

Study of aggregation behavior of predesigned azobenzene-cholesteryl derivatives in deep eutectic solvents

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Abstract

Structurally isomeric cholesteryl-appended azobenzene derivatives (azo-1 to azo-5) with various substituents, such as H/unsubstituted, ether, ester, and nitro at the terminal position of azobenzene units were designed, and synthesized. The gelation ability and aggregation behavior of the above synthesized azobenzene-cholesteryl derivatives in deep eutectic solvents (DES) such as Zinc Chloride: Ethylene Glycol (Zn:EG), Choline Chloride: EG (Ch:EG), Choline Chloride: Urea (Ch: Urea), and Choline Chloride: Glycine (Ch: Gly) were studied. The results revealed that all the azo derivatives formed semi-transparent and strong/hard eutectic gels in at least one DES except azo-4 which formed gel in two DES. The morphological analyses by scanning electron microscopy (SEM) exhibited entangled dense fibrous, flowers, and sheet-like textures, depending on the nature of DES as well as azo derivatives. Like all azobenzene-based organo-gelators, UV-triggered gel-to-sol transition was expected for these eutectic gels. However, these eutectic gels did not undergo the gel-to-sol transition under UV irradiation. This could be due to the hardness of the gel, which arrests the structural transformation from trans-to-cis during photolysis. It was further confirmed by absorption profiles of before and after irradiation of eutectic gels. Regarding application, an attempt has been made to use eutectic gels as a template for the synthesis of nanomaterials and the results revealed that the azo-4 gel can be used to prepare aggregated highly dense nanorods of copper chloride.

Keywords: Azobenzene; Cholesteryl derivatives; Eutectic gel; Morphology; Deep eutectic solvents.

Introduction

Supramolecular self-organization is one of the key techniques for the “bottom-up” nanotechnology approach. In this technique, small molecules form well-defined larger nanostructures via multiple non-covalent intermolecular forces, such as hydrogen-bonding, dipole–dipole, and van der Waals interactions (including π - π interactions) [1,2]. Based on this, much number of organic gelators was developed in which organic compounds formed gel in organic solvents. However, deep eutectic solvents (DES), considered green solvents, result from hydrogen bonds that occur between a hydrogen-bond acceptor (HBA) and a hydrogen bond donor (HBD). DES share some of the well-known characteristics of ionic liquids namely low volatility, high conductivity, wide liquid temperature range, and high solvation ability for a large number of compounds – and, additionally present high biodegradability, easy preparation, and renewable character [3-12].

Azobenzene is an aromatic molecule, derived by replacing the hydrogen atom of diazene (-NH=NH-) with phenyl ring. Azobenzene are well-known photochromic molecules and can undergo photo tunable isomerization. Moreover, azobenzene are easily tunable by substituting electron-donating or withdrawing substituents at the benzene ring of the azobenzene. Therefore, it has received much attention in research areas both fundamental and applied sciences [13-16]. Similarly, cholesteryl-based compounds have increased

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attention due to an attractive starting material, as a model system for organic synthesis, easy functionalization, and low cost [17-19]. Therefore, by combining both-azobenzene and cholesteryl units, many derivatives were developed especially for photo-tunable liquid crystalline materials, photo-tunable organogelators, photochemical molecular switches etc. In our earlier report, we have developed azobenzene-cholesteryl based organo-gelators and their gelation and aggregation phenomena were studied with respect to the length of their alkyl chains. These compounds act as good gelators and form gels in a variety of organic solvents [20]. In continuation of the study of self-assembly of azobenzene-cholesteryl derivatives, in this work, we would like to extend our studies on aggregation behavior in deep eutectic solvents. For that purpose, we prepared four different eutectic solvents such as Zinc Chloride: Ethylene Glycol (Zn:EG), Choline Chloride: EG (Ch:EG), Choline Chloride: Urea (Ch: Urea), and Choline Chloride: Glycine (Ch: Gly). The gelation ability of five different pre-designed azobenzene-cholesteryl derivatives namely azo-1, azo-2, azo-3, azo-4, and azo-5, and their aggregation behavior was studied by morphological analysis using scanning electron microscopy (SEM). The morphology, as well as optical properties of the eutectic gels, was studied in detail and their potential application as a template for the synthesis of nanomaterials was studied in detail.

