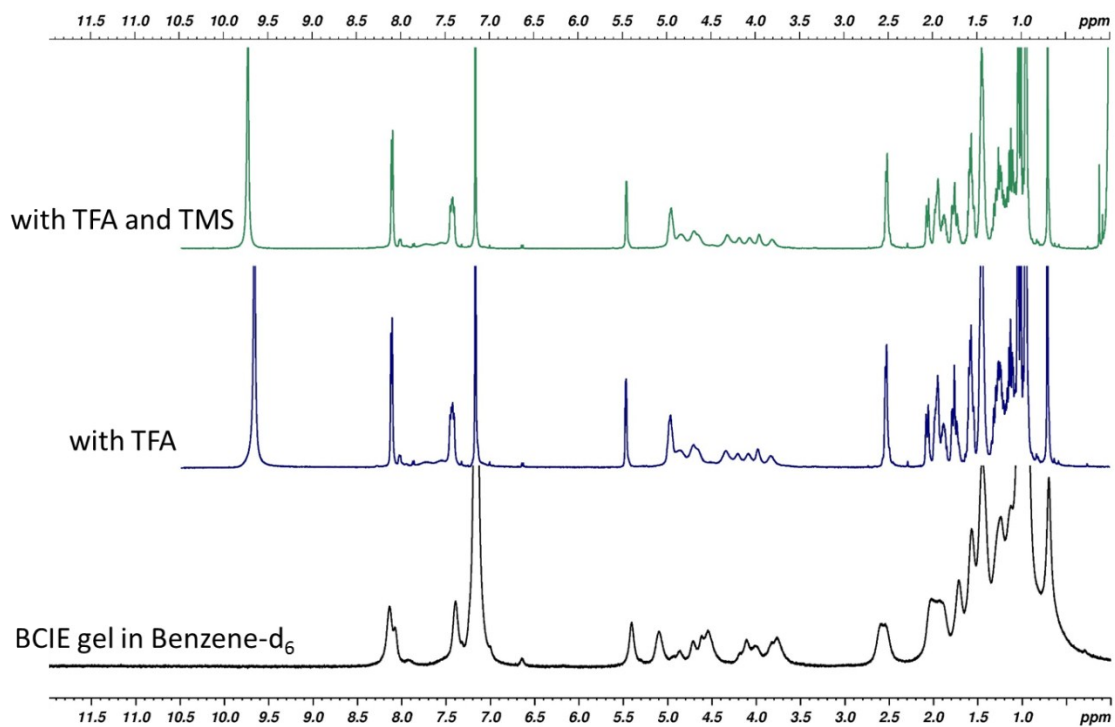


Fig.S11 ¹H-NMR spectra of **BCIE** gel in benzene-d₆ (a) before, (b) after addition of deuterated TFA and (c) along with TMS

