New gelators of urea-containing triazine derivatives: effects of aggregation and optical features in different organic solvents

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New gelators of urea-containing triazine derivatives: effects of aggregation and optical features in different organic solvents

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New gelators for urea-containing triazine derivatives were synthesised, and their gelation potential was examined using different organic solvents. These compounds were found to form the organogels with a variety of organic solvents, such as hexane and other solvents. The elongated alkyl tails of the gelators displayed an obvious decrease in the critical gelation concentrations of apolar solvents and an increase in the compatibility of gelation in polar solvents. The resulting thermo-reversible gels were characterised by using the dropping ball method and a number of other instruments. The melting temperature (Tm) of the gels in decalin and CCl_4 increased with the gelator concentrations. The intermolecular hydrogen bonding of gelation in different organic solvents was observed using an FT-IR spectrometer. Temperature-dependent UV–vis and fluorescence analysis showed that the organogels displayed diverse aggregations and various fluorescence effects in different organic solvents. Blue fluorescence and J-aggregation in decalin and the quenched effect and $\pi-\pi$ stacking in CCl_4 were observed. Further, the morphological self-assembled feature in different organic solvents was studied with a scanning electron microscope, and the morphological features demonstrated that there were different aggregations in different solvents. In conductivity electrolyte experiments, the organogel electrolytes exhibited high conductivity (σ) compared with the corresponding tetrabutylammonium perchlorate (TBAP)/THF solution. The conductivity of the gel electrolytes increased with the concentration of the electrolyte salts and temperature. When the sol–gel temperature was achieved, a high ion conductivity was observed compared with the corresponding TBAP/THF solution. When the ratio of the added electrolyte salts exceeded 5%, gelation was inhibited. Furthermore, the effect of the electrolyte salts on the Tm of the gel was confirmed. The added electrolyte salts affected the gelation ability, but did not affect the sol–gel temperature.

Keywords: gel; hydrozen bonds; triazin; self-assemble; ureas

Introduction

Supramolecular chemistry has attracted enormous interest and attention because of various factors, such as the use of hydrogen bonding, $\pi-\pi$ stacking, and solvophobic and donor–acceptor interactions to control the molecular order, thus making it a challenging topic for research (*1–7*). One of the challenges faced involves organogel, which is spontaneously self-assembled to form a soft solid-like mass by entrapping a large volume of solvent between the self-assembled formations. Organogel can be applied in a wide range of applications and to diversified fields. The base of the gelator consists of porphyrins, phthalocyanines, phenylenevinylenes and perylene bisi-mides, which have been discussed in other studies (*8–11*). The above-mentioned dyes have already been applied to light-harvesting systems, photovoltaic cells, field-effect transistors and light-emitting diodes (*12–14*). A number of research reviews have presented various types and applications of organogels (*15–17*). One study in the optoelectronic field that attracted our attention involved

the control of hydrogen-bonding interaction and ionic salts to induce aggregative changes (*18*).

New gelators for urea-containing triazine derivatives have yet to be studied. Therefore, this paper examines the development of organogels derived from triazine derivatives and the induced aggregative changes in gels using different organic solvents.

Results and discussion

Synthesis

The present 1,3,5-triazine-containing compound was synthesised from 2,4,6-trichloro-1,3,5-triazine and a nucleophile. Compound **2** was synthesised by using the di-*tert*-butyl dicarbonate in Scheme 1. In Scheme 2, the 2,4,6-trichloro-1,3,5-triazine and compound **2** were reacted in DMSO to obtain compound **3**. Further, compound **4** was obtained from the hydrolysis of compound **3**. Finally, compound **5** was synthesised from compound **4** and isocyannate reacted in dioxane.

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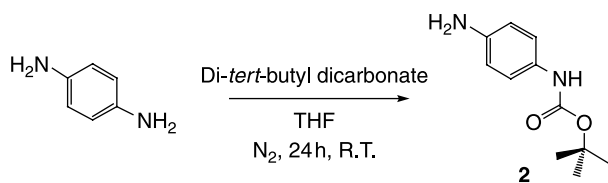
Scheme 1.   *tert*-Butyl *N*-(4-anilino) carbamate.

All of the reactions of the compounds were stirred and heated at reactive temperatures under N_2 to avoid oxidation of the amine. The following abbreviations for compound **5** were used: TLUAT, (2,4,6-tris(*p*-*N'*-laurylureido-anilino)-1,3,5-triazine); TOUAT, (2,4,6-tris(*p*-*N'*-octadecylureido-anilino)-1,3,5-triazine).

