

A novel photo-responsive organogel based on azobenzene

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A novel triarmed *cis*-1, 3, 5-cyclohexanetricarboxamides gelator, functionalized by three azobenzene moieties grafted with three long alkyl chains, was designed and synthesized. The gelator can gel most of the organic solvents in low concentration. The morphologies of the xerogels show one-dimensional aggregated bundles or helical fibres. The azobenzene groups in the gel state form H-type aggregation and perform expected *trans*–*cis* photoisomerization with a gel to sol phase transition upon irradiation of UV light. The main driving force for gelation is intermolecular hydrogen bonding between amides and π – π interaction of azobenzene moieties. Copyright © 2008 John Wiley & Sons, Ltd.

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INTRODUCTION

The design of self-assembling supramolecules becomes the charming target toward the development of new materials and nanoscale devices.^[1–6] As a novel class of self-assembled materials, low weight molecular (LWM) gels have received considerable attention in recent years because they can organize into regular nanoarchitectures through specific non-covalent interactions including hydrogen bonds, hydrophobic interactions, π – π interactions and van der Waals forces.^[7–13] The intermolecular hydrogen bonds or π – π interactions usually facilitate the growth of linear, elongated aggregates in the gels. Chiral diaminocyclohexane or *cis*-1, 3, 5-cyclohexanetricarboxamides are important organogelator cores for the formation of chiral organogel systems, which was reported by Hanabusa *et al.* for the first time.^[14,15] Shinkai *et al.* successfully transcribed the chiral, helical structures of the organogels into silica gel and got chiral silica with both right- and left-handed helical motif.^[16,17]

Azobenzene moieties are known to all for their photo responsive properties. The soft matter contained azobenzene groups can potentially be applied in message storage and transport, etc.^[4] In the organogel systems, azobenzene groups also acted as π system to enforce the interactions among the molecules. Feringa reported the chiral recognition through cooperative interactions between aggregates and gels of bis(ureido)-cyclohexane skeleton containing azobenzene chromophores.^[18] Kato introduced azobenzene based chiral gelator into liquid crystal systems to get photo responsive anisotropic liquid-crystalline physical gels.^[19,20] Zhao *et al.* achieved electrically switchable diffraction gratings based on light-induced reorganization process in two azobenzene contained gelators.^[21,22] In our previous work, we observed solvent tunable morphologies in an azobenzene gelator with several competitive or cooperative interactions^[23] and we also developed a new

system of two component photo-responsive gel.^[24] However, stimulus response operated in the self-assembled gel state is still a challenge. In this work, we synthesized a novel triarmed *cis*-1, 3, 5-cyclohexanetricarboxamides gelator **AZO-C16**, functionalized by three azobenzene moieties grafted with three long alkyl chains (Scheme 1). The cooperative interactions of hydrogen bonding, π – π interactions and van der Waals forces confirmed the compound an effective gelator for various organic solvents. The main attraction is that the self-assembly organization resulted in a chiral helical structure in a supramolecular level even using a non-chiral compound as a building block.

