Gelation of a highly fluorescent urea-containing triarylamine derivative: *N, N, N', N'*-tetrakis (*p*-octadecylureido-phenyl)-*p*-phenylenediamine in organic solvents

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Gelation of a highly fluorescent urea-containing triarylamine derivative: *N, N, N', N'*-tetrakis (*p*-octadecylureido-phenyl)-*p*-phenylenediamine in organic solvents

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An innovative gelator was synthesised by non-covalent interactions from triarylamine derivative as N, N, N', N'-tetrakis(*p*-octadecylureido-phenyl)-*p*-phenylenediamine (TOUPPD), and its gelation potential was examined in different organic solvents. The resulting thermo-reversible gel was characterised by using the dropping ball method and a number of other methods. The melting temperature of the gel increased with the TOUPPD concentration. Temperature-dependent UV–vis and fluorescence analysis revealed that the gel exhibited blue fluorescence and H-aggregation in decalin. Intermolecular hydrogen bonding in the TOUPPD gel was observed from FT-IR spectrometry. The morphological self-assembled feature of the gel was studied by atomic force microscopy (AFM). In conductivity and solid electrolyte experiments, the organogel electrolytes exhibited high conductivity (σ) comparable to the corresponding $NaClO_4$/THF solution. The conductivity of the gel electrolytes increased with the concentration of the electrolyte salt. The TOUPPD film exhibited well-defined conductivity of 2.5×10^{-4} to 3.5×10^{-6} S cm^{-1} in the solid state upon addition of a known concentration of trifluoroacetic acid (TFA).

Keywords: triarylamine; self-assembled; aggregation; supramolecular chemistry

Introduction

In recent years, supramolecular chemistry has attracted enormous interest and attention owing to various factors such as hydrogen bonding, $\pi-\pi$ stacking, solvophobic and donor–acceptor interactions, by using these factors to control the molecular order, thus making it a challenging topic for research (*1–7*). One of the challenges in this field is the synthesis of an organogel that spontaneously self-assembles to form a soft solid-like mass by entrapping a large volume of solvent between the self-assembled formations. Organogels can be used in diverse fields for a wide range of applications. Most gelators are based on porphyrins, phthalocyanines, phenylenevinylenes and perylene bis-imides, as reported previously in other studies (*8–11*). The abovementioned 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 of organogels and their applications (*15–17*). Ayyappanpillai and Vakayil presented a tutorial review describing recent developments in the design of chromophores to form organogels and their use as supramolecular scaffolds for research in excitation energy transfer. Moreover, Hoeben and Meijer presented a paper on the supramolecular assembly of π-conjugated systems. The extensive application of organogels derived from triarylamine derivatives is yet to be studied. Therefore, in this paper, the development of organogels derived from triarylamine derivatives is examined, and the actual applications of N, N, N', N'-tetrakis(*p*-octadecylureido-phenyl)-*p*-phenylenediamine (TOUPPD) in the field of optoelectronics are also provided. All the organogels used in optoelectronics exhibited well-defined properties.

Results and discussion

Synthesis

TOUPPD was synthesised as follows: compound 2 (*N, N, N', N'*-tetrakis(*p*-nitrophenyl)-*p*-phenylenediamine) was prepared by dissolving *p*-phenylenediamine and 4-fluoronitrobenzene in dimethyl sulphoxide (DMSO). K_2CO_3 was added to this solution, and the mixture was stirred and heated under N_2 atmosphere to avoid oxidation of the amine. Compound 3 (*N, N, N, N'*-tetrakis(*p*-aminophenyl)-*p*-phenylenediamine) was synthesised by catalytic hydrogenation of 2 in dioxane. TOUPPD was prepared by the reaction of 3 with octadecyl isocyanate in THF. The synthetic route is described in Scheme 1.

Gelation of organic solvents: critical gelation concentration (CGC)

TOUPPD has been found to form organogels with a variety of organic solvents such as hexane. The CGC values of TOUPPD in different solvents are summarised