Gelation of organic solvents: critical gelation concentration (CGC)

These compounds were found to form organogels with a variety of organic solvents, such as hexane and other solvents. The CGC of the compounds in different solvents is summarised in Table 1. From these values, it is apparent that TOUAT and TLUAT were the effective gelators. In apolar solvents, such as hexane, cyclohexane and decalin, TOUAT and TLUAT formed long alkyl chains to immobilise the solvents and yielded gels. The CGC of the gel increased with the polarity of the solvent. However, when the polarity of the solvent became too high, the gelation became solubilisation and precipitation occurred.

A comparison of the elongated alkyl tails of TOUAT with TLUAT clearly showed the decrease in the CGC in apolar solvents and the increase in the compatibility of gelation in polar solvents. This was clearly exhibited whether the intermolecular hydrogen bonds of the urea groups were destroyed or not. The longer alkyl chains could assist the gel formation in apolar solvents and increased the gelation ability through the van der Waals interaction in polar solvents (*17–20*). However, in chlorinated solvents, such as CCl_4 and others, the gels underwent a colorimetric change to blackish yellow, thus indicating a charge transfer.

The organogels listed in Table 1 were completely transparent and stable with mechanical agitation, except for those obtained from pyridine and dichloroethylene (DCE) (*17–19*).

Thermotropic behaviour of the gels

The relationship between the gel concentrations and the melting temperatures (Tms) of the gels was studied in decalin and CCl_4 by the dropping ball method, and the results are displayed in Figure 1. The Tm of the gels in decalin and CCl_4 increased with the gel concentrations. The TLUAT gel in decalin displayed an obviously higher sol–gel temperature and stability compared with the TOUAT gel. The Tm decreased with the elongation of the alkyl tail, which was ascribed to the fact that the TOUAT gelator with the longer alkyl tails was dissolved easily in decalin. In contrast, the TLUAT displayed a lower solubility in apolar solvents and hence a higher melting temperature. Furthermore, the TLUAT and TOUAT gels in CCl_4 exhibited lower sol–gel temperatures compared with the gels in decalin. Clearly, the gels in CCl_4 were easily destroyed by an increase in temperature.
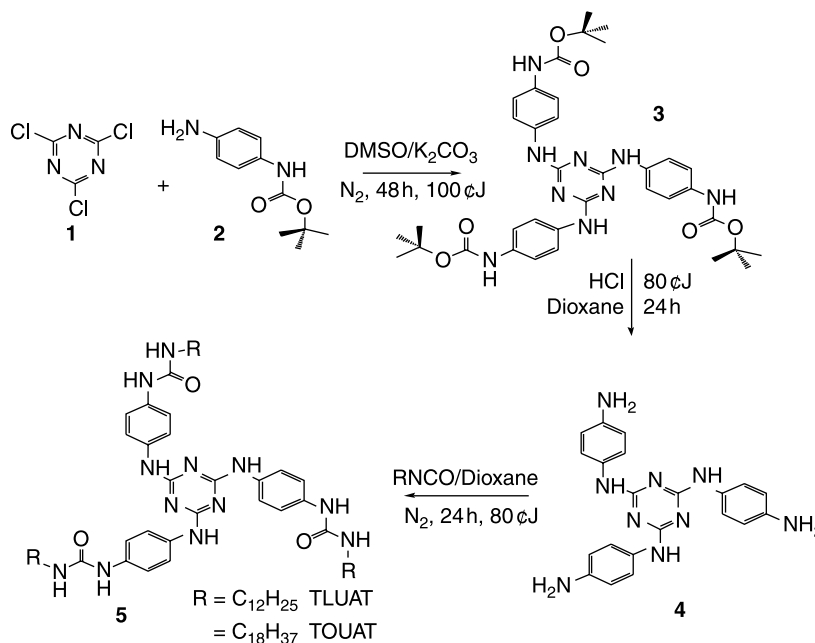

Scheme 2.   Synthesis of 2,4,6-tris(*p*-*N'*-alkylureido-anilino) triazine.

Table 1. Gelation properties and CGC[a].