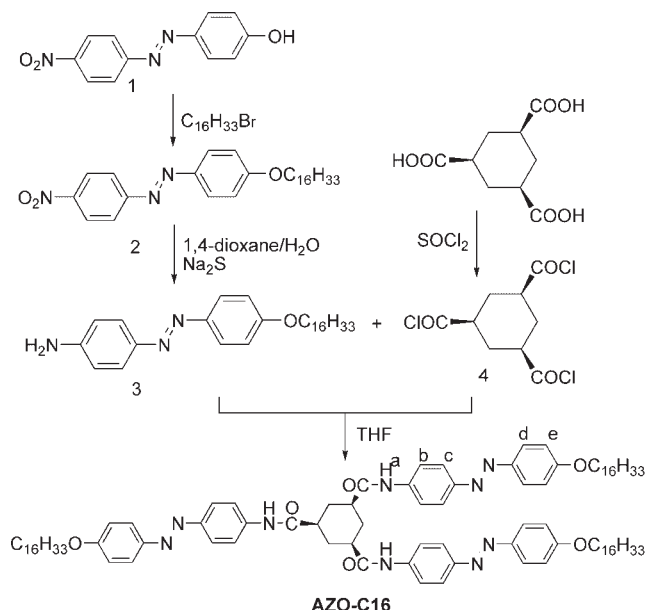
MATERIALS AND METHODS

General

All starting materials were obtained from commercial suppliers and used as received. Moisture sensitive reactions were performed under an atmosphere of dry argon. ¹H NMR and ¹³C NMR spectra were recorded on a Mercuryplus, at 400 and 100 MHz, respectively. Proton chemical shifts are reported in parts per million downfield from tetramethylsilane. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF-MS) was recorded on an AXIMA-CFRPLVS mass spectrometer (Shimadzu). Element analysis was carried out on a VARIOEL3 apparatus (ELEMENTAR).

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Scheme 1. Structure and synthesis process of compound **AZO-C16**

Synthesis of the gelator

(*E*)-4-(4-nitrophenyl diazenyl) phenol (**1**)

Yellow solid **1** was synthesized according to a previous report^[23,24] (95% yields). ¹H NMR (CDCl₃) δ 8.36 (d, *J* = 9.2 Hz, 2H), 7.93–7.99 (q, *J* = 8.8 Hz, 4H), 6.98 (d, *J* = 8.8 Hz, 2H).

(*E*)-1-(4-(hexadecyloxy) phenyl)-2-(4-nitrophenyl)diazene (**2**)

1-Bromohexadecane (6.1 ml, 20 mmol) was dropped into 50 ml of dry acetone solution containing **1** (2.43 g, 10 mmol) and anhydrous potassium (2.78 g, 20 mmol). The reaction mixture was refluxed, stirred for 8 h and then poured into excess water. **2**^[25] was obtained by filtration and purified by column chromatography on silica gel with chloroform/petrol ether (1:2, v/v) as the eluent, yield 4.20 g (90%). M.p. 87–88; ¹H NMR (CDCl₃) δ 8.36 (d, *J* = 8.8 Hz, 2H), 7.97 (q, *J* = 7.2 Hz, 4H), 7.02 (d, *J* = 7.2 Hz, 4H), 4.06 (t, *J* = 6.8 Hz, 2H), 1.80–1.86 (m, 2H), 1.26–1.50 (m, 28H), 0.88 (t, *J* = 6.4 Hz, 3H).

(*E*)-4-((4-hexadecyloxy phenyl) diazenyl) benzenamine (**3**)

Na₂S · 9H₂O (4.80 g, 20 mmol) was added to a suspension of **2** (2.72 g, 6 mmol) in 50 ml of H₂O/dioxane (1:1, v/v). The reaction mixture was stirred at 80 °C for 24 h. Crude **3** (2.62 g) was obtained and purified by column chromatography on silica gel with chloroform as the eluent, yield 60%. M.p. 88–89; ¹H NMR (CDCl₃) δ 8.83 (d, *J* = 8.8 Hz, 2H), 7.76 (d, *J* = 8.8 Hz, 2H), 6.98 (d, *J* = 9.2 Hz, 2H), 6.73 (d, *J* = 8.4 Hz, 2H), 4.02 (t, *J* = 6.4 Hz, 2H), 3.98 (s, 2H), 1.77–1.84 (m, 2H), 1.26–1.47 (m, 28H), 0.88 (t, *J* = 6.4 Hz, 3H).

(1*s*, 3*s*, 5*s*)-Cyclohexane-1,3,5-tricarboxylic acid (**4**)

SOCl₂ (1 ml; excess) was dropped into 10 ml of dry THF solution of (1*s*, 3*s*, 5*s*)-cyclohexane-1, 3, 5-tricarboxylic acid (0.43 g, 2 mmol). The reaction mixture was refluxed and stirred for 3 h. The solvent and excess SOCl₂ were evaporated under reduced pressure to

yield **4** as a white solid. The product was used in the next reaction without further purification.