Materials and Methods

Materials

All chemicals were purchased from Aldrich Chemicals and used without further purification. All solvents were purified before use. Aniline, p-anisidine, ethyl-4-aminobenzoate, (–)-cholesteryl chloroformate and 4-(dimethyl amino) pyridine were purchased from Sigma Aldrich and used as such without further purification. Trimethylamine and N, N'-dicyclohexyl carbodiimide (Aldrich) were used as received. All the chemicals for the preparation of deep eutectic solvents such as choline chloride, zinc chloride, ethylene glycol, and urea were purchased from Sigma Aldrich and used as received. Dichloromethane was distilled over calcium hydride under argon immediately before use and all the solvents were purified and dried by standard procedures before use. All the pre-designed azobenzene-cholesteryl compounds were synthesized according to our procedure reported in our earlier publications [20,21].

Instrumentation

Fourier transform infrared spectra (FTIR) were recorded using a Fourier transform infrared (FTIR) spectrophotometer (Spectrum One, Perkin Elmer). Nuclear magnetic resonance (NMR) spectra were obtained using a Bruker AMX-500 (Darmstadt, Germany) high-resolution NMR spectrometer, and the chemical shifts were reported in ppm with tetramethylsilane (TMS) as an internal standard. UV-Visible recording spectrophotometer in chloroform solution (10^{-6} M). The typical procedure adopted is as follows: The solution was objected to UV irradiation emanating from a 125 W medium pressure mercury lamp kept at a distance of 10 cm from the sample at various intervals of time followed by UV absorption measured on the spectrophotometer, respectively. This procedure was repeated until the reduction in absorption completed. The eutectic gels were subjected

to water exchange in order to remove the DES and freeze-dried. Thus obtained xerogels were used for morphological analysis. The dried samples held on glass substrates were attached to a copper holder for SEM by conductive adhesive tape and were coated with platinum.

Synthesis of compound Ia-Ie

Compound Ia-Ie was synthesized according to the reported procedures [22]. For example, compound Ic namely ethyl-4-[(4-hydroxyphenyl) diazenyl] benzoate was synthesized as follows: Typically, about 9.03 g (1.0 equiv, 55.0 m mol) of ethyl-4-amino-benzoate was taken in a round-bottom flask and dissolved in 1M HCl. The above solution was stirred at 0°C. To this solution, the aqueous solution of 3.80 g (1.0 equiv, 55.0 m mol) of sodium nitrite in 25 mL of water was added drop wise to produce a diazonium salt solution. Meanwhile, 9.61 g (1.65 equiv, 90.8 m mol) of sodium carbonate and 5.81 g (1.0 equiv, 55.0 m mol) of phenol were dissolved in 100 mL of water at 0°C. To this solution, the diazonium salt solution was added dropwise and stirred for 3 hrs at 0°C. Then the condense of the flask was neutralized with 1M hydrochloric acid to precipitate the product. Thus, the obtained precipitate was filtered off, air-dried, and recrystallized in ethanol to get pure compound as orange solid (yield of 74%). By using the same procedure, the other azo compounds were synthesized, in which respective amines were used instead of ethyl-4-amino-benzoate.

