Soft Matter

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Journal Name

ARTICLE

Click Chemistry-Assisted, Bis-cholesteryl-Appended, Isosorbide-Based, Dual-Responsive Organogelators and their Self-Assemblies

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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A new series of symmetric, **b**is-**c**holesteryl-appended, **i**sosorbide derivatives (**BCIE**, **BCIC$_2$** and **BCIC$_4$**) were designed as gelators to respond to changes to their environment and were synthesized successfully. Among these derivatives, **BCIE** can gel a wide variety of organic solvents (23 solvents), suggesting that **BCIE** acts as a more versatile gelator than **BCIC$_2$** and **BCIC$_4$**. The CGC of the gels varies from 1.53 mM in 1-hexanol to 23 mM in pyridine. The results from the gelation ability in different solvents revealed that changing the linking group (ester/carbamate) attached to the cholesteryl units can produce a dramatic change in the gelation behavior of the compounds. The morphology of the as-formed organogels can be regulated by changing the types of organic solvents. The results from the electron microscopy studies revealed that the gelator molecule self-assembled into different aggregates, from wrinkled fibers to dense fibers with the change of solvents. The gels of **BCIE** in 1-hexanol and 1-octanol exhibited strong CD (circular dichroism) signals, indicating that the gelation induced supramolecular chirality in these gel systems. Secondary forces of van der Waals and π-π stacking (from both 1,2,3-triazole and aromatic units) played important roles in the aggregation of compounds in the solvents according to the FTIR and variable temperature ^{1}H-NMR analysis, and a mechanism for the gel formation was proposed. The *gel-to-sol* phase transition can be triggered by the addition of trifluoroacetic acid (TFA), and the gel state was obtained slowly (after 1 day) when neutralizing with triethyl amine (TEA), which indicated that the sol⇆gel phase transitions are tunable by pH, which is further supported by the ^{1}H-NMR and SEM analysis. In addition, the gel stability of **BCIE** was investigated using Cu^{2+}, Cd^{2+}, Ag^{2+}, Fe^{3+}, Hg^{2+}, Mg^{2+}, Pd^{2+}, Al^{3+} and Zn^{2+}, and the results showed that the *gel-to-sol* phase transition process could be selectively controlled by interaction with Pd^{2+} and Zn^{2+} because complexation with 1,2,3-triazoles destroyed the interactions between the triazoles, collapsing the gel, which was further evidenced by the ^{1}H-NMR and SEM analysis. However, the gel stability of **BCIE** was enhanced by the addition of Pd^{2+} and Zn^{2+} in presence of pyridine, whereas the gel collapsed in other solvents, which may be due to the chelating effect of the pyridine moiety. Another interesting factor of this gel is that when using the gelator as a stabilizer, stable water in oil (W/O) gel-emulsions were created, in which styrene can be used as the continuous phase, water as the dispersed phase with a stabilizer in the continuous phase of only 2% (w/v). Gel-emulsions were observed with any ratio of water to styrene.

Introduction

Supramolecular organogel materials have attracted considerable attention due to their unique structures and diverse potential applications in sensors, drug-delivery systems and as templates for preparing nano-materials. These gel systems are collections of low-molecular weight organogelators (LMWOG) organized with a multitude of weak but cooperative, non-covalent bonds (hydrogen bonding, π-π stacking, metal coordination and van der Waals forces)[1-4]. In general, there are two possibilities to form a supramolecular gel. One can either start from a polymer that is cross-linked by additional supramolecular interactions between the polymer chains or one can rely on the self-assembly of small low molecular weight organic molecules[5]. The latter approach is more challenging because it requires very stable noncovalent interactions between the individual small building blocks to ensure a sufficient degree of polymerization needed to form a gel.

As reported by S-I Kawano et al, the critical gelation concentration (CGC), gel-sol transition temperature (T_{gel}) and the gelation versatility for various solvents are the important factors that determine the gelation ability of the compounds[6]. Among these properties, the gelation versatility for various solvents is more important than other factors because there is no systematic

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x guideline for the design of gelators. Moreover, several characteristics have been noted among the various organogelators, including limited solubility at room temperature, complete dissolution upon heating, and highly directional self-assembly into 1-dimensional (1-D) fibers. Therefore, to elucidate the driving force for gelation, researchers have focused on reducing the structural complexity of LMWOGs[7]. Among these gelators, cholesterol-based LMWOGs have attracted a considerable amount of attention because of their versatility in gelation and the diversity of their structures. Several studies have been reported on cholesterol-based organogelators[2-5]. We recently reported the self-assembly of mono- and bis-cholesteryl-appended organogelators based on anthracene[8], azobenzene[9] and pyridine[10] conjugates. We studied (1) the effect of the alkyl chain length, (2) positional effect (meta vs para substitution effect), (3) effect of the linker (alkyl chain/benzene) and (4) the nature of the solvent on the gelation ability, liquid crystalline properties, tuning of the sol-gel phase transitions and their aggregation phenomena. Therefore, in the continuation of our research on the structure-property relationship of the gelation and aggregation phenomena, we wanted to determine the scope and limitation of our approach by extending our study to other molecules. Therefore, in this report, we introduced isosorbide and 1,2,3-triazole between cholesteryl units, and their structure-property relationships were studied with respect to their gelation and aggregation phenomena. Isosorbide is regarded as a promising monomer for polycondensation due to its attractive rigidity, chirality and non-toxicity[11] and has been widely used for the synthesis of polycarbonates[12], polyesters[13] and polyurethanes[14]. 1,2,3-Triazole is being explored as a binding site, in addition to attractive connecting units by click reaction[15]. Moreover, it is expected that introducing 1,2,3-triazole may provide interaction that may strengthen the criteria of gel formation, as reported in uracil-based organogelators[16]. The structural effects and thermal properties of the gelator molecules and gel stability by external stimuli, such as temperature, pH, effect of solvents and metal cations, were studied with respect to gelation. In addition, using this versatile gelator as stabilizer, water in oil (W/O) gel-emulsions were created, and their morphologies were studied with respect to increasing water content within the system. Because, surfactants which are commonly used as a stabilizers for the stabilization of gel-emulsions, are not very efficient and the gel-emulsions stabilized by them may suffer from phase inversion when the volume fraction of the dispersed phase reaches 0.65−0.70. In contrast, cholesteryl derivatives are much more efficient, and 2% (w/v) or even less than that is enough to produce a gel-emulsion with good quality[17]. Additionally, gel-emulsions created by them possess superior rheological properties. Therefore, we try to use our versatile gelators as a stabilizer for the preparation of gel-emulsions in this study.