(1*s*, 3*s*, 5*s*)-*N*1, *N*3, *N*5-tris(4-((*E*)-(4-hexadecyloxy phenyl) diazenyl) phenyl) cyclohexane-1,3,5- tricarboxamide (**AZO-C16**)

4 (0.22 g, 1 mmol) in 5 ml THF was dropped into 30 ml THF solution of **3** (1.44 g, 3.3 mmol) under an atmosphere of dry argon, then 0.5 ml triethylamine (TEA) was added. The reaction mixture was stirred and refluxed overnight. The resulted precipitate was then filtered and washed with THF to obtained 0.96 g of **AZO-C16** (65% yields). M.p. 73–75 °C, ¹H-NMR (CDCl₃, 60 °C) δ 8.18 (br, NH, 3H), 7.83–7.85 (m, ArH, 12H), 7.69–7.71 (m, ArH, 6H), 6.95–6.98 (m, ArH, 6H), 4.02 (t, —OCH₂—, 6H), 3.58 (m, 3H), 2.05 (m, 3H), 1.79–1.82 (m, 9H), 1.44–1.49 (m, 6H), 1.30 (s, —CH₂—, 72H), 0.89 (t, —CH₃, 9H). Anal. Calcd (%) for C₉₃H₁₃₅N₉O₆: C 75.72, H 9.22, N 8.55; found: C 75.46, H 9.11, N 8.67. MALDI-TOF-MS: 1475.1 [M+H]⁺.

Instruments

Fourier transform infrared (FT-IR) spectra were performed using a Nexus 470 spectrometer (Nicolet Company). UV–visible spectra were recorded on an UV–vis 2550 spectroscope (Shimadzu). The UV and visible irradiation was carried out by a CHF-XM550W power system (China). Visible light was generated by a 500 W Xe lamp with a standard band-pass filter 440 AF10 (Omega). Irradiations in the UV region were effected at 365 nm. Scanning electron microscopy (SEM) images of the xerogels were obtained using an SSX-550 (Shimadzu) with an accelerating voltage of 15 kV. Samples were prepared by spinning the gels on glass slices and coating with Au.

RESULTS AND DISCUSSIONS

Gelation properties

A typical procedure for gelation test is described below: a weighed compound was mixed with a certain organic solvent in a sealed test tube and the mixture was heated until the solid was dissolved. The resulting solution was then cooled to room temperature. If the test tube with gelled sample was turned upside down without flow, the sample was labelled as 'gel'.^[14] The gelation properties of **AZO-C16** were tested in 20 kinds of solvents (Table 1). It shows excellent gelling capability with 13 kinds of the test solvents and all the gels were semitransparent and stable for months (Fig. 1). These gelling solvents ranged from hydrocarbon solvents and aromatic solvents to dipolar aprotic solvents. This indicates that **AZO-C16** acts as a versatile gelator.

UV–vis spectra and the photochromic properties of the gels

Electronic UV–vis absorption spectra of the gels were studied to obtain information about the aggregated state of azobenzene on the molecular scale. The concentration of both dioxane and DMF gels is 1.0×10^{-2} M and the concentration of both dioxane and DMF solution is 1.0×10^{-5} M. Dioxane and DMF solutions of **AZO-C16** have maximum absorbance at 367 and 372 nm, respectively, corresponding to the *trans*-azobenzene chromophore (Fig. 2a and 2b). In the gel state of the corresponding solvents, the absorption band of π – π^* transitions of the

Table 1. Gelation properties of **AZO-C16**

Solvents	State	CGC	Solvents	State	CGC
Dichloromethane	G	8 mg/ml	Ethanol	I	—
Chloroform	G	10 mg/ml	1-Butanol	I	—
Acetone	I	—	Benzene	G	10 mg/ml
Acetonitrile	I	—	Toluene	G	8 mg/ml
Ethyl acetate	G	6 mg/ml	Xylene	G	10 mg/ml
Hexane	I	—	Bromobenzene	G	10 mg/ml
Cyclohexane	I	—	1-Bromobutane	G	10 mg/ml
THF	G	10 mg/ml	1-Bromohexane	G	10 mg/ml
Dioxane	G	8 mg/ml	1,2-Dichloroethane	G	10 mg/ml
Methanol	I	—	DMF	G	6 mg/ml

CGC, critical gelation concentration, the minimum concentration necessary for gelation of solvents; I, insoluble; G, gel.