Synthesis of gelators

The procedure for the synthesis and spectral characterization of the gelators molecules is followed from our earlier report [21]. For example, compound Azo-1 was synthesized as follows: Compound 1a (1.98 g, 10 m mol) and triethylamine (3.036 g, 30 m mol) were placed in double neck round bottom flasks with nitrogen inlets and dissolved in dry chloroform. Next, a small amount of 4-(dimethylamino) pyridine (DMAP) dissolved in chloroform was slowly added to these solutions with constant stirring under a nitrogen atmosphere. Then, cholesteryl chloroformate (4.491 g, 10 m mol) that was dissolved in chloroform was added drop wise to the solutions through a funnel. After this addition, the reaction mixture was stirred at room temperature for 48 hrs. Next, the contents of the flasks were extracted with excess chloroform and washed with aqueous sodium bicarbonate, a brine solution, and water. This procedure was used to obtain the organic phase, which was dried over anhydrous magnesium sulfate and then concentrated. The resulting crude product was recrystallized from ethanol to obtain a pure final compound (yield 79%). A similar procedure was adopted for the synthesis of other compounds (Azo-2 to Azo-5).

Preparation of Deep Eutectic Solvents (DES)

All the DES was prepared according to the reported procedure [23]. About 1:2 mole ratio of choline chloride/ zinc chloride with any one of the compounds such as EG/ urea/glycine were mixed and heated (<80°C) till getting homogenous liquid. Then allowed to cool down to room temperature. There are 4 different DES were prepared such as Zinc Chloride: Ethylene Glycol (Zn:EG) (1:2 Mole ratio), Choline Chloride: EG (Ch:EG) (1:2 Mole ratio), Choline Chloride: Urea (Ch: Urea) (1:2 Mole ratio), and Choline Chloride: Glycine (Ch: Gly) (1:2 Mole ratio). Thus obtained DES is little to moderate viscous liquid in nature.

Procedure for gelation (DES)

About 3 mg of azo derivative was taken in a small vial. To this about 100 microliters of the above prepared DES was added. The resulting mixture was heated till the solution was homogeneous and then cools down. Gelation ability was observed by "inverted tube" method.

Template assisted synthesis of copper chloride nanomaterials

First, azo-4 eutectic gel was selected for the template assisted synthesis of nanomaterials. Therefore, azo-4 eutectic gel was prepared. Thus obtained gels were added to 0.22 g of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and then heated to 85°C till the gel become liquid state and stirred for 30 minutes. Once the added copper chloride was homogeneously mixed with the gelators and DES, it was allowed to stir for 4 hrs at 60°C and cooled to room temperature. Then the resulting mixture was diluted/extracted with DMF and gelators were removed by decantation method. The resulting compounds were washed with ethanol and minimum amount of water. The product was centrifuged and dried. For comparison, the neat experiments performed without using the Azo-4 in the above procedure. Instead, sodium bisulfite (NaHSO_3) was used as a reducing agent.

Results and Discussion

Characterization of Ia-Ie

The synthetic route for the preparation of azobenzene and cholesteryl-based conjugates (azo-1 to azo-5) is shown in (Figure 1). The photosensitive azo benzene derivatives (Ia-e) were obtained by reacting sodium phenoxide with respective p-substituted aniline in the presence of nitrous acid (diazonium salt). All the azoderivatives were purified by repeated recrystallization in hot ethanol.

FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$): 3463 (-OH), 1517, 1580 (C-C in Ar), 1728 (C=O). $^1\text{H-NMR}$ (CDCl_3 , 500 MHz, δ in ppm): 8.4 (d, 2H, Ar-C-COO), 8.19 (d, 2H, Ar-H), 7.9-8.0 (m, 4H, Ar-C-N), 7.0 (d, 2H, Ar-C-OH), 5.79 (broad, s, -OH), 4.38 (q, 2H, O- CH_2), 1.39 (t, 3H, O- CH_2 - CH_3).