Experimental

Instruments

All chemicals were purchased from Aldrich Chemicals and were used without further purification. All solvents were purified before use. Fourier transform infrared (FTIR) spectra were recorded using a Jasco VALOR III Fourier transform infrared spectrophotometer. Nuclear magnetic resonance (NMR) spectra were obtained using a Bruker AMX-400 (Darmstadt, Germany) high-resolution NMR spectrometer, and the chemical shifts were reported in ppm with tetramethylsilane (TMS) as an internal standard. The sample morphologies were characterized using field-emission scanning electron microscopy (FE-SEM, JSM-7001, JEOL, Japan) and transmission electron microscopy (TEM) with a JEOL JEM-1200 CX-II microscope and a Cu-grid substrate. The xerogel for the measurements (SEM and TEM) was prepared by vacuum freeze-drying of the gel formed in the solvent at the critical gelation concentration (CGC) for 12-24 h. The dried samples held on glass substrates were attached to a copper holder for SEM by conductive adhesive tape and were coated with platinum. For TEM, the gel was placed on a carbon-coated copper grid and then dried under vacuum. The X-ray diffraction (XRD) measurements of the xerogel were monitored by Rigaku RINT2000 with a scan rate of 1^{o}/min. Circular dichroism (CD) spectra were recorded using JASCO J-720 with a sample concentration of 10^{-4} M in an optical cell (0.1 mm optical path length). The sol-gel transition temperatures (T_{gel}) of the gelators were determined by the dropping ball method using a stainless steel ball (124 mg, Ø2.5 mm) placed on the top of the gel in a vial and then slowly heated at 1°C/min. The T_{gel} at which the steel ball reached the bottom of the vial was recorded.

Gelation Test

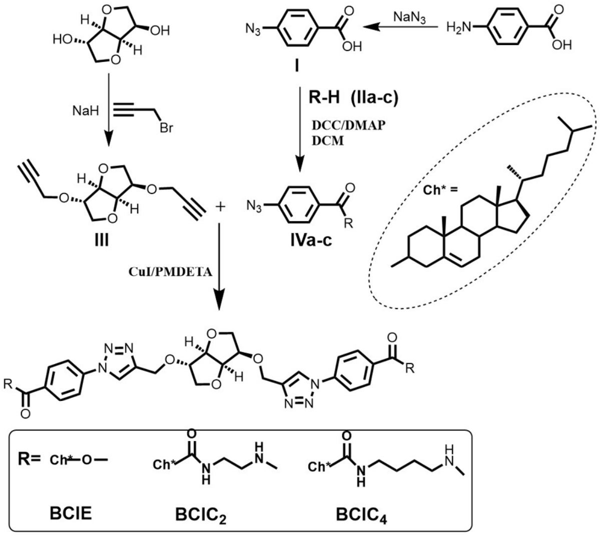
A pre-calculated weight of gelators (3 mg) and a measured volume of solvent (100 μL) were placed into a glass vial, and the system was heated until all solid materials were dissolved. The solution was then slowly cooled to room temperature, and the test tube was inverted to investigate gel formation. When an opaque or transparent gel formed, it was denoted by OG or TG; similarly, partial gelation was denoted by PG. Systems in which only solution remained throughout the tests were denoted by solution (S). The systems in which the gelator could not be dissolved even at the boiling point of the solvent were considered to be insoluble systems (I). Systems where heating resulted in the dissolution of the gelators and cooling resulted in their precipitation were denoted by P. In these experiments, the critical gelator concentration (CGC) was the lowest concentration that produced a gel. All concentrations were expressed in molar concentrations.

Preparation of Gel-Emulsion

Gel-emulsions were prepared according to the reported procedure[17]. In a typical preparation, 0.0040 g of the compound **BCIE** was added to a mixture of 0.2 mL of styrene and 0.8 mL of water at room temperature, and the resulting mixture was stirred and slightly heated if necessary to dissolve the compound. Then, the mixture was vigorously shaken by hand for 2 min; finally, a viscous and light yellow emulsion was produced. Formation of the gel-emulsion was confirmed by inverting the test tube to observe whether the mixture inside could still flow. A positive result was obtained when the mixture inside showed no fluidity.

Results and Discussion

The synthetic route for the designed symmetric dicholesterol-linked, isosorbide-based derivatives for gelators is shown in **Scheme 1**.



Scheme 1 Synthetic route for the designed organogelators

The designed molecule consists of cholesteryl (S), benzene (A) and ester/amide group (L), as in A(LS)2 type gelators. However, in our designed molecule, these ALS units were further connected to the isosorbide unit as building blocks through 1,2,3-triazole. These compounds (**BCIE**, **BCIC$_2$** and **BCIC$_4$**) were prepared from the azide derivatives (**IVa-c**), which were synthesized starting from 4-aminobenzoic acid and cholesteryl derivatives. The synthetic procedures and the spectroscopic characterizations of the precursors, intermediates and target compounds are provided in the supporting information. All of the spectral data for the synthesized intermediates and target compounds corresponded with the structures of the compounds.

The thermal behaviors of the synthesized compounds were evaluated by TGA analysis in nitrogen atmosphere at a heating rate of 10°C/min, and the representative thermograms are shown in **Fig. S1**. The results showed that all of the synthesized compounds are stable up to 200°C and start degrading thereafter in nitrogen. The degradation occurs in a three-step manner; the first step at approximately 205°C corresponds to cleavage of the ester/carbamate linkages. The second step at approximately 280°C is the outcome of cleavage of the ether linkage, and the third step at approximately 470°C is due to cleavage of the triazole ring.