azobenzene moiety became broad and the maximum absorbance blue shifted to 344 and 363 nm (Fig. 2c and 2d), respectively. The situation for the solution and gel state in THF solvent was similar to that of dioxane. This indicates that the azobenzene groups form H-type aggregation in the gel state (especially dioxane as the solvents). Under the irradiation of UV light (365 nm), these bands of azobenzene obviously decreased and two new bands at 318 and 450 nm in these solvents were observed. This indicated the transformation of the *trans* isomer to *cis* isomer of the azobenzene groups. Sequentially, the stable gels collapsed gradually and became homogeneous sol over 2 h. Moreover, the absorption bands of the *cis* isomer in collapse gel are almost the same with that of *cis* isomer in diluted solution, which means that the photochromic process destroyed the aggregates in the gel state, thus resulting in the collapse of the gel. The sol was deposited instead of recovering to homogeneous gel upon irradiation with the visible light of 440 nm for 30 min at room temperature in DMF or dioxane. The gel state can be restored again by heating the sample to solution (within 10 min, 95 and 105 °C for DMF and dioxane, respectively) and cooling to room temperature. However, for CHCl₃ gel (10 mg/ml) with *T_g* of 58 °C, the irradiation-induced sol could be directly back to the gel by visible light irradiation at room temperature.

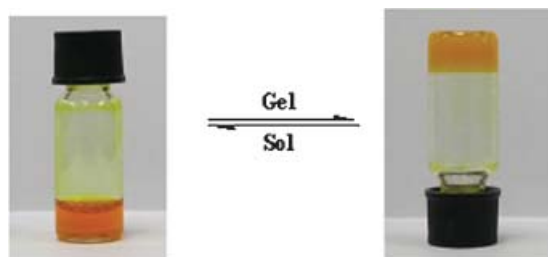
Morphologies of the xerogels

To obtain visual images of the assembled **AZO-C16** from various organic solvents, the morphologies of the xerogels obtained from **AZO-C16** were investigated by SEM. DMF and dioxane xerogels were obtained from corresponding initial gels with a concen-

tration of 10 mg/ml, while THF xerogel was obtained from the gel of 12 mg/ml. All of the micrographs of the xerogels from the above three solvents show one-dimensional aggregation (Fig. 3), but the solvent influences the morphology of the fibres to a certain extent. In the DMF xerogel, one can consistently observe a well-developed network structure composed of fibrous aggregates, with the length of several micrometres and the diameters of 100–200 nm (Fig. 3a). Some of the fibres self-assembled to form right- and left-handed helical structure (Fig. 3a and 3b). This result indicates the cyclohexyl core of the gelator induced the helically self-aggregated morphology. To our surprise, the helical self-assembly is not so clearly expressed at the supramolecular level in THF and dioxane gels. In THF, the xerogel has a smooth belt structure with the width of the belt in the range of 50–200 nm (Fig. 3c). The xerogel from dioxane also shows one-dimensional fibres, several of the fibres aggregated to form bundles with the width about 500 nm (Fig. 3d). After a gel to sol transition by 2 h UV irradiation (365 nm) in DMF, and followed by 30 min 440 nm visible light irradiation, the obtained precipitates gave a morphology as shown in Fig. 3e and 3f. It is obvious that the precipitates are in fact also composed of fibre-like entities (Fig. 3f). This implies that the packing of the molecules in the precipitates is similar to that in the gel. However, as the overall three-dimensional network of fibres cannot be fully developed at a temperature far from *T_g*, the reversibility of a gel upon visible light cannot be realized at room temperature in DMF. Whereas for the gel with a lower *T_g* such as CHCl₃ gel, the irradiation-induced *cis*-sol can be reverted to gel even at room temperature (20 °C).