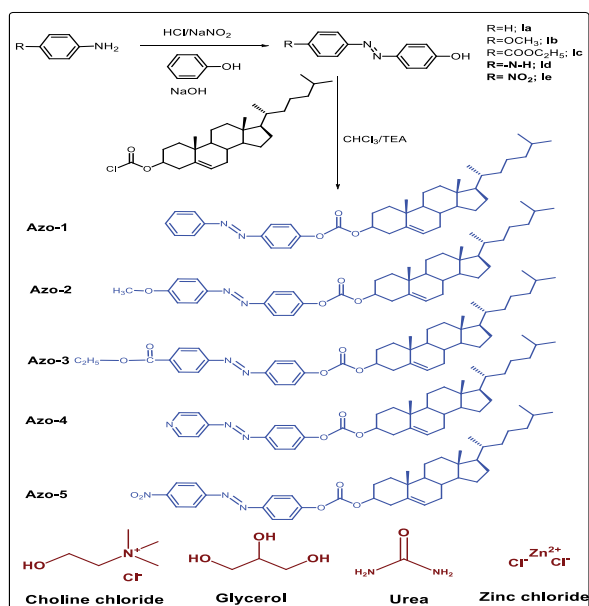


Figure 1: Synthetic routes and structures of azobenzene-cholesteryl derivatives and materials for DES.

Characterization of Azo-1 to Azo-5

The above-synthesized azo derivatives (Ia-e) were further subjected to react with cholesteryl chloroformate in presence of triethyl amine in chloroform or dichloromethane to get eutectic gelators (azo-1 to azo-5) with the yield of 59-79%. All the compounds were purified by recrystallization in ethanol. All the compounds were found to be soluble in DMF, CHCl_3 , CH_2Cl_2 , acetone and insoluble in ethanol, methanol and toluene. The structures of all the azo compounds were confirmed by ^1H and $^{13}\text{C-NMR}$ analysis.

Azo-1: Yield: 79%; FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$): 2868, 2947 (CH_2), 1764 (C=O), 1500, 1586 (C-C in Ar), 1247 (COC). $^1\text{H-NMR}$ (CDCl_3 , 500 MHz, δ in ppm): 7.97 – 7.90 (m, 4H), 7.53-7.47 (d, 2H), 7.36 – 7.34 (m, 2H), 7.26 (t, 1H), 5.44 (d, 1H), 4.66 (m, 1H), 2.51-1.33 (m, 28H), 1.09 (s, 3H), 0.93 (d, 3H), 0.87 (d, 6H), 0.69 (s, 3H). $^{13}\text{C NMR}$ (500 MHz, CDCl_3) δ 152.91, 150.21, 139.05, 131.07, 129.07, 124.05, 123.28, 121.65, 79.13, 77.25, 56.66, 56.12, 49.97, 42.30, 39.69, 39.50, 37.92, 36.82, 36.54, 36.17, 35.78, 31.90, 31.83, 28.21, 28.00, 27.63, 24.27, 23.82, 22.81, 22.55, 21.04, 19.27, 18.71, 11.85.

Azo-2: Yield: 73%; FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$): 2869, 2942 (CH_2), 1762 (C=O), 1503, 1593 (C-C in Ar), 1247 (COC). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.92 – 7.89 (m, 4H), 7.33-7.26 (d, 2H), 7.02 – 7.00 (m, 2H), 5.43 (d, 1H), 4.69 (m, 1H), 3.88 (s, 3H), 2.51-1.33 (m, 28H), 1.08 (s, 3H), 0.93 (d, 3H), 0.87 (d, 6H), 0.68 (s, 3H). $^{13}\text{C NMR}$ (500 MHz, CDCl_3) δ 162.11, 152.58, 150.34, 146.88, 139.06, 124.76, 123.69, 121.56, 114.19, 79.05, 77.25, 56.65, 56.11, 55.54, 49.95, 42.29, 39.68, 39.50, 37.91, 36.81, 36.53, 36.16, 35.17, 31.88, 31.82, 28.20, 27.99, 27.62, 24.26, 23.82, 22.80, 22.55, 21.03, 19.26, 18.70, 11.84