Compounds/solvents	Hexane	Cyclohexane	Decalin	Toluene	THF	Dioxane	Pyridine	DMF	NMP	DMSO	Chlorinated solvents			
											CCl$_4$	CHCl$_3$	DCM	DCE
TLUAT	>1.5	>2	>2	>4	>5	gp	s	s	s	s	>4	>6	>8	>10[b]
TOUAT	>1	>1.5	>1.5	>3	>5	gp	>6[b]	gp	s	gp	>3	>5	>8	>10[b]

[a]CGCs had been given in mg/ml.
[b]The following abbreviations were used: cc, colorific change; I, insoluble; p, precipitate; b, turbid; s, soluble; gp, gel-like precipitate.
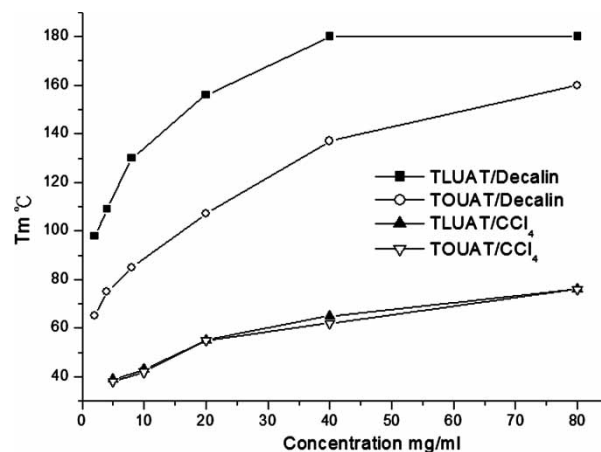

Figure 1. The Tms of the organogels in decalin and CCl$_4$ had been obtained by the dropping ball method.

It was suggested that the CCl$_4$ could affect the NH group of the gelators with an increase in temperature. Further, the intermolecular hydrogen bonds of the urea groups were destroyed. In addition, the gels in decalin displayed a higher sol–gel temperature compared with the gels in CCl$_4$ because decalin has a higher boiling point and slower volatility than CCl$_4$ (*4, 21, 22*).

FT-IR experiments

The relationship between the gelation ability and intermolecular hydrogen bonding was studied by FT-IR spectroscopy since the NH-stretching and the amide-I and Π bands of urea generally show large shifts in the IR spectrum upon the formation of hydrogen bonds. All the characteristic data for TLUAT and TOUAT are listed in Table 2. When the concentration of compounds (0.5 mg/ml) was lower than the CGC in decalin, the solution became viscous. The viscous solution of TOUAT in decalin showed absorption peaks at 3424 (N—H), 1630 (amide-I) and 1566 (amide-Π) cm^{-1}, as indicated in Table 2. When the gel was formed at 5 mg/ml, the peaks shifted towards 3316, 1632 and 1565 cm^{-1}. These spectral data indicated that the first peak at 3424 (N—H) was the characteristic peak for non-hydrogen-bonded urea groups (*13, 23–26*) and that the other peaks were characteristic of hydrogen-bonded urea groups. Apparently, gel formation was accompanied by the formation of intermolecular hydrogen bonds between the urea groups. The absorptions for solid TOUAT were in close agreement with these data (3313, 1632 and 1562 cm^{-1}, respectively). This clearly indicates that hydrogen bonding also occurred in the solid state. The characteristic data in Table 2 show that TLUAT in decalin and CCl$_4$ displayed the same properties as TOUAT.

Table 2. FT-IR data for TLUAT and TOUAT in the solid state, in the gel state[a].

Absorptions (cm^{-1})	NH-stretch	Amide-I	Amide-II	C—Cl stretch
TOUAT in decalin (viscosity sol. −0.5 mg/ml)	3424	1630	1566	N
TOUAT in decalin (gel − 5 mg/ml)	3316	1632	1565	N
TOUAT (solid)	3313	1632	1562	N
TLUAT in decalin (viscosity sol. −0.5 mg/ml)	3440	1633	1566	N
TLUAT in decalin (gel −5 mg/ml)	3314	1627	1565	N
TLUAT (solid)	3313	1626	1564	N
TLUAT in CCl_4 (viscosity sol. −0.5 mg/ml)	3440	1633	1567	749
TLUAT in CCl_4 (gel −5 mg/ml)	3312	1626	1565	789

[a] All spectra were recorded at RT.

Optical features of the gels

Temperature-dependent UV/vis and fluorescent analyses were carried out on the TOUAT gel in decalin in a temperature range of 65–20°C, and the behaviours of the gel and film are displayed in Figure 2. With a change in temperature, the gels were converted to the corresponding evaporated films, and the absorption spectra of the gels showed the bathochromic and hypochromic effects. Further, the fluorescent peak was shifted from 378 to 371 nm. The blue-shift effect was clearly observed. The features clearly indicate that the gelation of TOUAT in decalin displayed the J-type aggregation (*18*, *27*).