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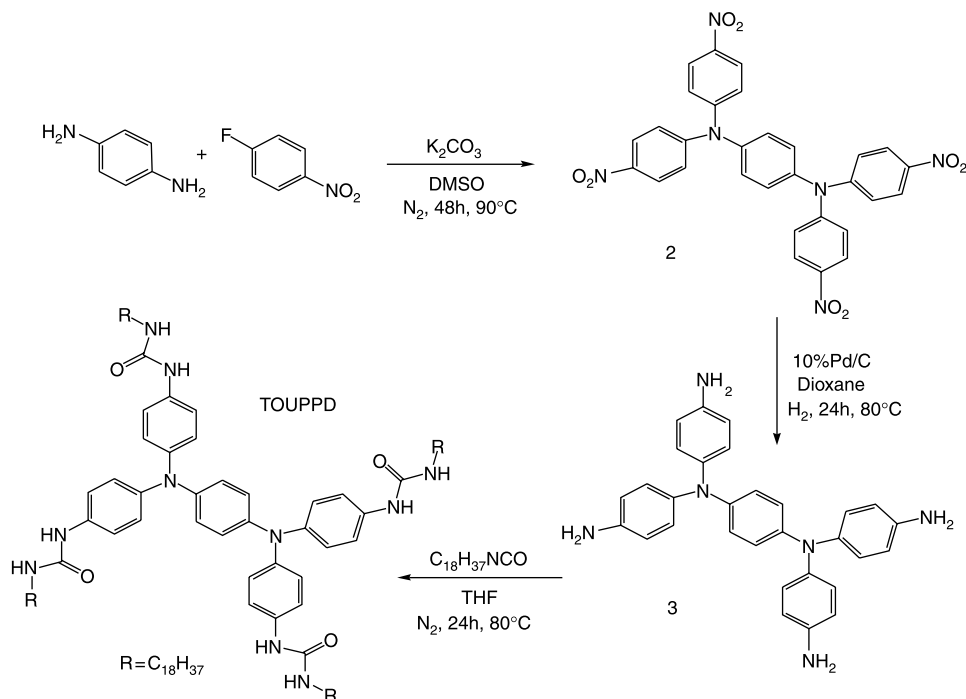
Scheme 1.   Synthesis of TOUPPD.

in Table 1. From these values, it is apparent that TOUPPD is an effective gelator. In polar solvents such as hexane, cyclohexane and decalin, TOUPPD formed long alkyl chains to immobilise the solvents and yielded gels. The CGC of the gel increased with the polarity of the solvents. However, when the polarity of solvents became too high, gelation was inhibited and precipitation occurred.

As a result, low concentrations of TOUPPD are thought to be suitable for gel formation in apolar solvents. However, in chlorinated solvents such as CCl_4, the CGC of TOUPPD increased to more than 18 mg/ml and the gels underwent a colorimetric change to blackish green, thus indicating charge transfer.

The organogels listed in Table 1 were completely transparent and stable towards mechanical agitation, except for those obtained from pyridine and chlorinated solvents (*17–19*). Furthermore, addition of trifluoroacetic acid (TFA) inhibited gelation in decalin, and the gels displayed the colorimetric change as blackish green owing to charge transfer.

Thermotropic behaviour of the gels

The relationship between the TOUPPD concentration and the melting temperature of the gel in decalin was studied by the dropping ball method, and the results are displayed in Figure 1. Decalin was selected for gel formation because of its higher boiling point and slower volatility than other solvents. The melting temperature of the gel

increased with the TOUPPD concentration. Clearly, the TOUPPD gel in decalin exhibited high sol–gel temperature and stability. A polar gelator would be less soluble in apolar solvents, and hence, would have a high melting temperature (*20, 21*). Therefore, it was clearly indicated that TOUPPD is a polar gelator.

FT-IR experiments

The relationship between the gelation ability and intermolecular hydrogen bonding has been studied by FT-IR spectroscopy since the NH-stretching and the amide-I and -II bands of urea generally show large shifts in the IR spectrum upon the formation of hydrogen bonds. When the TOUPPD concentration (0.5 mg/ml) was lower than its CGC in decalin, the solution became viscous. The viscous solution showed absorption peaks at 3413 (N–H), 1635 (amide-I) and 1562 (amide-II) cm^{-1}, as indicated in Table 2. When the gel was formed at 5 mg/ml, the peaks shifted toward 3332, 1641 and 1561 cm^{-1}. These spectral data indicated that the first peak at 3413 (N–H) is the characteristic peak for non-hydrogen-bonded urea groups (*13, 22–25*), and other peaks are characteristic of hydrogen-bonded urea groups. Apparently, gel formation was accompanied by the formation of the intermolecular hydrogen bonds between the urea groups. The wavelengths of the absorption peaks due to solid TOUPPD were in close agreement with these data. It clearly indicates that the hydrogen bonding also occurred in the solid state.

Table 1. Gelation properties and critical gelation concentration[a].