The structure investigation of the gels

To study the driving force of gel–sol process, temperature-dependent ¹H NMR spectra were examined. ¹H NMR spectra of **AZO-C16** (ca. 10 mg/ml in CDCl₃, *T_g* = 58 °C) at 20, 40 and 60 °C are shown in Fig. 4. ¹H NMR spectrum of aromatic proton in **AZO-C16** displayed broad signals at room temperature and became discriminable at higher temperature. The proton signal of the amide groups (Ha, Scheme 1) at 20 °C was very weak. At 40 °C, a broad signal at about 8.38 ppm assigned to the protons of amide groups was detected and high field shifted to 8.18 ppm at a temperature of 60 °C. Hb also slightly went to the higher field positions with the increase in the temperature (7.74–7.71 ppm from 20 to 60 °C). Other proton signals have almost no change

**Figure 1.** Pictures of the sol–gel transition of **AZO-C16** in DMF (10 mg/ml).

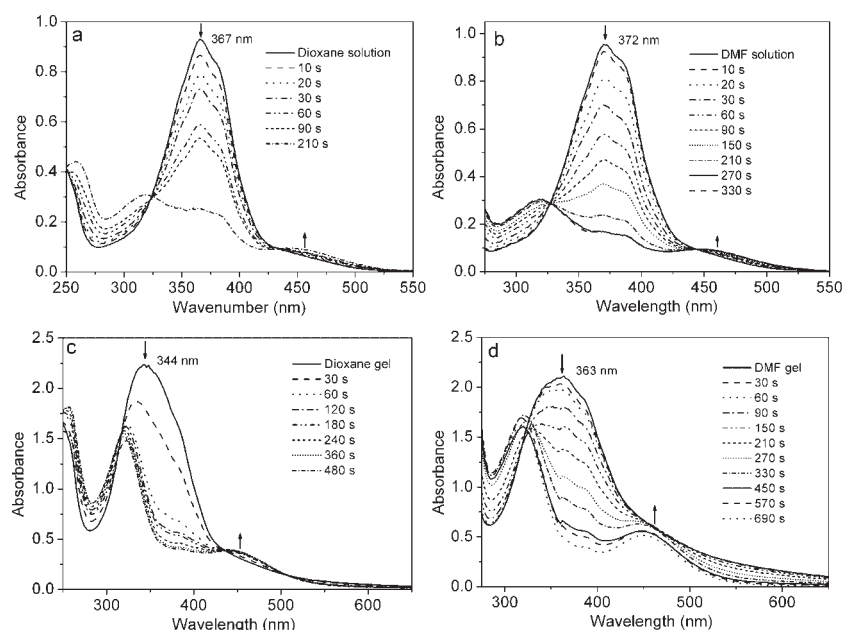


Figure 2. Absorption spectral changes of **AZO-C16** in the solutions of dioxane (a), DMF (b) (1.0×10^{-5} M, 10 mm cell) and gels of dioxane (c), DMF (d) (1.0×10^{-2} M, 1 mm cell), under the irradiation of 365 nm light at room temperature

with the temperature. These results implied that the intermolecular H-bonds were formed between neighbouring amide groups at room temperature. The intermolecular H-bonds became weaker by increase in the temperature, and as a result, the proton signal of amide groups upfield shifted. After the sample irradiated with 365 nm light for 3 h at room temperature, the gel was translated to sol. From NMR spectrum of the *cis*-sol sample, we can see that the amide proton Ha was obviously upfield shifted to 7.97 ppm, while Hc and Hd were downfield shifted to 7.87–7.85 ppm. These data indicate that the hydrogen bonds were destroyed by *trans*–*cis* transition, thus resulted in a gel to sol transition upon irradiation.

IR spectra of the gels were also studied to obtain the information of intermolecular interaction of these molecules. Figure 5A gives the comparison of the IR spectra of **AZO-C16** powder and its corresponding gel and solution in THF. The IR spectrum of pure THF was also measured as a reference. In the

powder, the NH and CO stretching modes of amide groups are located at 3286 and 1659 cm^{-1} , respectively. These two peaks only slightly move to 3284 , 1657 cm^{-1} in the THF gel, respectively. Whereas in the THF solution (5×10^{-3} M), the IR signals include a strong band at about 3386 cm^{-1} , attributed to the free NH stretching vibrational band of amide.^[15,26,27] The comparison of the IR spectra among solution, gel and solid state indicates that the formation of the hydrogen bond promotes the aggregation of **AZO-C16** molecules to form gel state; and the intermolecular hydrogen bonds in the gel state are essentially similar to that of the solid state.^[11,19,26,27] The IR spectra of the gel from different solvents of THF, dioxane and DMF are shown in Fig. 5B, from which we can see that the two amide bands in THF and dioxane gel are almost posited at same position. Whereas in the DMF gel, both the NH and C=O vibration move to a lower wavenumber (3279 , 1655 cm^{-1} , respectively). It is obvious that in a solvent containing amide C=O moiety such as DMF, the intermolecular

