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*

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**Fig. S22** Schematic representation of dropping ball method for the
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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 µA.

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 procedure\textsuperscript{1}. 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\textdegree 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\textdegree 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, $\nu_{\text{max}}$/cm$^{-1}$): 2100 (-N$_3$), 1684 (-C=O). $^1$H-NMR (DMSO-d$_6$, 500MHz, $\delta$ in ppm): 13.0 (s, 1H, -COOH), 7.9 (d, 2H, Ar-H), 7.0 (d, 2H, Ar-H).


Synthesis of compounds IIb and IIc:

The synthesis of compound IIb and IIc were given in our previous report\textsuperscript{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 Na$_2$SO$_4$ 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, $\nu_{\text{max}}$/cm$^{-1}$) : 3335 (NH stretching), 1714 (C=O), 1253 (COC). $^1$H-NMR (CDCl$_3$, 500MHz, $\delta$ 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$_2$-O-C=O), 3.22 (2H, t, CH$_2$-NH-C=O), 2.82 (2H, t, NH$_2$-CH$_2$-), 1.01 (s, 3H, CH$_3$ in Cholesteryl), 0.92 (d, 3H, CH$_3$ in Cholesteryl), 0.87 (s, 3H, CH$_3$ in Cholesteryl), 0.68 (s, 3H, CH$_3$ in Cholesteryl), 1.33 (t, 2H, CH$_2$ in Cholesteryl), 1.53 (t, 2H, CH$_2$ in Cholesteryl). $^{13}$C NMR (125.7 MHz, CDCl$_3$, $\delta$ in ppm): $\delta =$ 156.41 (C=O), 139.87, 122.46, 74.34, 56.72, 56.18, 50.06, 43.74 (CH$_2$ in ethylenediamine), 42.33, 41.83 (CH$_2$ 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, $\nu_{\text{max}}$/cm$^{-1}$) : 3330 (NH stretching), 1717 (C=O), 1250 (COC). $^1$H-NMR (CDCl$_3$, 500MHz, $\delta$ 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$_2$-O-C=O), 3.24 (2H, t, CH$_2$-NH-C=O), 2.80 (2H, t, NH$_2$-CH$_2$-), 1.50-0.66 (m, all protons in cholesteryl group are similar as in compound 4a). $^{13}$C NMR (125.7 MHz, CDCl$_3$, $\delta$ in ppm): $\delta =$ 156.21 (C=O), 139.83, 122.65, 75.26, 56.70, 56.16, 50.03, 43.32 (CH$_2$ in ethylenediamine), 42.33, 40.83 (CH$_2$ 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.


**Synthesis of III:**

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

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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, ν max/cm⁻¹) : 3280 (≡CH) and 2110 (C≡C); ¹H-NMR (DMSO-d₆, 500MHz, δ in ppm) : 2.50 (d, 2H, -C≡C-H), 4.20-4.40 (m, 4H, -O-CH₂-C-), 4.70 (m, 2H, -O-CH-), 4.50 (d, 2H, -O-CH-CH-O-), 3.90-4.10 (d, 4H, -O-CH₂- 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


**Synthesis of IVa:**

The 4-azidobenzoic acid (I) (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, ν max/cm⁻¹) : 1724 (C=O), 2106 (-N₃), 1253 (COC). ¹H-NMR (CDCl₃, 500MHz, δ in ppm) : 8.0 (s, 2H, HAr-C(=O)-), 7.6 (2H, d, ArH), 5.26 (s, 2H, C=CH in cholesteryl), 4.61 (t, 2H, Cholesteryl CH-O-C=O), 1.03 (m, 6H, CH₃ in Cholestryl), 0.93 (d, 6H, CH₃ in Cholestryl), 0.84 (m, 6H, CH₃ in Cholestryl), 0.67 (m, 6H, CH₃ in Cholestryl), 1.30 (t, 4H, CH₂ in...
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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 procedure¹a-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, ν_max/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
Cholestryl), 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, ν_max/cm⁻¹) : 3332 (NH stretching), 1710 (C=O), 2100 (-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.