Compounds\solvents	Hexane	Cyclohexane	Decalin	Toluene	THF	Dioxane	Pyridine	DMF	NMP	DMSO	CCl₄	CHCl₃	DCM	DCE
TOUPPD	>1.3	>1.5	>1.5	>3.5	>6	p	>15b	i	i	p	>18cc	>20cc	>22cc	>23cc

The following abbreviations are used: cc, colorimetric change; i, insoluble; p, precipitate; b, turbid. [a]Critical gelation concentrations have been given in mg/ml.
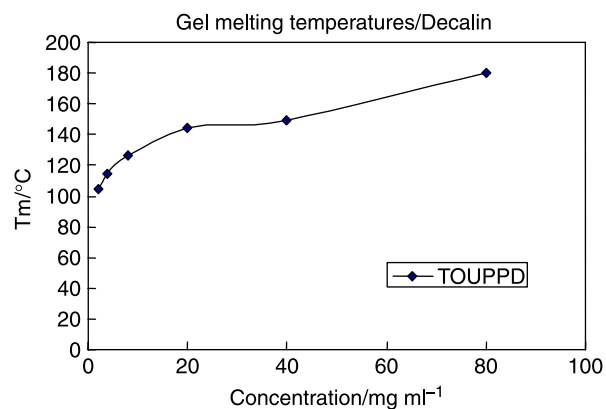

Figure 1. The melting temperatures of the gel in decalin obtained by the dropping ball method.

Optical features of the gels

The optical properties of the organogels in decalin and CCl₄ were studied by UV–vis and fluorescence spectroscopies. Figure 2 shows the different absorption spectra of the gels in decalin and CCl₄. Absorption peaks of the gel in decalin were observed at 348, 310 and 247 nm. In the absorption spectrum of the gel in CCl₄, the first absorption peak at 348 nm disappeared, and the absorption intensity upon 394 nm increased. The other peaks at 310 and 247 nm blue-shifted to 304 and 228 nm, respectively. Changes were also observed in absorption spectrum of the film in CCl₄. Furthermore, the fluorescence spectra of the gels in decalin and CCl₄ were found to be considerably different from each other. The gel in decalin showed fluorescence peaks at 437 and 419 nm. The fluorescence of the gel in CCl₄ was found to be quenched. All the gels in chlorinated solvents showed the same properties. The quenching of fluorescence, which was attributed to the chlorinated solvents and nitrogen atoms, resulted in contact ion pair formation (26). Figure 2 shows the occurrence of the charge transfer effect in chlorinated solvents. Therefore, the gels in decalin and chlorinated solvents exhibited blue fluorescence and quenching effect, respectively. As mentioned above, upon adding TFA, the TOUPPD gel in decalin underwent colorimetric change. The absorption and fluorescence effects of the gels in decalin upon the addition of TFA were in agreement with those of the gels in the chlorinated solvents. These phenomena suggest the stabilisation of the ion pairs formed. Since TFA is a strong carboxylic acid, it is frequently used to dope conjugated polymers to form *p*-type semiconductors. Hence, the addition of TFA to decalin results in protonation of the nitrogen atom in TOUPPD to afford a radical cation species (27). Further, ion pair formation also occurred. Consequently, TFA addition brings about fluorescent quenching and occurrence of the charge transfer effect.

Temperature-dependent UV–vis and fluorescence analyses have been carried out on the TOUPPD gel

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

Absorptions (cm^{-1})	NH-stretching	Amide-I	Amide-II
TOUPPD (gel-0.5 mg/ml)	3413	1635	1562
TOUPPD (gel-5 mg/ml)	3332	1641	1561
TOUPPD (solid)	3325	1643	1556

[a] All spectra were recorded at R.T.

in decalin in the temperature range from 65 to 20°C; the behaviours of the gel and the film are displayed in Figure 3. With a change in temperature, the gels were converted to the corresponding evaporated films, and the absorption spectra of the gel showed hypsochromic and hypochromic effects. These features clearly indicate H-aggregation (*28*). In general, fluorescence quenching is expected for H-type aggregates. In Figure 3, fluorescence quenching is observed, and the film is seen to exhibit weak fluorescence intensity, thus confirming H-aggregation. In addition, the photographs of the

