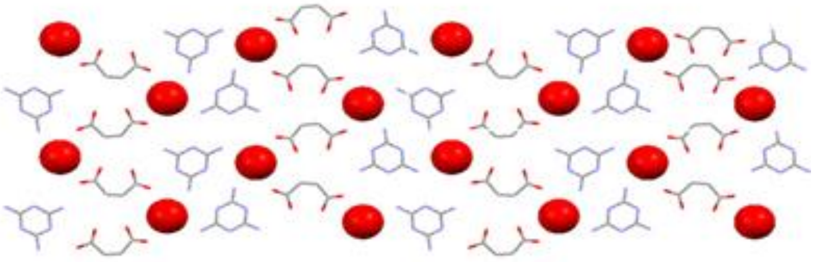
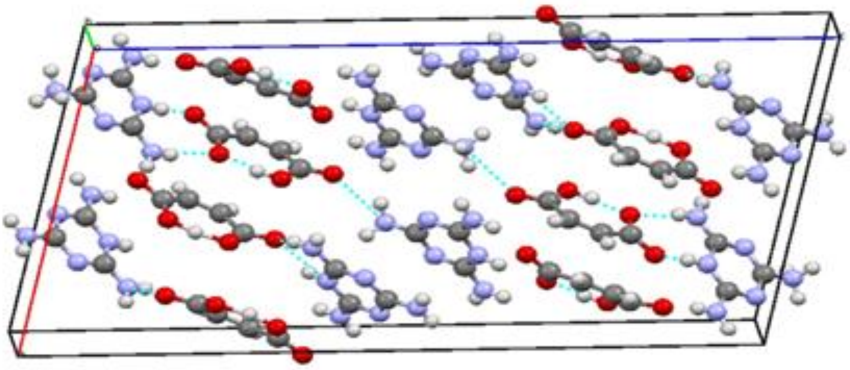
Chapter-2





Two -component supramolecular gelator based on melaminium salts: A step towards plausible mechanism of hydrogelation

Published in Colloids and Surfaces A: Physicochem.Eng. Aspects, 2012, 414, 333-338