The optical properties of the organogels in decalin and CCl_4 were studied by UV/vis and fluorescence spectroscopies. Figure 3 shows that absorption peaks for the gel and evaporated film in CCl_4 were observed at 282 and 293 nm, respectively. The bathochromic effect was clearly observed. With the transition from the gel to the evaporated film in CCl_4, the fluorescent peak shifted to a longer wavelength and the fluorescent intensity was clearly quenched. The gelation of TOUAT in CCl_4 exhibited the $\pi-\pi$ stacking. The aggregation was obviously affected by using the different solvents.

Figure 3 shows the different absorption spectra of the gels in decalin and CCl_4. The absorption peaks of the gels in decalin and CCl_4 were at 271 and 282 nm, respectively. Further, the fluorescence spectra of the gels in decalin and CCl_4 were found to be considerably different from each other. The gel in decalin showed a fluorescence peak at 378 nm. The fluorescence of the gel in CCl_4 was found to be quenched drastically. The quenching of fluorescence, which was attributed to the TOUAT and CCl_4, resulted in contact-ion-pair formation. The mechanism of quenching processes are: (1) light absorption by TOUAT molecules; (2) the electron transfer from singlet excited TOUAT to CCl_4 molecule in the transient excited complex; (3) the dissociation of the CCl_4 anion to chloride ion and trichloromethyl radical; and (4) formation of contact ion pair between TOUAT radical cation and chloride ion (*27*). Further, all the gels in chlorinated solvents showed the same properties. Figure 3 shows the occurrence of the charge transfer effect in chlorinated solvents. Therefore, the gels in decalin and chlorinated solvents exhibited blue fluorescence and the quenching effect, respectively.

In addition, photographs of the inverted gel in decalin under UV light showing the blue emission have been inset in Figure 2. Figure 4 shows the inverted gels and film under UV light. The gel (left) and evaporated film (right) in decalin displayed the highly fluorescent effects.
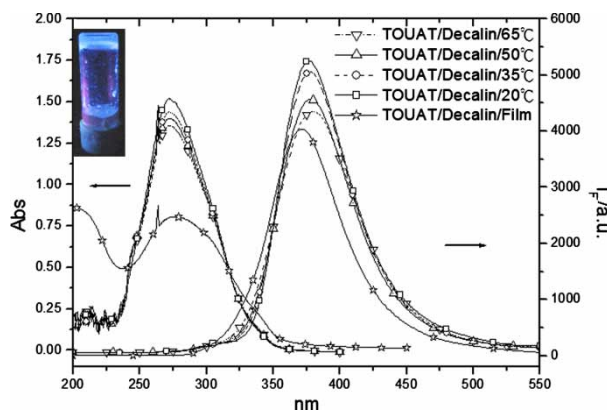

Figure 2. Temperature-dependent UV/vis and fluorescence analysis had been carried out for the gelation of TOUAT in decalin from 65 to 20°C and the behaviours of gel and film were displayed. Inset: the photograph of the inverted organogel in decalin under UV light showed the blue emission.
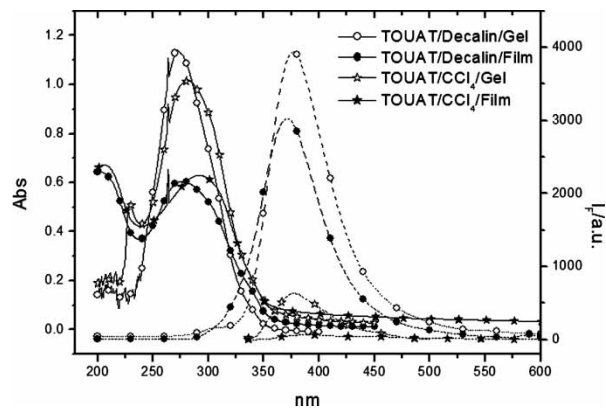

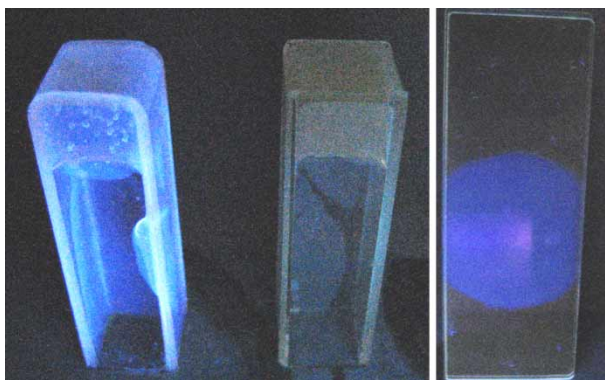Figure 3. The UV/vis and fluorescent spectroscopy of gels and evaporated film in CCl_4 had been performed.