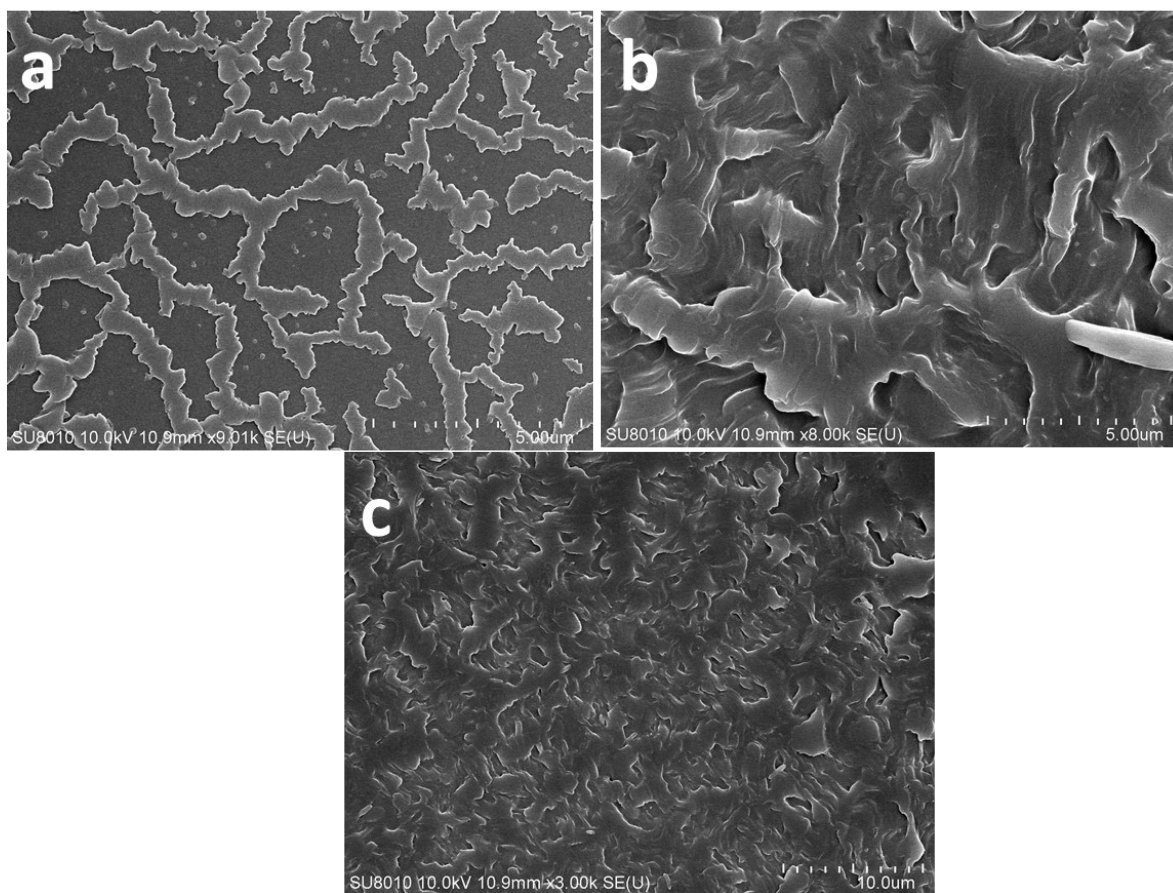


Fig.S12 Representative SEM images of BCIE gel after treated with TFA in (a) benzene, (b) 1-hexanol and (c) BCIE gel+TFA+TEA in 1-hexanol (fibrous textures of **BCIE** in 1-hexanol has been retained).

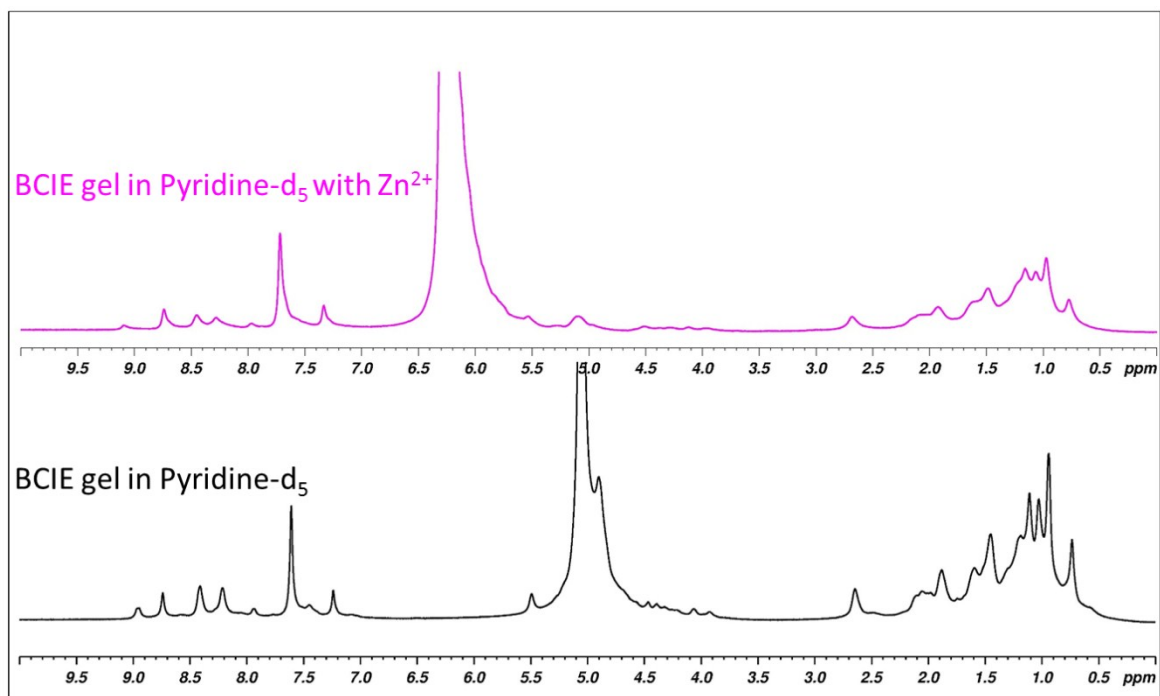


Fig.S13 $^1\text{H-NMR}$ spectra of **BCIE** gel in pyridine- d_5 before and after addition of Zn^{2+}