Figure 2. UV–vis absorption and fluorescence spectra of gels in different solvents.
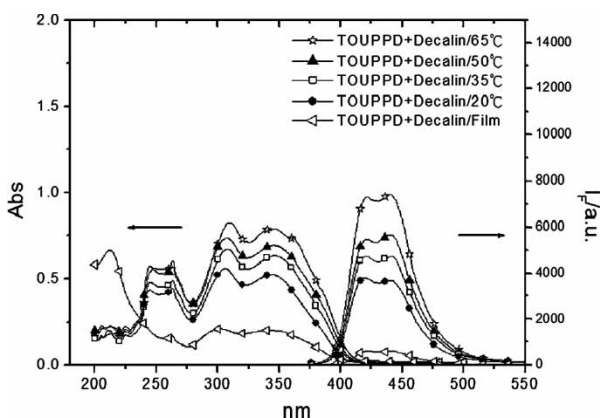
Figure 3. Behaviour of gel and film in decalin studied by temperature-dependent UV–vis and fluorescence analysis from 65 to 20°C.

organogels shown in Figure 4 display fluorescent effect in decalin (left) and charge-transfer effect in CCl_4 (right).

Morphological features of gels

As discussed above, the optical properties of the gels were different in decalin both with and without the addition of TFA. Further, H-aggregation and charge-transfer effect were observed. The morphological self-assembled patterns of the TOUPPD gel formed in decalin with and without the addition of TFA were studied by atomic force microscopy (AFM). When the TOUPPD concentration in decalin was lower than the CGC, the aggregated gels appeared as twisted ropes (Figure 5(a)) and entangled ropes (Figure 5(b)) in the AFM phase and height images, respectively. Each twisted rope was 100–200 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(c). When the TOUPPD concentration exceeded the CGC, a twisted rope extended and these extended ropes entangled to form a network, as can be clearly observed from Figure 5(d,e), respectively. Each extended rope was 250–350 nm wide and several micrometers long. After, the addition of TFA in decalin, a porous film was formed, as shown in Figure 5(f). Obviously, the crystal structures in decalin with and without TFA were different. The gelators could form twisted ropes and crystal films, irrespective of the addition of TFA. From Figure 5(a)–(e), it is evident
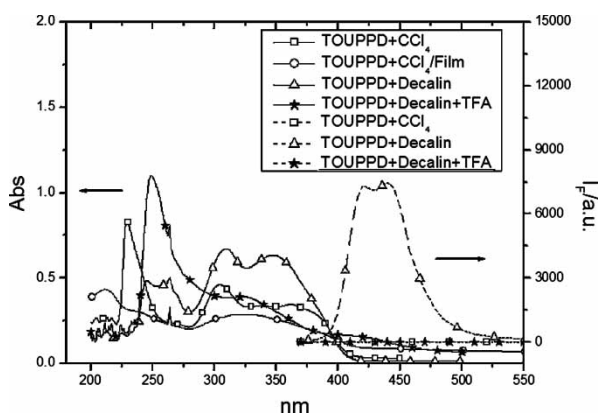