Gelation Properties

The ability of the compounds (**BCIE**, **BCIC$_2$** and **BCIC$_4$**) to self-assemble was first tested by the formation of organogels in a variety of solvents of different polarity, and the results are summarized in **Table 1**.

Table 1 Gelation properties of representative compounds in various solvents [G=gel; WG=weak gel; TG= transparent gel; OG= opaque gel; P=precipitate; S=soluble; I= insoluble; GE= gel emulsion; CGC values (mM) were given brackets]

Solvents/Compound	BCIE	BCIC$_2$	BCIC$_4$
n-Hexane	I	I	I
n-Heptane	I	I	I
n-Octane	I	I	I
n-Decane	I	I	I
Cyclohexane	WG	I	TG (6.6)
Cyclopentanone	S	S	TG (9.9)
Cyclohexanone	TG	TG (5.14)	TG (6.6)
Methyl ethyl ketone	TG (7.68)	S	P
1-Propanol	I	I	P
2-Propanol	I	I	P
1-Butanol	I	I	I
2-Butanol	I	I	I
1-Hexanol	TG (1.53)	P	S
1-Octanol	OG (2.07)	S	S
m-Cresol	S	S	S
Benzene	TG (7.68)	S	S
Toluene	TG (1.92)	P	S
Xylene	TG (11.52)	PG (10.28)	TG (13.2)
1,4-Dioxane	S	S	S
DMF	TG (2.3)	S	P
DMSO	I	P	TG (4.95)
Pyridine	TG (23)	S	S
Diphenyl ether	TG (5.76)	S	S
Chloroform	S	S	S
THF	S	S	S
Anisole	TG (7.68)	S	S
Water	I	I	I
t-BMA	I	I	I
MMA	I	I	I
Styrene	S	S	S
Styrene:Water	GE	P	P

In the case of A(LS)$_2$ type molecules, the cholesteryl groups at the terminal positions have a profound effect on gelation. Therefore, it was expected that all of the designed molecules would exhibit gelation in a variety of solvents. However, only **BCIE** formed gel in multiple solvents; the other compounds formed gel in limited solvents. Therefore, the structure property relationships of these compounds were compared. In **BCIE**, the cholesteryl unit is directly attached to the aromatic ring through ester linkage [C(=O)-O-], whereas **BCIC$_2$** and **BCIC$_4$** were attached to the aromatic ring through carbamate linkages [C(=O)-HN-(CH$_2$)$_n$-NH-C(=O)-O-] with varying alkyl chain lengths.

Unlike esters, the carbamates [HN-C(=O)-O-] can form hydrogen bonding. Esters can participate in hydrogen bonds as hydrogen-bond acceptors, but cannot act as hydrogen-bond donors. Therefore, the compounds containing carbamate linkages are expected to form gel in many solvents than ester linkage due to their hydrogen bonding ability. However, in our case, the compounds containing ester linkages (**BCIE**) formed gel in more of the solvents than the carbamate compounds (**BCIC$_2$** and **BCIC$_4$**), which may be due to the sterically hindered structures of the **BCIC$_2$** and **BCIC$_4$,** as shown in **Fig. S2**. Since unlike amides, esters are structurally flexible functional groups because rotation about the C-O-C bonds and they tend to be less rigid than the corresponding amides. From the **Fig. S2**., it was noted that **BCIE** is less crowded than **BCIC$_2$** and **BCIC$_4$**, and it is possible that several molecules come close together and aggregate in an ordered fashion. However, in the case of **BCIC$_2$** and **BCIC$_4$**, only random cholesteryl-cholesteryl interactions are possible so that it can gel only a limited number of solvents compared to **BCIE**. Moreover, the other factor affecting the gelation of **BCIC$_2$** and **BCIC$_4$** is intramolecular hydrogen bonding. Strong intramolecular hydrogen bonding leads to high solubility (*i.e.* dissolution of the gelator) [18a], which may be the reason why **BCIC$_2$** and **BCIC$_4$** did not form gel in many of the solvents. When comparing the structurally isomeric compounds with varying spacer lengths (**BCIC$_2$** and **BCIC$_4$**), **BCIC$_4$** forms gel in more solvents than **BCIC$_2$**. These results indicate that the length of the flexible alkyl chain between the aromatic and cholesteryl units significantly affected the gelation of the compounds. This phenomena was further supported by our previous report, in which we found that increasing the alkyl chain length up to a six carbon chain enhance the gelation ability in bis-cholesteryl-appended derivatives with azobenzene/pyridine as building blocks[8-10].

The compound **BCIE** formed gel in cyclic solvents, such as cyclohexane and cyclohexanone, and long chain linear alcohols, such as 1-hexanol and 1-octanol. Polar solvents, such as DMF, methyl ethyl ketone, pyridine, and anisole, and low polar solvents, such as benzene, toluene, xylene, and diphenyl ethers, also resulted in gelation. Among the synthesized compounds, **BCIE** resulted in gel formation in 12 solvents (**Table 1**). **BCIC$_2$** formed gel in 2 solvents, in which one was a partial gel (PG), which means that CGC is not sufficient to make a strong gel and a higher concentration (>10 mM) is needed to form a strong gel. **BCIC$_4$** formed gel in 4 solvents, in which 2 solvents resulted in partial gels. The CGC varied from 1.53 mM in 1-hexanol to 23 mM in pyridine. When comparing the critical gelation concentrations of all compounds, the compound with ester linkers with no alkyl chains (**BCIE)** required very low concentrations for effective gelation relative to the other compounds with carbamate linkers and increasing spacer lengths (**BCIC$_2$** and **BCIC$_4$**). This finding indicated that the effect of linker on the ability of gelation and **BCIE** was better gelation ability than the other compounds studied. The gel color varied from dirty white to pale yellow or orange and depended on the color of the synthesized compound. The color of the gels had no apparent change during heating and cooling in solvent (**Fig. 1a**).