Azo-3: Yield: 76%; FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$): 2867, 2949 (CH_2), 1763 (C=O), 1718 (C=O), 1497, 1602 (C-C in Ar), 1255 (COC). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.20-8.19 (d, 2H), 8.18 (d, 2H), 7.99 – 7.92 (m, 4H), 7.37 – 7.36 (m, 2H), 7.26 (t, 1H), 5.43 (d, 1H), 4.43-4.39 (m, 1H), 2.50-1.33 (m, 28H), 1.17 (s, 3H), 0.99 (d, 3H), 0.87 (d, 6H), 0.68 (s, 3H). $^{13}\text{C NMR}$ (500 MHz, CDCl_3) δ 165.99, 154.92, 153.48, 150.10, 139.01, 132.24, 130.55, 124.38, 123.30, 122.60, 121.74, 79.21, 77.25, 61.25, 56.65, 56.12, 49.96, 42.29, 39.68, 39.49, 37.90, 36.81, 36.53, 36.16, 35.77, 31.89, 28.20, 27.99, 27.61, 24.26, 23.81, 22.80, 22.54, 21.03, 19.26, 18.70, 11.84.

Azo 4: Yield: 69 %; FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$): 2874, 2947 (CH_2), 1759 (C=O), 1721 (C=O), 1490, 1606 (C-C in Ar), 1251 (COC). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.36 (d, 2H), 7.94-8.34 (m, 4H), 7.01 – 7.26 (d, 2H), 5.39 (d, 1H), 4.04 - 4.12 (d, 2H), 2.39-1.85 (m, 28H), 1.11 (s, 3H), 0.97 (d, 3H), 0.87 (d, 6H), 0.66 (s, 3H). $^{13}\text{C NMR}$ (500 MHz, CDCl_3 , δ in ppm) 162.94, 156.06, 154.68, 148.18, 146.17, 139.40, 125.60, 124.68, 123.07, 122.88, 114.91, 77.62, 77.25, 77.00, 76.74, 68.51, 67.84, 56.67, 56.12, 49.98, 42.29, 39.50, 38.05, 36.85, 36.53, 36.16, 35.77, 31.88, 31.83, 28.20, 28.00, 27.70, 25.96, 25.70, 24.26, 23.81, 22.80, 22.54, 21.02, 19.24.

Azo-5: Yield: 59 %; FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$): 2862, 2949 (CH_2), 1756 (C=O), 1726 (C=O), 1484, 1607 (C-C in Ar), 1254

(COC). ^1H NMR (500 MHz, CDCl_3) δ 8.30 (d, 2H), 7.99-8.79 (m, 4H), 7.14 - 7.32 (d, 2H), 5.37 (d, 1H), 4.06 - 4.13 (d, 2H), 2.39-1.85 (m, 28H), 1.14 (s, 3H), 0.99 (d, 3H), 0.88 (d, 6H), 0.63 (s, 3H). ^{13}C NMR (500 MHz, CDCl_3 , δ in ppm): 156.41, 154.48, 148.32, 146.14, 139.14, 125.63, 124.49, 123.27, 122.79, 114.77, 77.59, 77.35, 77.09, 76.44, 68.61, 67.69, 56.71, 56.11, 49.89, 42.29, 39.54, 36.99, 36.61, 36.14, 35.66, 31.80, 31.76, 28.19, 28.02, 27.54, 25.79, 25.65, 24.29, 23.71, 22.78, 22.49, 21.00, 19.16.

All the spectral values are in accordance with the assigned structures. For example, the ^1H -NMR spectrum of compound azo-4 is shown in (Figure 2). The presence of aromatic protons between 7.01-8.36 ppm and the presence of alkene proton ($\text{C}=\text{CH}$) at 5.39 ppm confirm the presence of azobenzene and cholesteryl unit in the structure. All other alkane protons in the cholesteryl units are resonated between 0.5-2.0 ppm. The ^{13}C -NMR for compound azo-4 was depicted in (Figure 3). The presence of peaks around 154 ppm and 122 ppm corresponding to carbonyl ($\text{C}=\text{O}$) and $-\text{C}=\text{CH}-$ carbon (in cholesteryl unit) confirmed the successful formation of azo-4. All the spectral values are in accordance with the structure of the molecule.