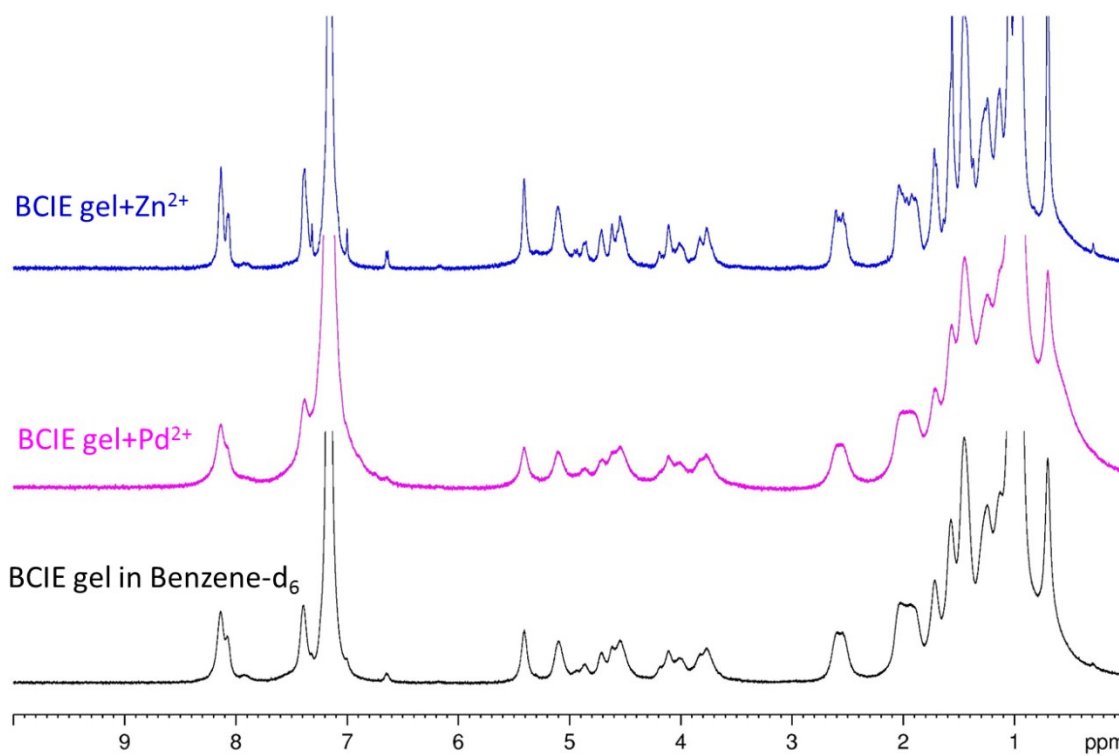


Fig.S14 $^1\text{H-NMR}$ spectra of **BCIE** gel in benzene- d_6 before and after addition of Pd^{2+} and Zn^{2+}