2.1 Introduction

Gels, a type of colloidal system, where the liquid phase is immobilized by a solid phase, is always an attractive system for study and research, due to its interesting properties, and numerous applications such as templating agent for inorganic/organic materials, opto-electronic, smart materials sensitive towards various external stimuli such as pH, light, sound and temperature.[1–3] Two decades have witnessed an exponential growth of thermo reversible gel materials based on small molecules commonly known as low molecular mass organic gelators (LMOGs). Numerous systems (hydrogelator or organogelator) with a plethora of structural diversity are reported in the literature; however, most of them are discovered by chance than design. Therefore, numerous scientists working in the area of research are contributing their efforts to understand the probable mechanism of metastable gel formation in organic solvent and/or water. Although, considerable progress has been made in finding more and more fascinating applications of LMOGs, a working principle for designing new gelators with tailor made properties and applications, is still desired. In recent years, a working rule for designing and synthesis of a new organogelator is established that one-dimensional (1D) hydrogen bond favours gelation, as 1D hydrogen bonding may lead to the formation of anisotropic growth of molecular assemblies, namely, ribbon, fibre, rods and tube, which further entangle among themselves through weak non-covalent interaction to give three-dimensional (3D) network capable of immobilizing organic solvents[3]. However, designing a non-polymeric hydrogelator is still a formidable task. Many questions need to be answered before a tailor made hydrogelator is realized in future. Few of the fundamental questions are (i) how hydrogen bonded supramolecular assembly gets affected in the presence of highly polar solvents like water? (ii) role of π-π and van der Waals interactions in supporting hydrogelation, (iii) how packing of a molecules in the crystalline state is associated with packing in metastable gel state? To answer the last related query, Weiss et al.[4] had developed an indirect method to investigate the packing of gelator molecule in gel, xerogel (dried gel) and bulk state by comparing powder X-ray diffractogram (XRD) of gelator molecule with simulated single crystal of gelling agent, if any. This method suffers from inherent drawback as growth of single crystal of gelator molecule is mostly unsuccessful, particularly in its gelling solvent. Secondly, packing of gelator molecules in bulk crystalline state is mostly different from xerogel or gel state,[3] thirdly; PXRD of gel is masked by strong scattering from solvents making the diffractogram unreliable. Even though, the method developed by Weiss et al. suffers from some shortcomings, it is frequently being used for explaining the mechanism and probable packing of gelator molecules in the gel state. A gelator molecule with structural complexity and predictable hydrogen bonding aggregation pattern may acts as a model system for understanding the probable mechanism of hydrogelation using X-ray diffraction studies. One of the simplest gelling systems is two-component gelator such as an organic acid/amine salt, charge transfer complex and hydrogen bonded complex, which provide an opportunity to systematically vary one of the components and study structure–property correlation. In recent years, 1, 3, 5-triazine moieties have emerged as one of the most robust supramolecular scaffold for designing new gelators. [5–17] Nandi et al. [11–16] had discovered many two-component hydrogelators system using melamine as one of the components. This new class of supramolecular hydrogelators have many hydrogen donor and acceptor sites which make the overall supramolecular assembly very intricate. As a result, it becomes very difficult to understand or predict the role of various hydrogen bonding sites and probable van der Waals interaction in immobilization of solvents. So, hydrogelators based on a simple system with fewer number of hydrogen bonding sites and functionality is beneficial, which may act as a model system to decipher the probable mechanism of hydrogelation and eventually, leads to design of new hydrogelators with tuneable properties. We decided to synthesize new organic salts of melamine with few simple aliphatic dicarboxylic acids **(Scheme 2.1)**, primarily due to following reasons, (a) to understand the role of π–π interaction in supramolecular assemblies such as gel, (b) to understand the role of hydrophobic interaction (by varying chain length of dicarboxylic acid) in highly polar environment, (c) role of spatial arrangement of molecule (fumaric acid and maleic acid) on plausible packing and its effect on gelation behaviour, (d) ease of synthesis of organic salts as compared with other multistep synthesies of other class of gelators, (e) supramolecular synthons with less number of functional groups which can be predictably ascertained due to well-known supramolecular synthons of melamine and related compounds,[18] (f) to understand the probable causes for the formation of hydrogel in melamine based system using structure–property correlation, and (g) application of gelator fibres as a template for nano-material synthesis. So, we have synthesized various melamine based salts (1a–1g) with simple aliphatic dicarboxylic acids. Two salts (1a and 1e) turned out good hydrogelators. Fortunately, we could able to grow single crystal of 1a with and without gelling solvent i.e. water. The literature search revealed that the single crystal X-ray structure solved by us, i.e. melaminium maleate monohydrate, matches exactly with a known single crystal structure.[19] A detailed study was undertaken to establish the packing of gelator molecules in the gel state, xerogel state, bulk solid and compared it with simulated powder XRD pattern generated using single crystal of 1a (with or without gelling solvent, i.e. water).To the best of our knowledge, this is a first report which directly correlates the structure of gelator molecule interacting with gelling solvent in the gel state and packing of the gelator molecules after evaporation of solvent i.e. xerogel. Furthermore, the gelator molecule 1a was successfully utilized for the synthesis of silver nano-particles by simple UV treatment method of silver salt.

2.2 Experimental section

2.2.1 Materials and physical measurements

2.2.1.1 Materials

Various aliphatic dicarboxylic acids (a–g) (maleic acid, fumaric acid, malonic acid, succinic acid, adipic acid, suberic acid and sebacic acid), and melamine were purchased from Aldrich. The other chemicals were of the highest commercial grade available and were used without further purification. The solvents for the preparation of gels were of reagent grade. All solvents used in the synthesis were purified, dried and distilled as required.

2.2.1.2 SEM measurement

Hot solution of a gelator was placed on a SEM sample holder and allowed to cool at room temperature to form gel, which is then dried under vacuum. The dried gel was subjected to gold sputtering by using Polaron SC 7620 sputter coater. The gold-coated sample 1a is used for direct viewing using JEOL JSM5610 LV SEM instrument. The SEM image of xerogel of 1e was recorded on JEOL JSM5610 LV SEM instrument after carbon coating.

2.2.1.3 FT-IR measurement

FT-IR spectra was recorded on perkin elmer –RX FTIR. The solid sample was ground together with anhydrous KBr using mortar pestle, and a pallet was made for FT-IR analysis.

2.2.1.4 Powder X-ray diffraction study

Powder diffraction patterns of neat gelator (bulk), xerogel (water slowly evaporated) and gel of 1a were recorded on XPERT Philips (CuK_α radiation) and PXRD of xerogel of 1a loaded with silver nanoparticle was recorded on Bruker D8(CuK_α radiation).