Figure 4.   The gel (left) and evaporated film (right) in decalin displayed the highly fluorescent effect. Then, the gelation in CCl$_4$ displayed the quenched effect (middle).

The gelation in CCl$_4$ displayed the quenched effect (middle).

Morphological features of gels

As discussed above, the optical properties of the gels were different in decalin and CCl$_4$. Further, the aggregation was affected by using the different solvents. In order to demonstrate the different aggregations, the morphological self-assembled feature in different organic solvents was studied with scanning electron microscope (SEM). When the TOUAT concentration in decalin was lower than the CGC, the aggregated gels appeared as twisted ropes (Figure 5(a)) in the SEM images. Each twisted rope was 100–400 nm wide and several micrometers long. As the CGC was reached, the entangled ropes extended to form networks that retained the solvent within the pores, as shown in Figure 5(b). When the TOUAT concentration exceeded the CGC, a twisted rope extended and these extended ropes entangled to form the lamellar structures, as can be clearly observed from Figure 5(c). When the TOUAT concentration in CCl$_4$ was lower than the CGC, a porous structure was formed, as shown in Figure 5(d) and (e). The TOUAT gelators obviously aggregated to form the ropes, and the ropes entangled to form the porous structure that retained the solvent within the pores. As the CGC was reached, the entangled ropes extended to form networks that retained the solvent within the pores, as shown in Figure 5(f). From Figure 5(a)–(f), the morphological features demonstrate that there were different aggregations in different solvents (*15–17, 28*).

Conductivities of gel electrolytes

In recent years, organogel electrolytes have received considerable attention due to their excellent characteristics, such as high reliability, non-leakage of electrolyte solution, thin film formation and flexibility, improvement of the contact between the electrodes and the solid electrolytes and so on. Therefore, the relationship between the ion conductivity and concentration of gelators and the sol–gel temperature and electrolyte salts as tetrabutyl-ammonium perchlorate (TBAP) in THF was measured using a vector impedance meter in the frequency range of 20 Hz–1 MHz. Since THF is highly polar and is more stable towards agitation than other solvents, it was selected to form the organogel electrolytes. As shown in Figure 6, the organogel electrolytes exhibited high ion conductivity (σ) compared with the corresponding TBAP/THF solution. The conductivity of the gel electrolytes increased with an increase in the electrolyte salt concentration and temperature. When the sol–gel temperature was achieved, a high ion conductivity was observed compared with the corresponding TBAP/THF solution. When the ratio of the added electrolyte salts exceeded 5%, gelation was inhibited. It was clearly demonstrated that the anion could inhibit the gel formation. The anion binding had been reported to inhibit the gel formation as result of specific binding interaction (*18*). Furthermore, by controlling the TOUAT concentration, the ion conductivity was decreased slightly. When the TOUAT concentration was increased to more than 30 mg/ml, an opaque gel was formed. It was suggested that this opaque gel does not affect ion diffusion in large interconnected liquid domains (*29, 30*). ($\sigma_{max20°C}$: 2.75 × 10^{-3} S cm^{-1} for the gel of TOUAT in 5% TBAP/THF; $\sigma_{Sol-gel°C}$: 4.2 × 10^{-3} S cm^{-1} for the sol of TOUAT in 5% TBAP/THF; $\sigma_{max20°C}$: 3.522 × 10^{-3} S cm^{-1} in TBAP/THF; $\sigma_{Sol-gel°C}$: 5.607 × 10^{-3} S cm^{-1} in 5% TBAP/THF; all the conductivity data are supplied in the supporting information.)

Furthermore, the effect of the electrolyte salts on the Tm of the gel was confirmed in Table 3. The added electrolyte salts affected the gelation ability, but did not affect the sol–gel temperature.