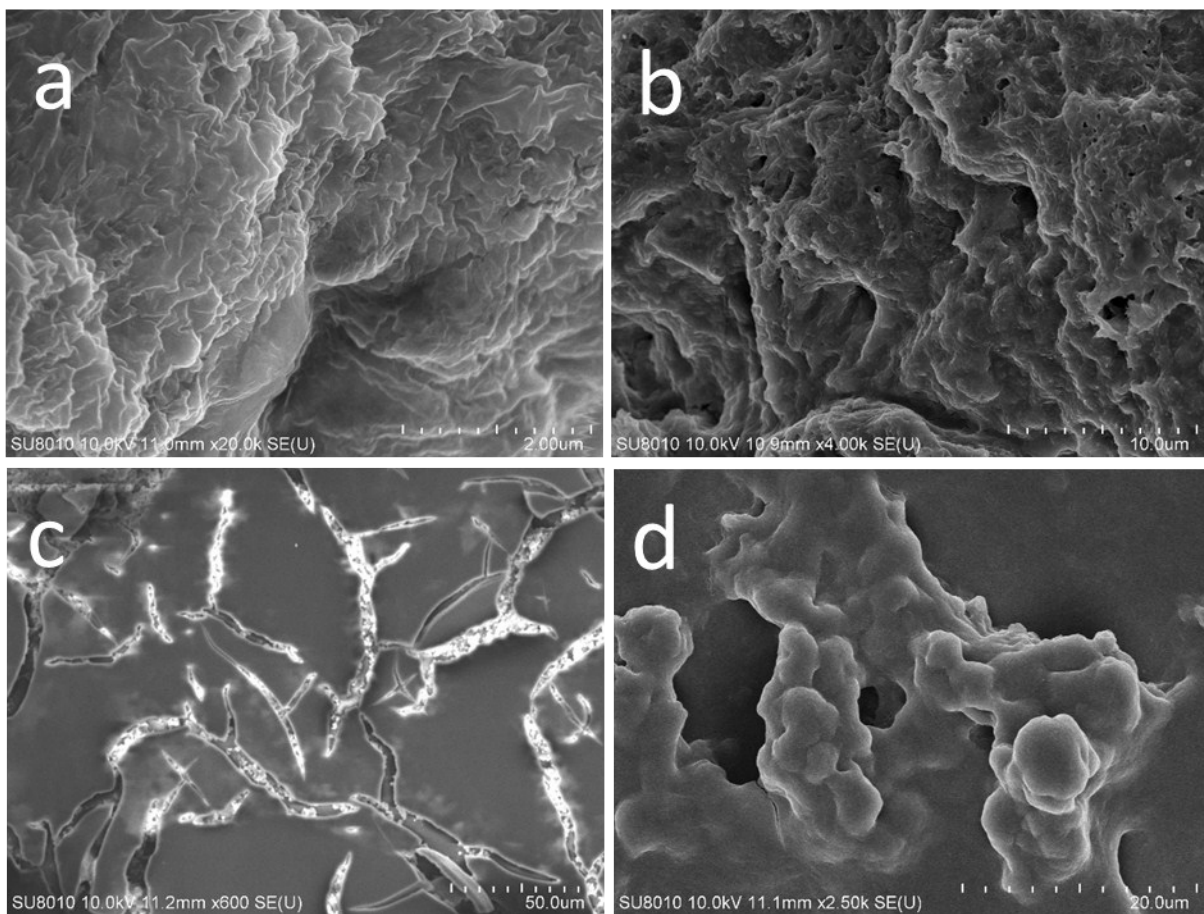


Fig.S15 Representative SEM images of BCIE gel (a) Zn²⁺ in pyridine (b) Pd²⁺ in pyridine (c) Zn²⁺ in benzene and (d) Pd²⁺ in benzene.