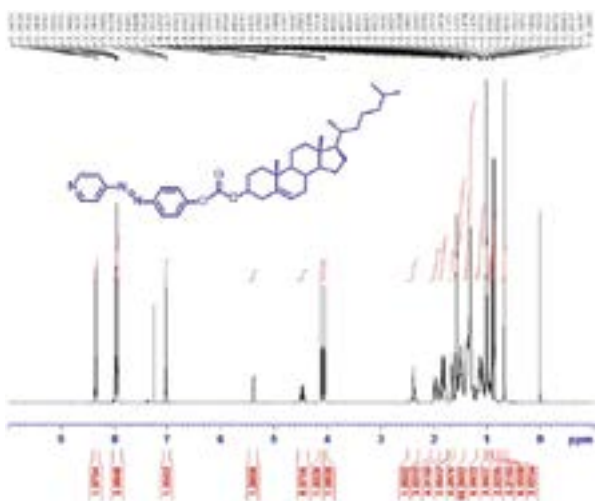


Figure 2: ^1H -NMR spectrum of Azo-4.

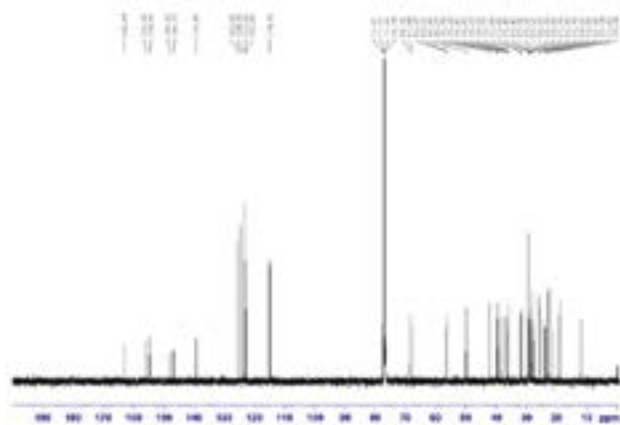


Figure 3: ^{13}C -NMR spectrum of Azo-4.

Gelation ability of predesigned azo derivatives in DES

The gelation ability of all the azo compounds (Azo-1 to Azo-5) is shown in (Table 1).

Compound/DES	Azo-1	Azo-2	Azo-3	Azo-4	Azo-5
Zn:EG	Insoluble	Insoluble	Insoluble	Insoluble	Gel
Ch:EG	Soluble	Gel	Insoluble	Insoluble	Insoluble
Ch:Urea	Gel	Insoluble	Gel	Gel	Insoluble
Ch:Gly	Insoluble	Insoluble	Insoluble	Gel	Insoluble

Table 1: Gelation ability of Azo-1 to Azo-5 in DES.

From the table, it was observed that all the derivatives form gel in at least one of the DES studied. For example, azo-1 and azo-2 form gel in Ch:Urea and Ch:EG respectively. whereas, azo-3 and azo-4 were form gel in Ch:Urea and Ch:Gly. Azo-5 form gel in Zn:EG. All the derivatives are structurally isomeric with varying substitutions such as hydrogen, ether, ester, nitro etc at the terminals of azobenzene. This indicates that the substituents at the terminals of azobenzene play a crucial role in gelation ability in DES.

The gel color varied from light orange to dark red color depended on the color of the synthesized compound as well as the type of DES. The gelators molecules formed semi-transparent gels (Figure 4) and demonstrated thermos-reversibility, 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.

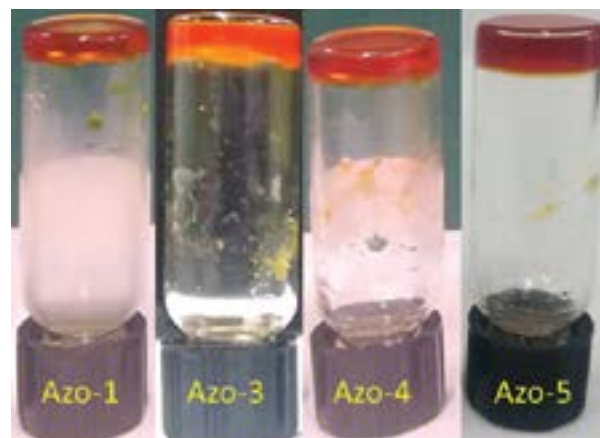


Figure 4: Representative pictures of eutectic gels.