Conclusion

In this study, new gelators for urea-containing triazine derivatives were synthesised, and their gelation potential was examined in different organic solvents. These compounds were found to form organogels with a variety of organic solvents, such as hexane and other solvents. The elongated alkyl tails of the gelators displayed an obvious decrease in the CGC in apolar solvents and an increase in the compatibility of gelation in polar solvents. The resulting thermo-reversible gels were characterised by using the dropping ball method and a number of other instruments. The Tm of the gels in decalin and CCl$_4$ increased with the gelator concentrations. The inter-molecular hydrogen bonding of gelation in different organic solvents was observed using an FT-IR spectro-meter. It was seen from temperature-dependent UV–vis and a fluorescence analysis that the organogels displayed diverse aggregations and various fluorescence effects
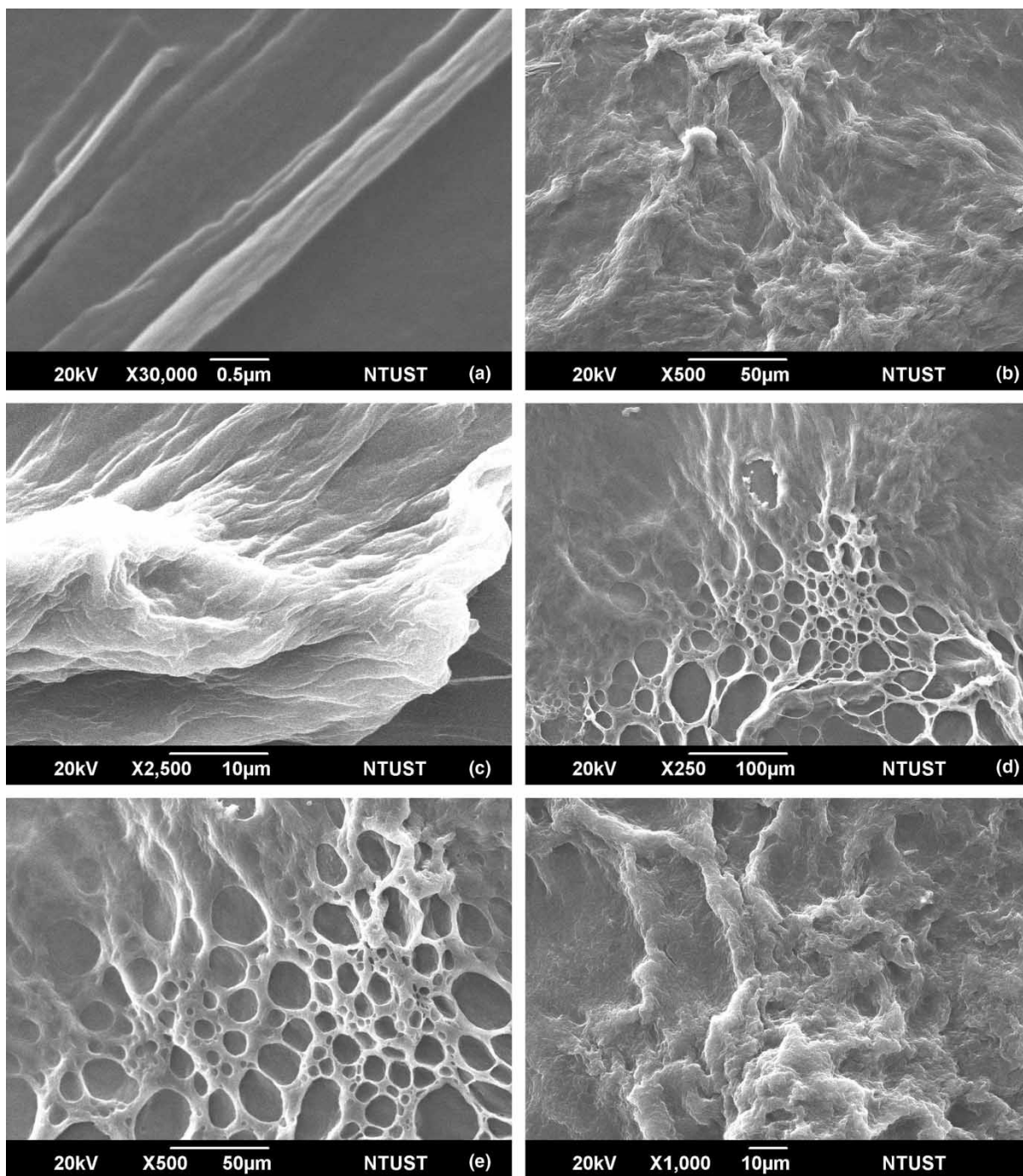
Figure 5. Morphological features of the self-assembled TOUAT. (a) When the TOUAT concentration in decalin was lower than the CGC, the aggregated gels appeared as twisted ropes. Each twisted rope was 100–400 nm wide and several micrometers long. (b) At the CGC was reached, the entangled ropes extended to form networks that retained the solvent within the pores. (c) When the TOUAT concentration exceeded the CGC, a twisted rope extended and these extended ropes entangled to form the lamellar structures, as can be clearly observed. (d) and (e) When the TOUAT concentration in CCl_4 was lower than the CGC, a porous structure was formed. Obviously, the TOUAT gelators aggregated to form the ropes, and the ropes entangled to form the porous structure that retained the solvent within the pores. (f) As the CGC was reached, the entangled ropes extended to form networks that retained the solvent within the pores.