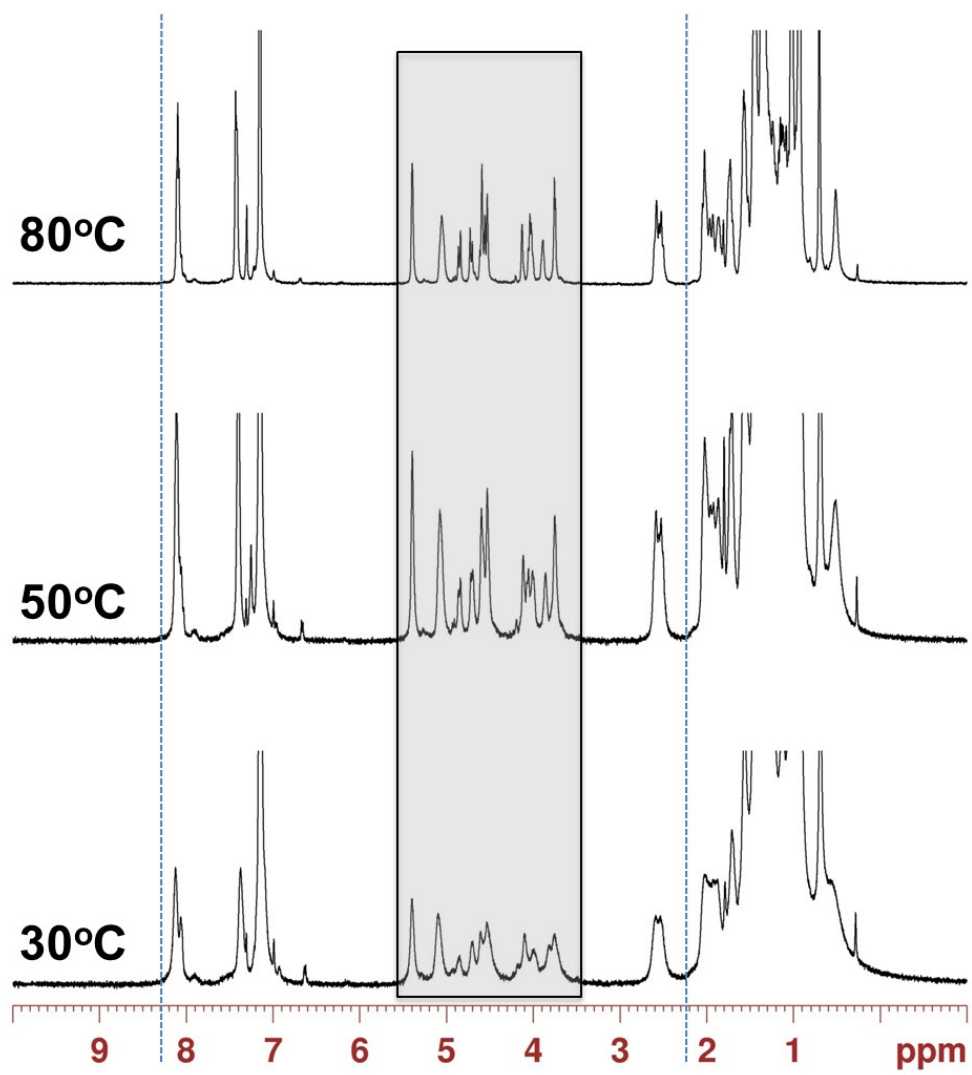


Fig. S16 Temperature-dependent ¹H-NMR spectra of BCIE/benzene-d₆ gel over the temperature range of 30 ~100 °C.

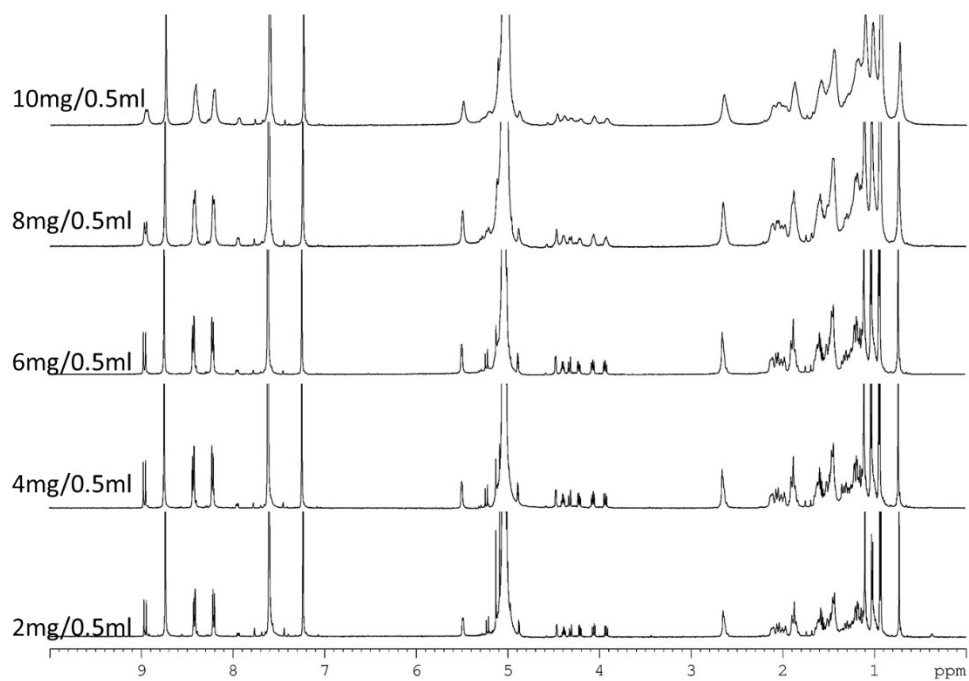


Fig. S17 Concentration-dependent ¹H-NMR spectra of BCIE/benzene-d₆ gel over the temperature range of 30 ~100 °C.