Morphological studies

To gain visual insights regarding the morphologies of the molecular aggregation modes, all the eutectic gelators were subjected to SEM analysis, and the results are depicted in (Figure 5). The gelators exhibited as self-assembled flower-like, micro plates/sheets and bundle fiber-like aggregates with several lengths to breadth ratio as shown in the figure. Azo-1 exhibits a more crystalline-like structure than azo-2. In the case of azo-4 both in Ch:urea and Ch:EG exhibit similar flower-like aggregates with porous structure. However, unlike Ch:urea, entangled fibrous textures were seen on Ch:EG based gels. These morphologies indicate that the nature of the eutectic solvent is crucial in the aggregation of the gelators.

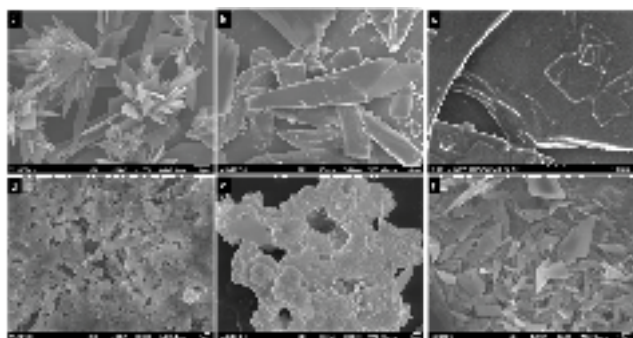


Figure 5: The SEM morphology of gels from (a) azo-1 in Ch:Urea, (b) azo-2 in Ch:EG, (c) azo-3 in Ch:urea, (d) azo-4 in Ch:urea, (e) azo-4 in Ch:Gly and (f) azo-5 in Zn:E.

Potential applications

In general, the organo/hydro gelators can be used as a template or support for the synthesis of nanoparticles such as silver nanoparticles (AgNP), gold nanoparticles (AuNPs), and iron nanoparticles (FeNPs). Since the gelators possess a 3D network structure, a large number of functional groups can provide space for the nucleation and growth of the noble metal nanoparticles [24-26]. Therefore, we attempt to use our eutectic gelators as template/structure-directing agents for the synthesis of copper chloride nanoparticles (CuCl NPs). For that, the gelator azo-4 in Ch:Urea was chosen and applied as a template for the synthesis of CuCl NPs as shown in the experimental section.

Thus obtained copper chlorides from both neat and azo-4 based eutectic gels were subjected to morphological analysis by SEM and the results were merged in (Figures 6a-d).

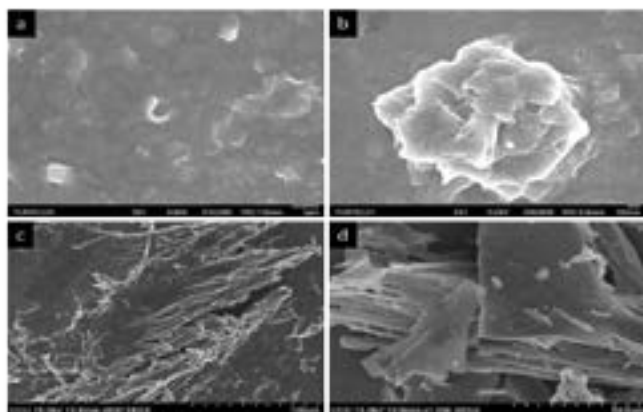


Figure 6: The SEM morphology of gels from (a and b) CuCl₂ in Ch:Urea, (c and d) CuCl₂ in Azo-4 eutectic gel.

From the morphology, it can be observed that the neat eutectic solvent exhibited self-assembled CuCl nanoparticles (Figure 6a and 6b), whereas eutectic gel exhibited aggregated nano-rods-like textures (Figure 6c and 6d).