Figure 6.   The relationship between the ion conductivity and the concentration of gelator and sol–gel temperature and electrolyte salts has been measured using a vector impedance metre in the frequency range from 20 Hz to 1 MHz.
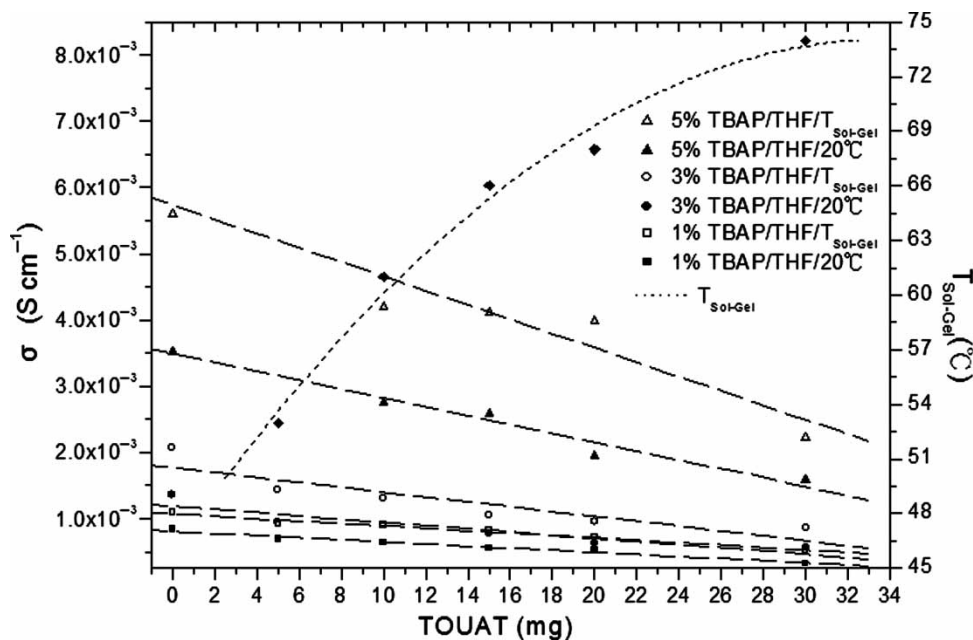
in different organic solvents. Blue fluorescence and J-aggregation in decalin and the quenched effect and $\pi-\pi$ stacking in CCl_4 were observed. Further, the morphological self-assembled feature in different organic solvents was studied with SEM, and the morphological features demonstrated that there were different aggregations in different solvents. In electrolyte conductivity experiments, the organogel electrolytes exhibited high conductivity (σ) compared with the corresponding TBAP/THF solution. The conductivity of the gel electrolytes increased with the electrolyte salt concentration and temperature. When the sol–gel temperature was achieved, a high ion conductivity was observed compared with the corresponding TBAP/THF solution. When the ratio of the added electrolyte salts exceeded 5%, gelation was inhibited, it was clearly demonstrated that the anion could inhibit the gel formation. Furthermore, the effect of the electrolyte salts on the Tm of the gel was

confirmed. The added electrolyte salts affected the gelation ability, but did not affect the sol–gel temperature.

In future work, this organogel will be studied extensively for applications in the optoelectronic field.

Experimental section

Materials and methods

All solvents used were reagent grade and were distilled before use. Reagents were purchased from Acros, Aldrich or Fluka and used without purification. The ^{1}H NMR (300 MHz) spectra were recorded on a Varian VXR-300 spectrometer at ambient temperature or the Tm of the gel. Chemical shifts are denoted in δ units (ppm) relative to the solvent signals DMSO (^{1}H NMR: $\delta = 2.49$ ppm). Mass spectra (EI and MALDI-TOF) were performed at the Department of Chemistry, National Taiwan Normal University and National Taiwan University, respectively. Elemental analyses were performed at the University of Tatung.

Table 3.   The effect of electrolyte salts on the Tm of the gel[a].

TOUAT (mg/ml)	1% (°C)	3% (°C)	5%
5	53	53	N
10	61	62	62°C
15	66	66	67°C
20	68	68	69°C
30	74	74	74°C

[a] The following abbreviations were used: N, gel-like precipitate; TOUAT, 2,4,6-tris(p-N'-octadecylureido-anilino)-1,3,5-triazine.