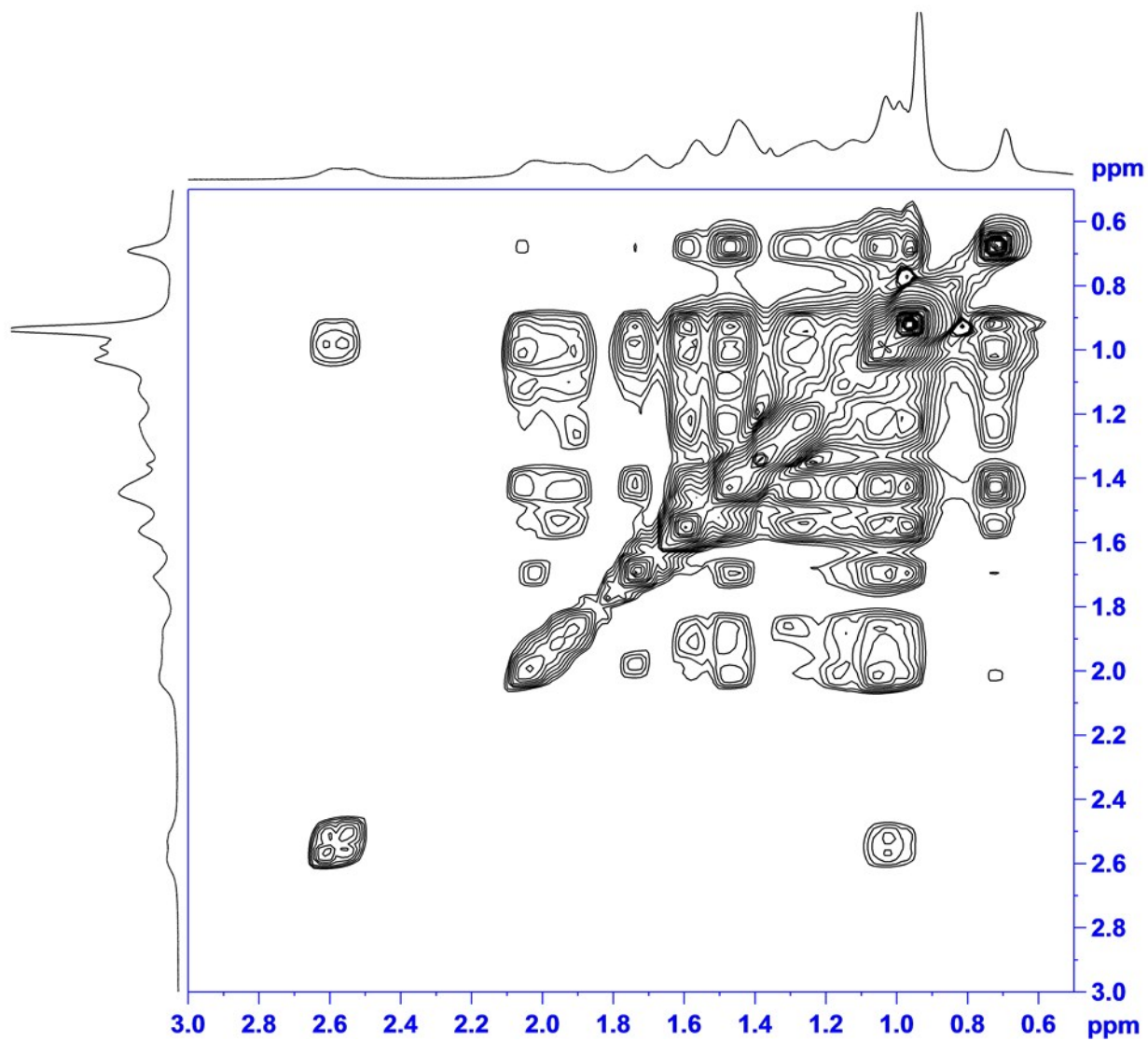


Fig. S18 Partial 2D-NMR spectrum of BCIE/benzene-d₆ gel

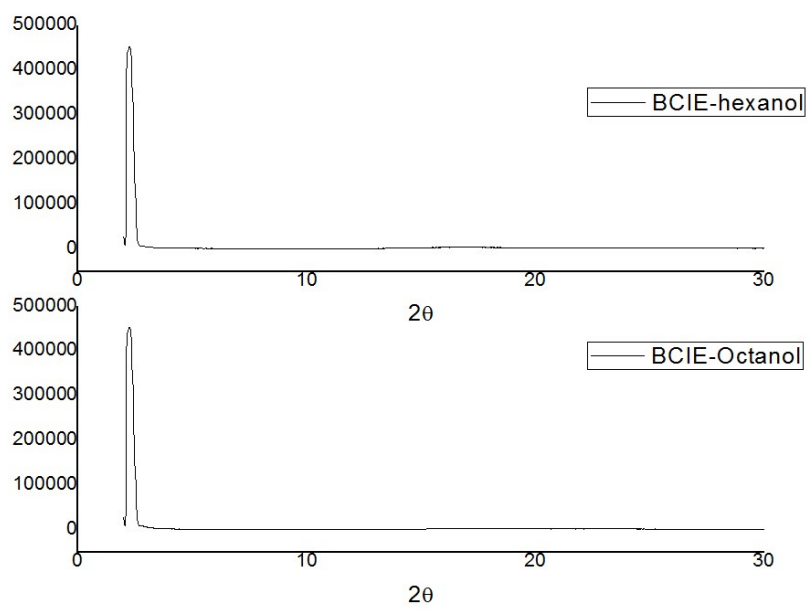


Fig. S19 XRD analysis of BCIE gels in 1-hexanol and 1-octanol