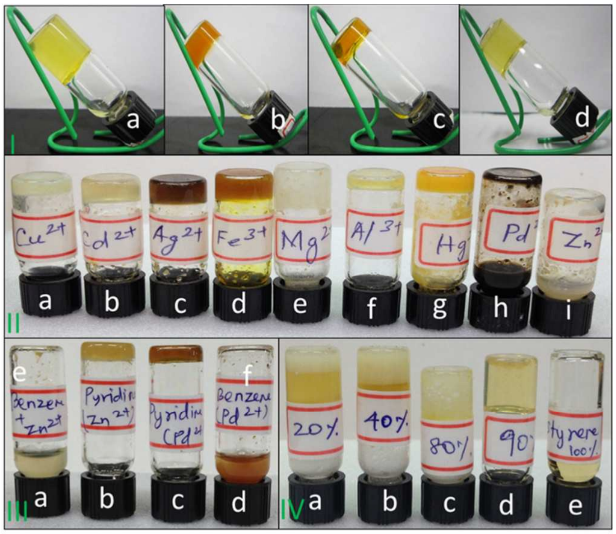


Fig. 1. Representative real images of (I) gels of BCIE in (a) 1-hexnol, (b) pyridine (c) anisole and (d) 1-octanol; (II) stability of BCIE gels in presence of different metal ions in 1-hexanol; (III) stability of BCIE/benzene and BCIE/pyridine gels in presence of Pd^{2+} and Zn^{2+} (IV) Gel-emulsions of BCIE(2

wt%)/Styrene/water in which water content (a) 20% (b) 40% (c) 80% (d) 90% and (e)without water

The gelator molecules formed transparent gels in most of the tested solvents, with the exception of 1-octanol, which resulted in opaque gel and demonstrated excellent thermoreversibility, which means the compounds could be brought into solution by heating and the hot solution could be converted back to the gels upon cooling to room temperature. This cycle could be repeated several times. The gel-sol transition temperatures (T_{gel}) of the gelators were determined by the dropping ball method[10, 18b-c] (naked eye detection) and were further supported by DSC analysis. The naked eye results were in accordance with the DSC analysis. The results from the DSC analysis of the gels are shown in **Fig. S3,** and the data are given in **Table S1**. The results from the DSC analysis of the gels revealed that the T_{gel} values of the gelators were above 60°C. These results indicate that the gels were not dissociated up to 60°C, suggesting that the gels were thermally durable, which may be due to the strong interactions between the gelators and solvent molecules. The gels kept in sealed vials were stable for more than 6 months, demonstrating their long-term stability at room temperature.

Table 1 shows that none of the compounds (**BCIE**-**BCIC$_4$**) formed gel in any of the linear alkane solvents, such as *n*-hexane, *n*-hexane, *n*-heptane, *n*-octane and *n*-decane or in monomers, such as tertiary butyl methacrylate (*t*-BMA), methyl methacrylate (MMA) and styrene. However, **BCIE** gels the mixture of water and styrene at room temperature. To investigate the effect of the water content on the phase behavior of the gel-emulsions, **BCIE**/water/styrene with different water contents, including 0, 20, 40, 60,70, 80, 90 and 100%, was studied. The systems with 0% and 100% water did not form gel, whereas all other proportions formed strong gels. However, the systems below 80% formed heterogeneous gel, whereas the 90% water content formed homogeneous gel, as shown in **Fig. 1 (IVd). BCIE** is insoluble in water but highly soluble in styrene. However, the mixture of styrene and water formed typical gel-emulsions when the water content exceeded 80% (v/v).

Morphological studies

To gain visual insights regarding the morphologies of the molecular aggregation modes, all of the gelators were subjected to SEM analysis, and the results are depicted in **Fig. 2** and **Fig. S4-S6**. As observed in the SEM images of the xerogels, all of the derivatives existed as self-assembled, one-dimensional, fiber-like aggregates with lengths of several micrometers and diameters of approximately 100-300 nm. These xerogels undergo further entanglement to form bundles of fibrous aggregates (**Fig. 2a-d**). The nanostructures of the xerogels in different solvents are significantly different, and the morphologies of the aggregates change from sponge, fiber, and rod, to wrinkled textures with the change of solvents.

For example, the xerogel of **BCIE** exhibited fibrous networks in 1-butanol, 1-octanol, MEK, DMF, xylene, benzene and cyclohexane, and cross-linked, interconnected, spherical spheres were observed for anisole, pyridine and DPE. Moreover, the xerogel of **BCIE** in cyclohexanone exhibited long and straight rod-like morphologies, whereas toluene exhibited flower-like morphologies at the critical gelation concentration. Similarly, the xerogel of **BCIC$_2$** in cyclohexanone exhibited fibrous networks, whereas in xylene, interconnected uniform spherical spheres were observed. The xerogel of **BCIC4** exhibited entangled spherical spheres in xylene, whereas flower-like morphologies were observed in DMSO and cyclohexane.

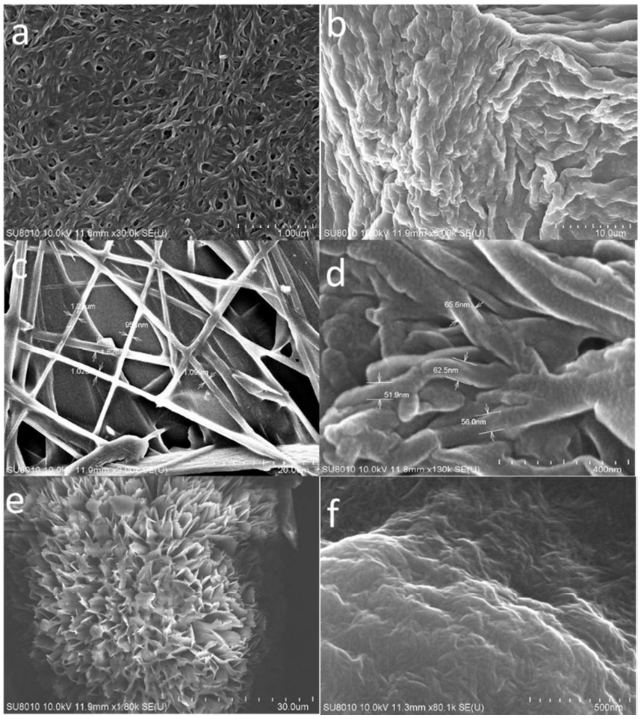


Fig. 2. Representative SEM images of BCIE in (a) 1-hexanol (1μm), (b) 1-octanol (10μm), (c) cyclohexanone (20μm); (d) BCIC2 in cyclohexanone (400 nm); (e) BCIC4 in DMSO (500 nm) and (f) Gel-emulsions in styrene-water (90:10).