**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, v 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-
CH$_2$-and-O-CH- ), 3.65-4.25 (m, 6H, isosorbide ring protons), 0.70-2.49 (m, 45H, in Cholesteryl). $^{13}$C NMR (125.7 MHz, CDCl$_3$, 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

BCIC$_2$: Yield 44%; FT-IR (KBr, $\nu_{\text{max}}$/cm$^{-1}$) : 3334 (NH stretching),1714 (C=O), 1532, 1614 (C-C in Ar), 1258 (COC). $^1$H-NMR (CDCl$_3$, 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-CH$_2$-), 4.50 (t, 2H, Cholesteryl CH-O-C=O), 3.3 (4H, t, CH$_2$-NH-C=O), 1.14 (m, 6H, CH$_3$ in Cholesteryl), 0.97 (d, 6H, CH$_3$ in Cholesteryl), 0.86 (m, 6H, CH$_3$ in Cholesteryl), 0.66 (m, 6H, CH$_3$ in Cholesteryl), 1.32 (t, 4H, CH$_2$ in Cholesteryl), 1.49 (t, 4H, CH$_2$ in Cholesteryl). $^{13}$C NMR (125.7 MHz, CDCl$_3$, 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.

BCIC$_4$: Yield 51%; FT-IR (KBr, $\nu_{\text{max}}$/cm$^{-1}$): 3331 (NH stretching),1718 (C=O), 1528, 1617 (C-C in Ar), 1260 (COC). $^1$H-NMR (CDCl$_3$, 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-CH$_2$-), 4.47 (t, 2H, Cholesteryl CH-O-C=O), 3.28 (4H, t, CH$_2$-NH-C=O), 1.14 (m, 6H, CH$_3$ in Cholesteryl), 0.97 (d, 6H, CH$_3$ in Cholesteryl), 0.86 (m, 6H, CH$_3$ in Cholesteryl), 0.66 (m, 6H, CH$_3$ in Cholesteryl), 1.28 (t, 4H, CH$_2$ in Cholesteryl), 1.50 (t, 4H, CH$_2$ in Cholesteryl). $^{13}$C NMR (125.7 MHz, CDCl$_3$, 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 BCIC$_2$ (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 \( T_{gel} \) values are in accordance with the dropping ball method).

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**Fig. S4** Representative SEM images of BCIE in (a) toluene (2μm), (b) MEK (50μm), (c) DPE (10μm); (d) pyridine (30μm); (e) DMF (40μm) and (f) benzene (50μm).
Fig. S5 Representative SEM images of BCIE in (a) xylene (500 nm), (b) anisole (20 μm), (c) BCIC₂ in xylene (10 μm); (d) BCIC₄ in xylene (40 μm); (e) BCIC₄ in cyclohexane (10 μm) and (f) Gel-emulsions in styrene-water (90:10) (5 μm).
**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 BCIC$_2$ (up) and BCIC$_4$ 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 $^1$H-NMR spectra of BCIE gel in benzene-d$_6$ (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 $^1$H-NMR spectra of BCIE gel in pyridine-d$_5$ before and after addition of Zn$^{2+}$

Fig. S14 $^1$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) Zn$^{2+}$ in pyridine (b) Pd$^{2+}$ in pyridine (c) Zn$^{2+}$ in benzene and (d) Pd$^{2+}$ in benzene.
**Fig. S16** Temperature-dependent $^1$H-NMR spectra of BCIE/benzene-d$_6$ gel over the temperature range of 30 ~100 °C.
**Fig. S17** Concentration-dependent $^1$H-NMR spectra of BCIE/benzene-d$_6$ gel over the temperature range of 30 ~100 °C.
Fig. S18 Partial 2D-NMR spectrum of BCIE/benzene-d$_6$ 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, Ø2.5 mm, placed on the top of the gel, heating rate 5°C/min)