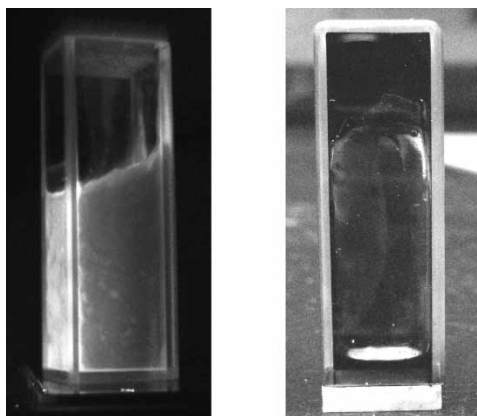Figure 4. Photographs of organogels showing strong fluorescence in decalin (left) and charge transfer in CCl_4 (right).
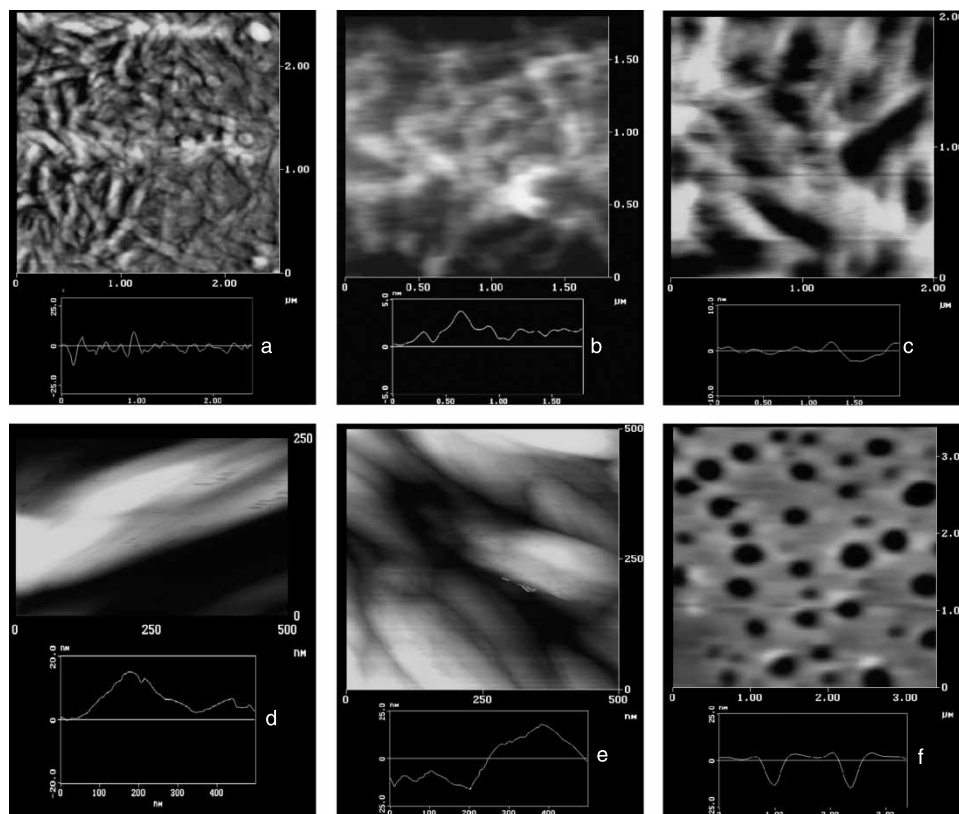
Figure 5. Morphological patterns of the self-assembled TOUPPD gels in decalin (a, b) at TOUPPD concentration lower than the CGC, the phase image of twisted ropes and the height image of entangled ropes were observed; (c) as the CGC was reached, the entangled ropes extended to form the networks that retained the solvent within the pores; (d, e) when TOUPPD concentration exceeded CGC, a twisted rope extended and the extended ropes entangled to form the network were clearly observed; an extended rope was 250–350 nm wide and several micrometers long; (f) a porous film was observed upon adding TFA in decalin.

that the morphological patterns supported the formation of gel aggregations, which in turn entangled to form three-dimensional networks. From Figure 5(f), it was observed that the addition of TFA affects the TOUPPD aggregation in decalin and results in a decrease in the gelation ability in decalin (*15–17, 29*).

Conductivities of gel electrolytes and solid 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, and improvement of the

contact between the electrodes and the solid electrolytes. Therefore, the relationship between the ion conductivity and the concentrations of TOUPPD and electrolyte salts ($NaClO_4$) in THF has been measured using a vector impedance meter in the frequency range from 20 Hz to 1 Mz. Since THF is highly polar and is more stable toward agitation than other solvents, it was selected to form organogel electrolytes. As shown in Table 3, the organogel electrolytes exhibited high ion conductivity (σ) comparable to the corresponding $NaClO_4$/THF solution. The conductivity of the gel electrolytes increased with the concentration of the electrolyte salts. When the ratio of the added electrolyte salts exceeded 10%, gelation was inhibited. Furthermore,

Table 3. Conductivities of gel electrolytes and solid electrolytes.

Concentration	2.5% (S cm^{-1})	5.0% (S cm^{-1})	7.50% (S cm^{-1})	10% (S cm^{-1})
TOUPPD-10 mg/ml	3.5×10^{-4}	9.2×10^{-4}	7.7×10^{-4}	3.2×10^{-3}
TOUPPD-30 mg/ml	4.3×10^{-4}	21.04×10^{-3}	1.8×10^{-3}	2.1×10^{-3}
TOUPPD-50 mg/ml	4.0×10^{-4}	7.8×10^{-4}	2.1×10^{-3}	3.5×10^{-3}
$NaClO_4$/THF	6.7×10^{-3}	1.5×10^{-3}	4.6×10^{-3}	5.4×10^{-3}
Doped TFA in decalin	1%	2%	4%	5%
The film of TOUPPD	3.5×10^{-6}	6.9×10^{-6}	7.8×10^{-5}	2.5×10^{-4}