The morphology of CuCl nanoparticles from the neat is almost similar to the reported textures by Ying Huang et al, in which the author used PVP [27]. But in our case, sodium bisulfite was used. However, the size of the particles is found to be too high (<500 nm) when compared to the reported one. This may be due to the fact that the addition of PVP which preventing the aggregation and controlled the size of the nanoparticles, whereas in our case we didn't add any size

controlling reagent. In the case of eutectic gelators-based synthesis, nanoparticles were expected. But, interestingly, aggregated rods with lengths of several micrometers and diameters of approximately 200-400 nm were observed. This may be due to the fact that the complexation of copper with the nitrogen of pyridine units of the azo-4 gel may assist or direct nanoparticles aggregated into form nanorods. However, the exact mechanism of the formation of nanorods is unclear. These results revealed that the azo-4 eutectic gelators can act as a template for the synthesis of nano-rods. However, this preliminary studies need to go a long way in order to optimize the conditions and reagents if need to be added to form nanorods of <100 nm, and the mechanism of formation of nano-rods by various analytical techniques such as XRD and XPS analysis are under progress.

Photolysis

The effects of photo-irradiation of all the compounds were studied by irradiating under UV-vis light and the changes were recorded. The representative results of photo-irradiation of azo-4 in DES were shown in (Figure 7). From the figure, it was observed that azo-4 eutectic gel exhibited an absorbance at 331 nm. Since azobenzene undergoes trans-to-cis isomerization under UV light, the gel-to-solution transition was expected similar to the corresponding organ gels.

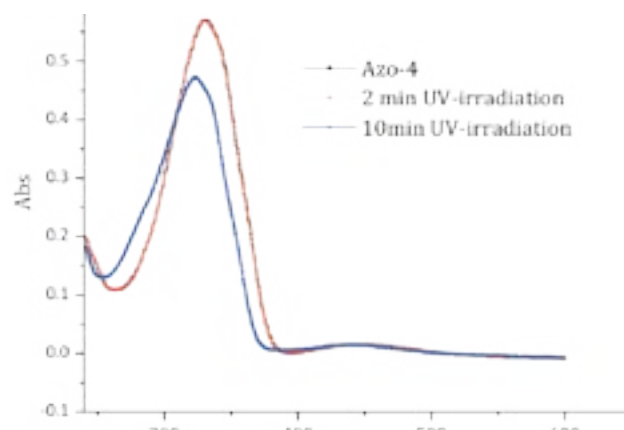


Figure 7: Changes in UV spectral characteristics during photolysis of Azo-4 gel in eutectic solvent.

However, in azo-4 eutectic gels did not undergo gel to sol transition; moreover, the corresponding absorption profiles also revealed that there was no change after irradiation of azo-eutectic gel by UV light for 2 min. After 10 min of irradiation showed no obvious or little changes in the absorption profile. However, there is no change in the nature of the gel even after irradiated over 30 min under UV light, indicating that azo-4 eutectic gel didn't undergo isomerization under UV light. It may be due to the formation of strong/hard gel as well as high viscosity of the eutectic solvent in which the azo molecule remains in the stable trans form.

Conclusion

The cholesteryl appended azobenzene derivatives with varying terminal substituents were synthesized and their gelation ability in deep eutectic solvents was studied. All the gels are hard, semi-transparent, and thermally reversible. The morphology of eutectic gels by SEM analysis

revealed dense fibrous, flower-like, and sheet-like textures, depending on the type of deep eutectic solvents used. Unlike azobenzene organogelators, these azobenzene eutectic gels did not undergo gel-to-sol transition during photolysis, which may be due to the hardness of the gel which restricts the transformation of trans-to-cis form, which was further supported by their absorption profiles before and after photolysis. Finally, an attempt has been taken to use this eutectic gel as a template for the synthesis of copper chloride nanorods. These primary studies investigated the designing of novel eutectic gels and their applications for nanomaterial synthesis.

Acknowledgments

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Competing Interests

The authors declare no competing interests.

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