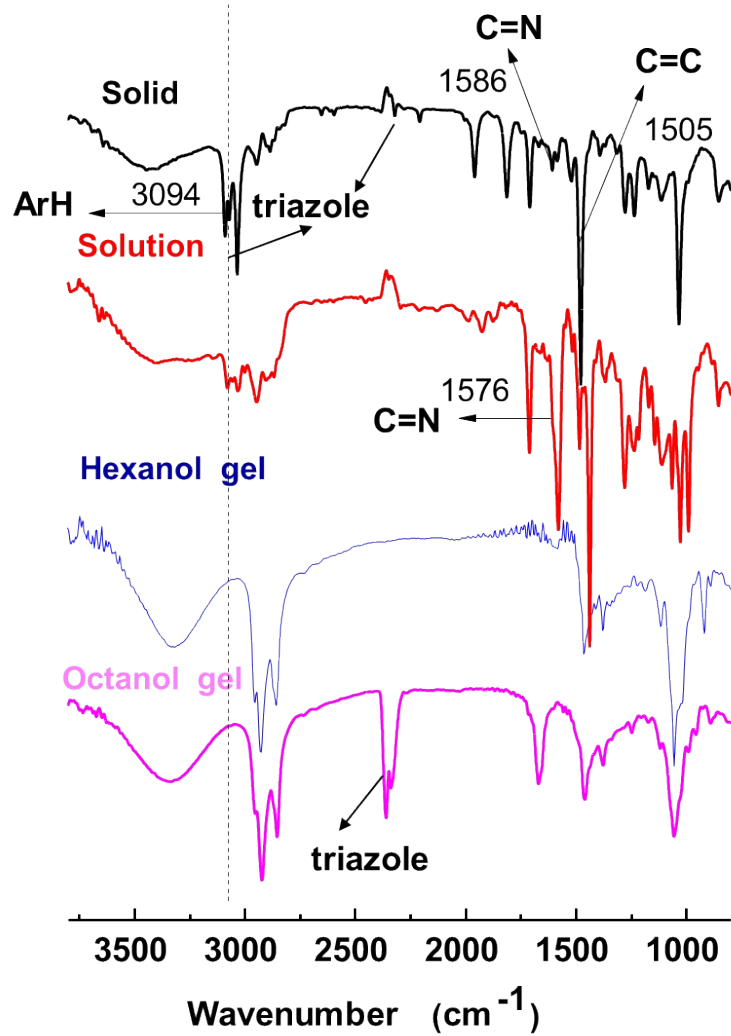


Fig. S20 FTIR spectra of BCIE as (a) solid, (b) CHCl_3 solution, (c) gel in 1-hexanol and (d) gel in 1-octanol