In some cases (**BCIE** in 1-hexanol, xylene, and cyclohexane, and **BCIC$_2$** in cyclohexanone), twisted helical fiber structures were observed (**Fig. 2a** and **2d**), which resulted from the presence of a cholesteryl group, which provided a chiral environment that induced the helical self-assembly structure. Such twined structures were expected for all of the gel systems but were only observed in a few compounds. In most cases, highly dense fibrous structures composed of several long-range fibrous aggregates were observed, which indicated very strong inter-fiber interactions. The xerogels of **BCIC$_2$** and **BCIC$_4$** exhibited identical textures of microspheres of uniform size in toluene, and **BCIC$_4$** exhibited similar morphology both in cyclohexane and DMSO. The difference in morphologies is attributed to the various assembly modes and forces between gelators and solvent molecules. The differences of the morphologies between different organogels is due to the different strengths of the hydrophobic forces between cholesteryl segments, π-π stacking and steric hindrance between aromatic rings, which played an important role in regulating the intermolecular orderly staking and formation of special aggregates or twisted fibrous structures[9, 19].

The morphology of the gel-emulsions, the functions of the stabilizer, and the structures of the aggregates of the stabilizer in the gel-emulsions were studied by SEM analysis, and the results are shown in **Fig. 2** and **Fig. S5-S6**. The stabilizer in all of the gel-emulsion systems was always maintained at 2% (w/v). The xerogels of 10% water content gel-emulsions exhibited a number of long fibrous structures as observed for the corresponding gelator **BCIE** in xylene and cyclohexane. The 10% water content maintained the fibrous structure of the gelator (here stabilizer) **BCIE**. However, after increasing the water content to ≥ 20%, the fibrous structure vanished and the agglomeration of sheet-like structures was observed. These results suggested the formation of a heterogeneous system when increasing the water content over 20%. Therefore, the gel-emulsion of the 10% water content was used for further study.

The morphological behavior of the xerogels was further supported by the TEM analysis, the results of which are depicted in **Fig. 3** and **Fig. S7-S8**. A small, frizzled, fibril structure with a diameter of 100-150 nm was observed from the xerogel of **BCIE** in cyclohexane, which shows a highly dense fibrous structure under SEM analysis (Fig. 2e). The xerogel of **BCIE** in 1-hexanol and 1-octanol exhibited twined fibers with right-handed helical structures, which cannot be seen clearly under SEM. The presence of helical structures was further supported by the circular dichroism (CD) analysis of the **BCIE** gels at room temperature, and the results are shown in **Fig. S9**. From the figure, it was observed that **BCIE** in 1-hexanol and 1-octanol exhibited very strong positive cotton effect at 285 and 288 nm respectively. These results revealed that the strong interactions (π-π stacking from the aromatic/triazole unit and hydrophobic interactions from the cholesteryl units) between the molecules self-assembled in the gel resulted in gelation-induced supramolecular chirality, which caused strong CD signals[20]. However, in many cases, the helical structures could not be observed in the TEM images because the dense network of the entangled fibrils affected the clarity of the structures of the single fiber textures. The xerogel of **BCIE** in cyclohexanone exhibited long-range rod-like structures, which corresponded with the SEM results.

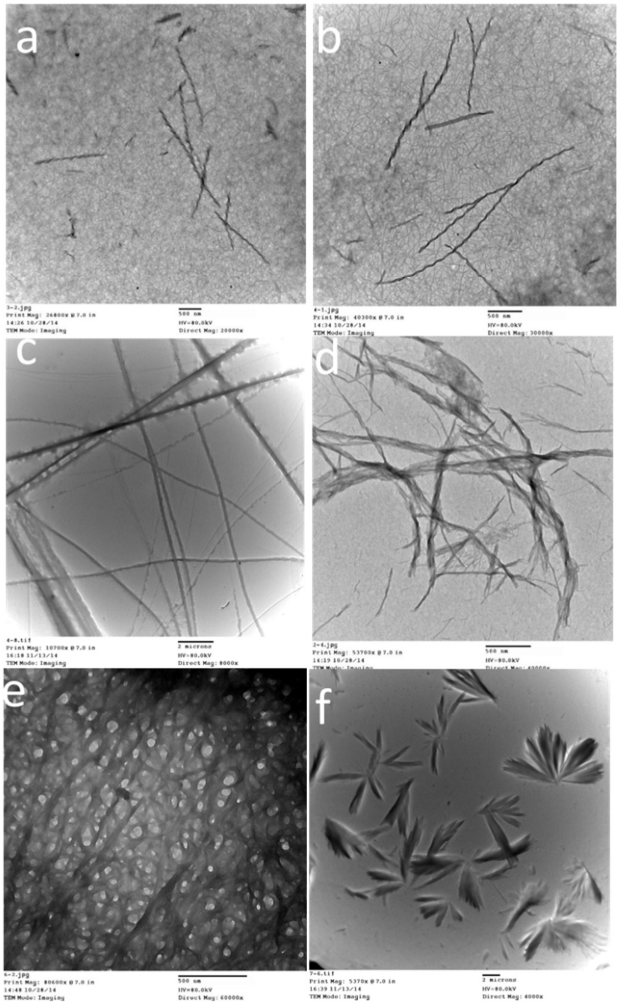


Fig. 3. Representative TEM images of BCIE in (a) 1-hexanol, (500nm), (b) 1-octanol (500nm), (c) cyclohexanone (2μm), (d) cyclohexane (500nm), (e) toluene (500 nm); (f) BCIC4 in DMSO (2μm).