Critical gelation concentration

The CGC was determined by gradually lowering the gelator concentration by subsequently adding more solvent and repeating a heating and cooling cycle in a 3-ml closed vial (diameter 10 mm). The CGC was considered to be reached when the gel network was not able to support the solvent (inverted test tube method).

Dropping ball experiment

Gels were made at least 1 day before actual melting. A stainless steel ball with a diameter of 2.5 mm was placed on the gels and the gels were heated at $6°C\,h^{-1}$ in an oil bath regulated by a thermostat. The gel was considered melted as the ball had reached the bottom of the vial. The dropping-ball experiments were carried out and the Tms obtained were reproducible to within $\pm 1°C$.

Fourier-transformed infrared spectroscopy

Spectra were recorded on a Varian 1000 FT-IR instrument. Solid samples were recorded as the intimate mixture with KBr powder. Liquid and gel samples were recorded in a liquid cell equipped with CaF2 windows.

Temperature-dependent UV/vis and fluorescence spectroscopy

Temperature-dependent UV/vis and fluorescence spectroscopy were performed on a Hewlett–Packard HP 8453 spectrophotometer and Hitachi F-4500 spectrophotometer, respectively. The samples were prepared in the 0.3 ml quartz cell by injecting a hot solution containing gelator molecules. Usually, this will lead to the formation of gel in the cell, and a homogenous sample was obtained by heating and subsequent cooling of the sample.

Scanning electron microscope

The SEM measurements were performed on a Cambridge SEM S360 operating at 2.0 kV. The gels in different solvent were deposited on a piece of mica on which 20 nm of gold was sputtered. The samples were dried at ambient temperatures and used without additional staining.

Conductivities of gel electrolytes and solid electrolytes

The controlled concentration of organogel containing the different concentration of electrolyte salts ($NaClO_4$) in THF was placed in glass cell with the platinum electrodes. Ionic conductivities were measured by the vector impedance meter at a frequency range from 20 Hz to 1 MHz.

Syntheses

2,4,6-Tris(p-N^l-octadecylureido-anilino)-1,3,5-triazine (TOUAT)

The compound (TOUAT) was synthesised by the reaction of the compound **4** (2 mmol) and octadecyl isocyannate (10 mmol) in 100 ml THF. The solution was stirred and heated at 80°C for 24 h under N_2 to avoid oxidation of the amine. During the synthesis of this compound in THF, a clear and transparent gel was formed. The viscosity solution was allowed to cool to room temperature and filtered this solution. Then, the precipitate was washed several times with THF and methanol.

Data for compound: ^{1}H NMR (300 MHz, *d*-DMSO): δ 8.922 (NH, 1H), 8.233 (NH, 1H), 7.582 (CH, 2H), 7.225 (CH, 2H), 5.996 (NH, 1H), 3.194 (CH_2, 2H), 1.229 (CH_2, 30H), 0.835 (CH_3, 3H). IR (KBr): ν_{max} 3317, 3122, 2919, 2850, 2361, 1898, 1632, 1562, 1515, 1432, 1302, 1224, 1122, 873, 763 cm^{-1}. Anal. calcd for $C_{78}H_{132}N_{12}$: C, 72.85; H, 10.35; N, 13.07. Found: C, 72.93; H, 10.63; N, 13.42. MS: cal. for, 1285.05, found: 1285.51.

2,4,6-Tris(p-N^l-laurylureido-anilino)-1,3,5-triazine (TLUAT)

The compound (TOUAT) was synthesised by the reaction of the compound **4** (2 mmol) and lauryl isocyannate (10 mmol) in 100 ml THF. The solution was stirred and heated at 80°C for 24 h under N_2 to avoid oxidation of the amine. During the synthesis of compound in THF, a clear and transparent gel was formed. The viscous solution was allowed to cool to room temperature and filtered this solution. Then, the precipitate was washed several times with THF and methanol.

Data for compound: ^{1}H NMR (300 MHz, *d*-DMSO): δ 8.902 (NH, 1H), 8.243 (NH, 1H), 7.574 (CH, 2H), 7.235 (CH, 2H), 5.009 (NH, 1H), 3.012 (CH_2, 2H), 1.223 (CH_2, 20H), 0.835 (CH_3, 3H). IR (KBr): ν_{max} 3313. 3119, 3042, 2924, 2859, 2380, 2303, 2141, 2057, 1893, 1628, 1565, 1512, 1422, 1297, 1234, 1095, 806 cm^{-1}, Anal. calcd for $C_{63}H_{102}N_{12}$: C, 70.35; H, 9.56; N, 15.63. Found: C, 70.53; H, 9.174; N, 15.66. MS: cal. for, 1074.82, found: 1075.35.

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