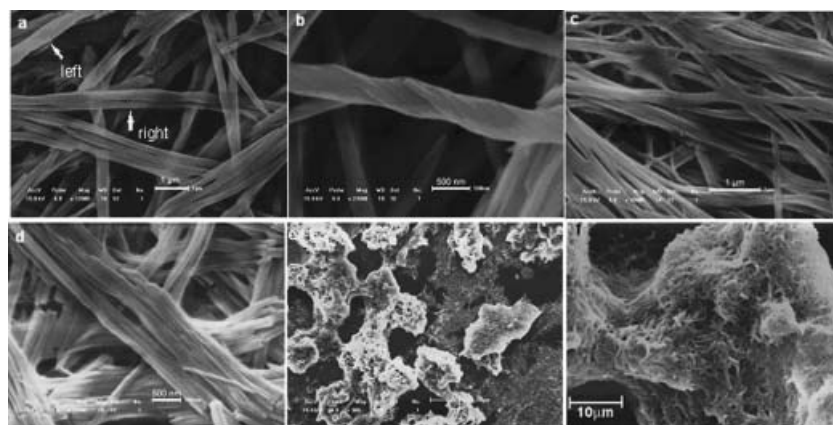


Figure 3. SEM images of xerogels from DMF (a, b, the arrow pointed to the right- and left-hand helix), THF (c), dioxane (d), precipitates after a gel–sol transition by UV (365 nm) and visible light (440 nm) in DMF (e, $50\text{ }\mu\text{m}$ and f, $10\text{ }\mu\text{m}$)

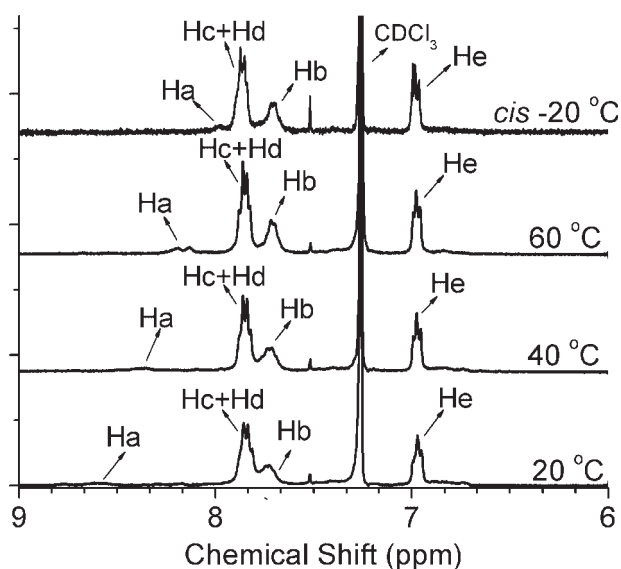


Figure 4. Partial ^1H -NMR spectra of **AZO-C16** (10 mg/ml) in CDCl_3 at temperatures of 20, 40, 60 $^\circ\text{C}$ and that after 365 nm irradiation for 3 h at 20 $^\circ\text{C}$

hydrogen bonds were enhanced, which suggests that DMF may participate in the formation of the aggregates.

As it pointed out in the above section, the *cis*-1, 3, 5-cyclohexanetricarboxamides core reacted on the formation of the hydrogen bonding; however, the π - π stacking of azobenzene moieties and hydrophobic interactions of long alkyl chains may also influence the large aggregate of the molecules in the gel state (Scheme 2). By the molecular modelling studies,^[2,15,28] it can

be deduced that the three amide-CO and NH of **AZO-C16** can direct themselves parallel to each other and perpendicular to the cyclohexane ring by intermolecular hydrogen bonds as described in Scheme 2a. Similar type of stacked amide hydrogen-bonding arrangement has been observed in a crystal structure of *cis*-1, 3, 5-cyclohexanetricarboxamide derivative reported by Hamilton, in which the molecules packed as a non-central arrangement in the structure.^[28] The presence of the azo group in the *trans* form is important for the formation of the complete intermolecular hydrogen bonding between amide as well as the π - π interaction between azo. The irradiation of UV light could induce *trans* to *cis* transition of the AZO group. As shown in Scheme 2b, the spatial block in the *cis* isomer resulted in the incomplete hydrogen bonding of **AZO-C16**, which destroyed the huge aggregate of the molecules necessary for the gelation formation. As a result, a gel to sol transition happened upon irradiation of the UV light in the gel state of **AZO-C16**.