The xerogels of **BCIC$_2$** and **BCIC$_4$** in xylene resulted in the entanglement of spherical nano-spheres, as observed from the SEM analysis. Similarly, the xerogel of **BCIC$_4$** in DMSO resulted in feather-like structures, whereas flower-like morphologies were observed in the SEM analysis. The difference in morphologies were ascribed to the difference in interaction between substrate and solvents. The xerogel of the **BCIE** gel-emulsion with a 10% water content exhibited fibrous structures, whereas other proportions did not exhibit remarkable textures under TEM, which may be due to the heterogeneity of the system.

Stability of the gels as a function of pH

The stability of the gels as a function of pH and sonication was investigated. Ultrasound did not affect the gels or solution state, indicating that the phase transitions could not be tuned by sonication. The 20 mM solutions of **BCIE** in 1-hexanol and DMF solvents were prepared, and acid-base titrations were conducted using trifluoroacetic acid (TFA) and triethyl amine (TEA)[21]. The addition of 10 equivalents of TFA to the 20 mM solution of **BCIE** affected the gel formation, and the addition of TFA to the gel resulted in dissolution (**Fig. S10**). However, after neutralization with 10 equivalents of TEA, the gel state could be retained after 1 day. However, the obtained gel after neutralization was not as strong as the "as prepared" gel. The gel was stable during inversion of the tube; however, the gel state collapsed to a partial gel if any strong mechanical force, like vigorous shaking, occurred, unlike the "as prepared gel". These results indicate that phase transitions can be triggered rapidly in acidic medium but slowly in basic medium. However, these cycles could be repeated only two times; afterwards, the solution state remained constant. These sol ⇆ gel phase transitions were further supported by the ^{1}H-NMR analysis of the **BCIE** gel in pyridine-d5 along with TFA, and the results are shown in **Fig. S11**. The broad signals observed in the gel state became sharper upon addition of TFA. Moreover, the observation of a new peak at 9.8 corresponds to the TFA, and there are no changes observed after addition of TMS. After the addition of triethyl amine (TEA) as a base to the BCIE-pyridine gel/TFA mixture, the gel state recovered and the NMR results showed the same pattern of the "as prepared gel" (result not shown). In addition, the SEM analysis of the **BCIE** gel treated with TFA in benzene and 1-hexanol solvents were performed, and the results are shown in **Fig. S12**. When comparing the morphology of the "as prepared" gel and the TFA-treated samples, the highly entangled dense fibers of the "as prepared" gel were collapsed when treated with TFA in both cases (**Fig. S12a** and **b**), and the fibrous textures were almost regained after neutralization with TEA (**Fig. S12c**). These results revealed that **BCIE** gels could be triggered by pH.

Stability of the gels over metal cations

1,2,3-Triazole provided a coordination site in the formation of stable metal complexes[15,16]. The gel stability of **BCIE** (in 1-hexanol) was tested with the influence of Cu^{2+}, Cd^{2+}, Ag^{2+}, Fe^{3+}, Hg^{2+}, Mg^{2+}, Pd^{2+}, Al^{3+} and Zn^{2+}. With progressive addition of 10 equiv of these cations, only the gel phases treated with Zn^{2+} and Pd^{2+} w collapsed, and the other gels phases were stable with Cu^{2+}, Cd^{2+}, Ag^{2+}, Fe^{3+}, Hg^{2+}, Al^{3+} and Mg^{2+} [**Fig. 1 (IVa-i)**]. The results demonstrated that the gel phase had a selectively responsive nature to metal cations, which is acceptable because both of these metal ions can be selectively complexed by 1,2,3-triazole-oxygen (ether/amide) linkages (as coordination sites), as shown in **Fig. 4,** as observed from the reported literature[22], in which the coordination sites acted as excellent sensors for Zn^{2+} and Pd^{2+}.