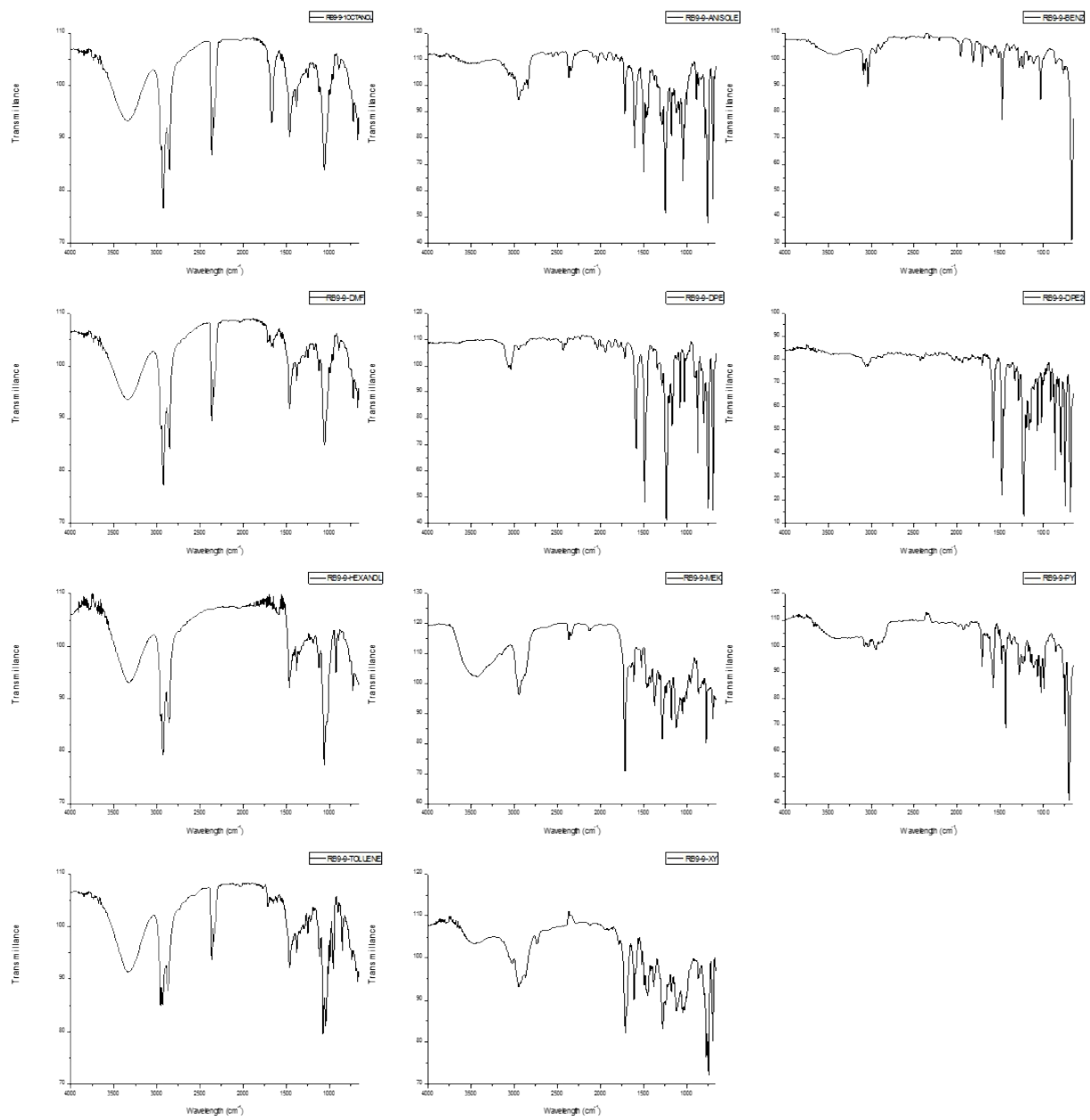


Fig.S21. Representative ATR analysis of the BCIE gels in different solvents

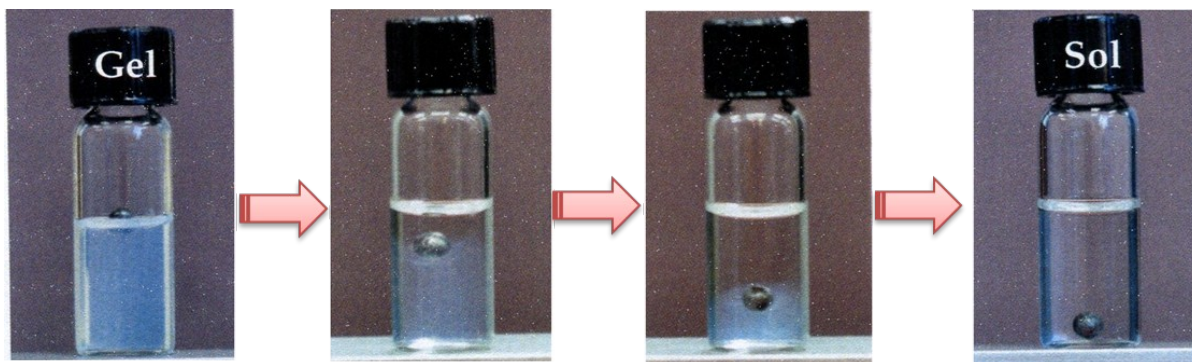


Fig. S22 Schematic representation of dropping ball method for the determination of T_{gel}
(Stainless steel ball: 124 mg, $\text{Ø}2.5$ mm, placed on the top of the gel, heating rate $5^{\circ}\text{C}/\text{min}$)