by controlling the TOUPPD concentration, the ion conductivity could be decreased, but no supposition was observed. When the TOUPPD concentration was increased to more than 30 mg/ml, an opaque gel was formed. It was suggested that the opaque gel does not affect ion diffusion in large interconnected liquid domains (30, 31). ($\sigma_{max\,25°C}$: 3.5×10^{-3} S cm^{-1} for the TOUPPD gel in NaClO$_4$/THF; $\sigma_{max\,25°C}$: 5.4×10^{-3} S cm^{-1} for NaClO$_4$/THF). In order to demonstrate an efficient intermolecular charge transport in a self-assembled structure, the solid-state conductivity of TOUPPD film was measured at controlled TFA concentration. The TOUPPD film exhibited well-defined conductivity of 2.5×10^{-4} to 3.5×10^{-6} S cm^{-1} in the solid state when a controlled amount of TFA was added, thus showing that an efficient intermolecular charge transport can be established in a self-assembled structure.

Conclusion

In this paper, an innovative gelator (TOUPPD) has been synthesised by non-covalent interaction and, its gelation potential in different organic solvents was investigated. The resulting thermo-reversible gel has been characterised by using the dropping ball method and a number of other methods. All applicable organogel characteristics have exhibited well-defined properties. The melting temperature of the gels increased with the TOUPPD concentration. Temperature-dependent UV–vis and fluorescence analyses reveal that the gels exhibited blue fluorescence and H-aggregation in decalin. Further, charge-transfer effect was observed in chlorinated solvents. FT-IR spectrometric analysis showed the presence of intermolecular hydrogen bonds in the TOUPPD gels. The morphological self-assembled patterns of the gels have been studied by AFM. Furthermore, it is found that the addition of TFA can inhibit the gelation in decalin, and the resulting charge-transfer effect affects TOUPPD aggregation. The organogel electrolytes exhibit high conductivity (σ) comparable to the corresponding NaClO$_4$/THF solution. The conductivity of the gel electrolytes increased with the concentration of the added electrolyte salts. The TOUPPD film exhibits a well-defined conductivity of 2.5×10^{-4} to 3.5×10^{-6} S cm^{-1} in the solid state upon the addition of a controlled amount of TFA, showing that an efficient intermolecular charge transport is established in the self-assembled gel structure. In future, these organogels will be studied extensively for applications in the field of optoelectronics.

Experimental section
Materials and methods

All the solvents used were reagent grade and were distilled before use. Reagents were purchased from Acros, Aldrich or Fluka and used without purification. ^{1}H NMR (300 MHz) spectra were recorded on a Varian VXR-300

spectrometer at ambient temperature or the melting temperature of the gel. Chemical shifts are denoted in δ units (ppm) relative to the solvent signals DMSO (1Proton 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.

Critical gelation concentration (CGC)

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 gels were considered melted as the ball reached the bottom of the vial. The dropping ball experiments were carried out and the melting temperatures obtained were reproducible to within ± 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 CaF$_2$ windows.

Temperature-dependent UV–vis and fluorescence spectroscopy

Temperature-dependent UV–vis and fluorescence spectroscopy were performed on 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.

Atomic force microscopy (AFM)

A sample of the gel was placed on a glass (0.5 × 0.5 cm) or a sample of the solution of compound at high temperature was poured on a glass at two kinds of process treatment as quenching or drawing. After drying at low pressure, the glass was examined with a Nanoscope III instrument.

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 Mz. The evaporated organogel controlling the TFA concentration was placed on the glass (1.5 × 1.5 cm) with aluminium electrodes. Solid conductivities were measured by the vector impedance meter at a frequency range from 20 Hz to 1 Mz.

Syntheses

N,N,N′,N′-tetrakis(p-*octadecylureido-phenyl)*-p-*phenylenediamine (TOUPPD)*

The compound (TOUPPD) was synthesised by the reaction of compound **3** (2 mmol) and octadecyl isocyanate (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 synthetic process of the TOUPPD in THF, the solution became viscous. The viscous solution was allowed to cool to room temperature and filtered. Then, the precipitate was washed several times with THF and methanol. Data of compound: IR (KBr): v_{max} 3325, 3107, 3042, 2922, 2852, 2360, 1897, 1643, 1556, 1504, 1265, 1155 and 829 cm^{-1}. Analysis calculated for $C_{106}H_{176}N_{10}O_4$: C, 76.95; H, 10.72; N, 8.47. Found: C, 76.93; H, 10.59; N, 8.75 MS (MALDI-TOF): Calcd. for, 1654.39. Found, 1654.23.

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