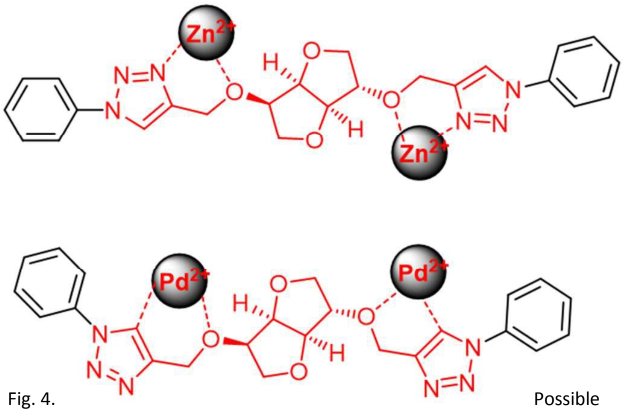


Fig. 4. Possible coordination of **BCIE** with Zn^{2+} and Pd^{2+}

To support this phenomenon, the ^{1}H-NMR spectra of **BCIE** gel treated with Zn^{2+} and Pd^{2+} were recorded in pyridine-d$_5$. The addition of Zn^{2+} and Pd^{2+} to **BCIE**-pyridine gel did not result in the *gel-sol* phase transition as was observed in 1-hexanol solvent; instead, the addition enhanced the stability of the "as prepared gel" (became hard gel) [**Fig. 1** (**III b-c**) and **Fig. S10**). Moreover, from the NMR results with the Zn^{2+} hard gel, the peaks between 4.5 and 5.5 ppm, were shifted to 5.5-6.5 ppm (**Fig. S13)**. The experiments were repeated with benzene-d6, which resulted in *gel-sol* phase transitions, as was observed for 1-hexanol (**Fig. 1**). Therefore, these results suggested that the addition of metal ions to the pyridine (hetrocyclic solvents) gels enhances the gel stability, which may be due to the chelating effect of pyridine. The ^{1}H-NMR analysis of the **BCIE** gels (in benzene) is shown in **Fig. S14**. The broad signals observed in the gel state became sharper upon addition of Zn^{2+}. However, the signals remained or became broader with the Pd^{2+} addition due to the paramagnetic relaxation effect exerted by the Pd^{2+}ions. The *gel-sol* phase transition occurred in solvents like benzene and 1-hexanol (other than pyridine) because the binding behavior of 1,2,3-triazole with Pd^{2+} and Zn^{2+} destroyed the π-π interaction between 1,2,3-triazoles, which resulted in the collapse of the gel because the formation of complex caused the environment to be highly sterically hindered, which prevented the other molecules from coming close to each other for aggregation, thereby reducing the chances of π-π interactions to allow *gel-to-sol* phase transitions. These results proved that 1,2,3-triazole was involved in the formation of the gel through π-π interactions, in addition to the aromatic units. These phenomena were further supported by the SEM analysis of the **BCIE** gels (both in benzene and pyridine) treated with Zn^{2+} and Pd^{2+}, and the results are depicted in **Fig. S15**. The results revealed that the addition of Zn^{2+} and Pd^{2+} in pyridine maintained and even improved the entangled fibrous textures compared to the morphology of the “as prepared” gels, respectively, whereas the fibrous networks disappeared in benzene. These results indicated that metal ion-induced *gel-sol* phase transitions occurred only in benzene, whereas in pyridine, the gelation ability was improved by the addition of metal ions.

To study the formation and the thermoreversibility of the gels, the temperature-dependency of the ^{1}H-NMR spectra was determined for **BCIE** in pyridine-d_5 and in benzene-d_6 [14]. These results are shown in **Fig. 5** and **S16**. In pyridine-d_5, with increasing temperature, the peaks at approximately 2 ppm and 8.8 ppm, corresponding to cholesteryl and aromatic protons, respectively, became sharp and well-separated compared to the room temperature spectra. Moreover, the peak at 4.3 ppm, corresponding to the O-CH- group of the cholesteryl unit, shifted downfield at 50°C and then shifted upfield thereafter with increasing temperature, which revealed that the van der Waals interactions between the cholesteryl groups were disturbed at this temperature range, leading to spreading of the speaks and a consequent sharpening of the signals. Increasing the temperature disrupted the supramolecular arrangement and decreased the effects of the secondary forces. Similarly, the concentration-dependent ^{1}H-NMR results (**Fig. S17**) revealed the broadening of peaks, especially for the cholesteryl region between 2.5 and 1 ppm, suggesting a strong interaction between cholesteryl units, which was further supported by the partial 2D NMR of the **BCIE** gel in benzene shown in **Fig. S18**. These observations revealed that the van der Walls forces and π-π stacking of the aromatic moieties played important roles in gel formation. In the case of benzene-d6, there was no remarkable changes, except the sharpening of the peaks.

Further attempts to study the aggregation phenomena by the XRD pattern of the gels failed because the results from the XRD showed no reflection peaks (**Fig. S19**) in both the small and wide angle for **BCIE** gels (1-hexanol, 1-octanol and benzene) because the molecular arrangement in the organogelators was disordered [23].

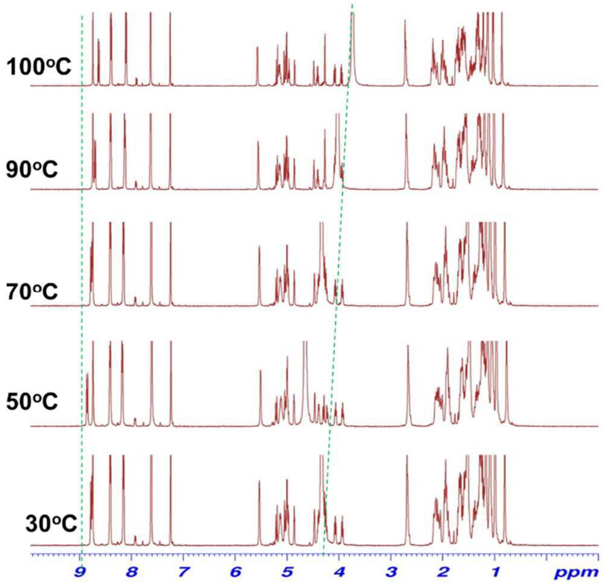


Fig. 5 Temperature-dependent ^{1}H-NMR spectra of BCIE/pyridine-d_5 gel over the temperature range of 30 ~100 °C

Moreover, the FT-IR spectra of the gelator **BCIE** in the solid, solution ($CHCl_3$) and gel state, both in 1-hexanol and 1-octanol, were recorded, and the results are shown in **Fig. S20**. From the figure, it was observed that the peak for aromatic hydrocarbons (ArH) at 3094 cm^{-1} and C=C stretching at 1505 cm^{-1} in the solid state were shifted to 2950 cm^{-1} and 1465 $cm^{-1,}$ respectively, in the gel state, which indicated that aromatic protons were involved in the gel formation. The presence of a new broad peak for the 1-hexanol and 1-octanol gel at approximately 3300 cm^{-1} resulted from the OH stretching of the solvents. The reason for the new peak at approximately 2350 cm^{-1} for the 1-octanol gel was unknown. The peak for the 1,2,3-triazole ring at 1586 cm^{-1} was merged after the gel was obtained. Similar results were observed for other gels of **BCIE** (**Fig. S21**). These results support the above phenomena of gel formation using the cooperative effect of van der Walls forces and π-π stacking of aromatic moieties and triazole units. Therefore, based on the available evidence, the mechanism of aggregation was proposed, and the schematic representation[24] of the aggregation of gelator **BCIE** is shown in **Fig. 6**.