CONCLUSIONS

In conclusion, by introducing *cis*-1, 3, 5-cyclohexanetricarboxamides core, azobenzene moieties and long alkyl chains into one system, we obtained a versatile gelator which can widely gel varieties of organic solvents. Electron microscopy and spectral studies show that the gel formation is due to the aggregation of **AZO-C16** molecules into helical fibres or aggregated bundles, through cooperative interactions of hydrogen bonding of amide moieties, π - π interactions of azobenzene groups and hydrophobic interactions of alkyl chains. From this research, we have obtained new insight toward the molecular design in the more effective organogelator for organic solvents. Moreover, the gel is

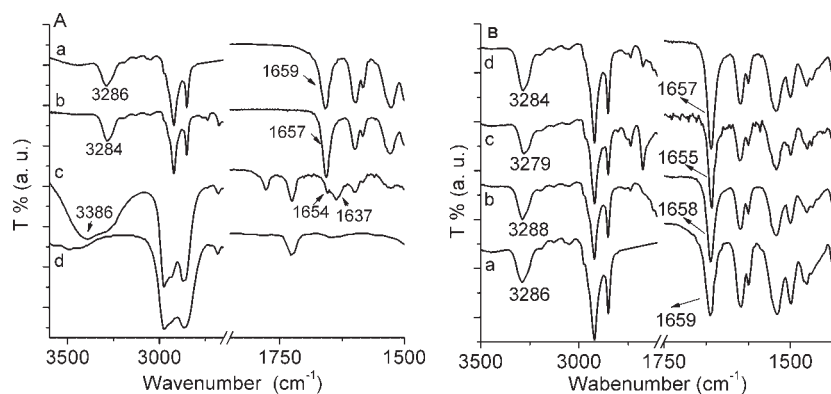
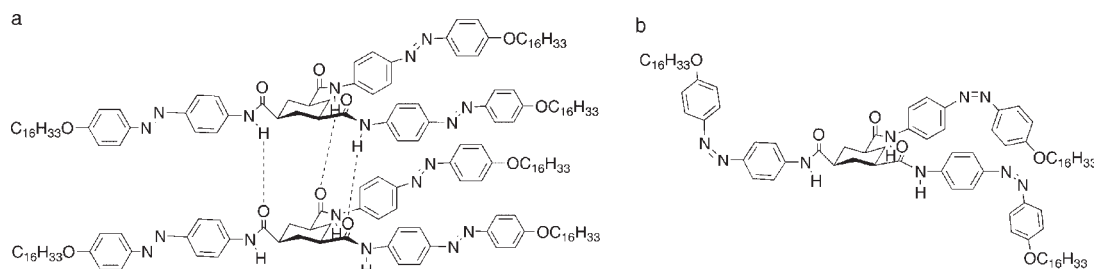


Figure 5. A: IR spectra of **AZO-C16** in powder (a), the gel (b), (20 mg/ml), the solution (c, 5×10^{-3} M) from THF and the spectrum of pure THF (d). B: The IR spectra of the powder (a) and the gels (20 mg/ml) of dioxane (b), DMF (c) and THF (d), respectively



Scheme 2. Schematic presentation of the intermolecular hydrogen bonds between *trans* **AZO-C16** molecules in the gel state (a), the structure for the *cis* **AZO-C16** molecule (b)

sensitive to light irradiation and performs photochromism and gel–sol transition by UV irradiation at room temperature. The stimuli responsive smart supramolecular system is important in biological application, molecular (drug) release system, sensors, molecular devices, etc. Therefore, this research affords a good example for design and investigation of the environment responsive soft materials.

Acknowledgements

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