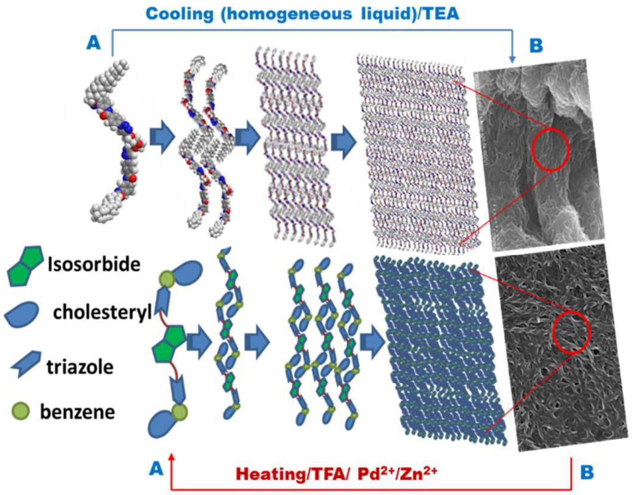


Fig. 6 Schematic representations of bundle aggregation and organogel formation

Conclusion

In summary, a new family of symmetric isosorbide derivatives (BCIE, BCIC$_2$ and BCIC$_4$) was designed, synthesized and characterized spectroscopically. **BCIE** was a more versatile gelator than BCIC$_2$ and BCIC$_4$ in different organic fluids, ranging from non-polar to highly polar. The aggregation phenomena of the gels by SEM and TEM analysis revealed the formation of fibrous structures. The gels were affected by temperature, pH and metal cations, like Pd^{2+} and Zn^{2+}. Regarding effect of temperature on the BCIE gels, the sol-gel phase transitions occurred after any number of cycles without change. Regarding the pH, sol-gel phase transitions occurred only after two cycles, and the solution state was then constant. Regarding the addition of metal ions, BCIE gels were selectively affected by Pd^{2+} and Zn^{2+}, which enhanced the gel stability of **BCIE** in pyridine solvent, whereas the gels collapsed and turned to the solution state in the other solvents. These effects of external stimuli on the BCIE gels were further supported by the ^{1}H-NMR and SEM analysis. The solution and gel state investigation by FTIR and variable temperature ^{1}H-NMR spectroscopy of compound **BCIE** suggested that both ⍰π-π stacking interactions (from aromatic and triazole rings) and van der Waals forces between the cholesteryl units were the driving forces for the process of self-aggregation, and a gel formation mechanism was proposed. In addition, **BCIE** is also an efficient stabilizer for gel-emulsions of water/styrene at room temperature. These systems represent an example of smart gels, which display the ability to respond to various changes in their environment. The use of gel-emulsions as a template for the preparation of silver nanowires and single-crystal halide salt wires is under progress.

Acknowledgements

The authors thank the National Science Council (NSC) of the Republic of China (Taiwan) for financially supporting this research under Contract no. NSC 101-2221-E-006- 074-MY3 and MOST 104-2221-E-006-242. This research was, in part, supported by the Ministry of Education, Taiwan, R.O.C. The Aim for the Top University Project to the National Cheng Kung University.

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Graphical Abstract

Click Chemistry-Assisted, Bis-cholesteryl-Appended, Isosorbide-Based, Dual-Responsive Organogelators and their Self-Assemblies

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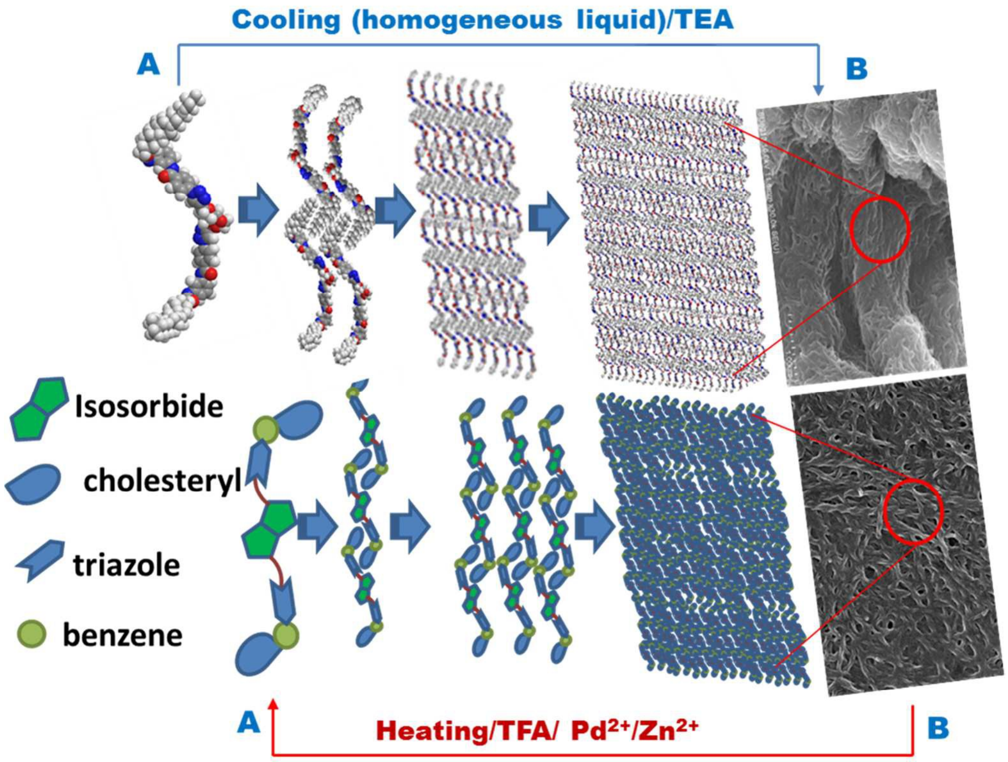

The aggregation of bis-cholesteryl-appended, isosorbide derivatives (**BCIE, BCIC$_2$ and BCIC$_4$**) in solvents and their response to external stimuli (temperature, pH and metal cations) were explored. By using the **BCIE** gels as stabilizers, gel-emulsions were created in styrene-water mixtures.