2.2.1.5 Single Crystal X-ray study

Crystals of 1a and 1e were obtained from ethanol and water respectively in a slow evaporative condition at room temperature. Diffraction data for 1a was collected using MoKα (λ=0.7107Å) radiation on a SMART APEX diffractometer equipped with CCD area detector. While single crystal X-ray study of compound 1e was carried out using CuKα (λ=1.5418Å) radiation on Xcalibur, EOS, Gemini diffractometer. Data collection, data reduction, structure solution/refinements were carried out using the software package of SMART APEX. Graphics were generated using MERCURY 3.0. All structures were solved by direct methods and refined in a routine manner. In all cases, nonhydrogen atoms were treated anisotropically. Whenever possible, the hydrogen atoms were located on a difference Fourier map and refined. In other cases, the hydrogen atoms were geometrically fixed.

2.2.1.6 UV-Vis spectroscopy study of Nanoparticles

Characteristic optical properties of synthesized silver nanoparticles were recorded using Perkin Elmer Lambda 35 UV–vis spectrophotometer.

2.2.1.7 TEM Studies

TEM images were taken using Philips CM200 operated at 20-200 kV. TEM image of nanoparticles formed within the gel has been recorded. Sample was prepared by evaporating the solvent (water) from the gel network, which resulted xerogel containing nanoparticles within the xerogel matrix. The powder sample was dispersed in water by sonication. Sample was deposited on carbon- coated copper grid and directly imaged after drying under IR lamp.

2.2.1.8 Gelation Test

Salts 1a- 1g were tested for their gelation behavior in various solvents of different polarity by test tube method. 10 mg of sample was taken in a test tube and 1mL of solvent was added to it. The suspension of salt in solvent was heated in an oil-bath for few minutes untill the solute dissolved completely. The hot solution was kept at the ambient temperature for observation. The test tube was inverted to confirm the gel formation.

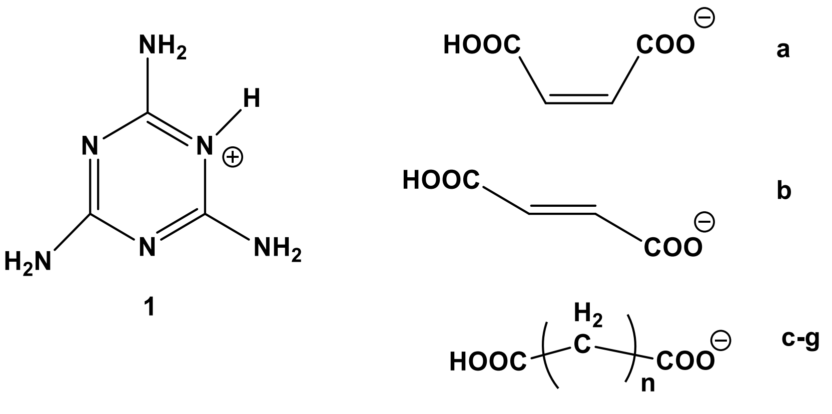
2.2.1.9 T_{gel} measurements

T_{gel} (gel-to-sol conversion temperature) was measured using a small glass bead placed on the upper surface of gel formed in a glass tube. The test tube was heated in oil-bath untill the glass ball (weighing about 63 mg) reaches to the bottom of the test tube. The temperature at which semi-solid mass lost its weight-bearing capacity, and gel convert into a sol was noted as T_{gel}.

2.2.2 Synthesis

2.2.2.1 Synthesis of organic salts

Organic salts (**1a-1g)** were prepared by mixing hot methanolic solution of Dicarboxylic acids (a-g) with a hot aqueous solution of Melamine in a 1:1 molar ratio. The mixtures were cooled slowly and kept at room temperature for drying. The white powders obtained were subjected to characterization by various physico-chemical techniques. The salt formation was confirmed by Fourier transform infrared (FT-IR) spectroscopy. All the synthesized salts showed the characteristic bands for -COOH (1697-1720 cm^{-1}) and -COO^- (1650-1680 cm^{-1}), which clearly indicated deprotonation of one of the carboxylic acids. The 1:1 stoichiometry of the synthesized salts was confirmed by NMR Spectroscopy and elemental analyses.



Where n=1,2,4,6,8

Scheme 2.1 List of organic salts synthesized (1a- 1g)

2.2.2.2 Synthesis of silver nanoparticles

Silver nanoparticles were synthesized by a simple method of reduction of silver salts using UV radiation.[20-21] $AgNO_3$ (5mg) and compound **1a** (40 mg) were dissolved in water (2ml) by heating in a quartz test tube. After formation of stable colorless gel at the ambient temperature, it was irradiated with a mercury vapor UV lamp. The silver salt loaded gel showed remarkable color change from colorless to pale pink within 15 minutes of irradiation. Prolong exposure of UV light for an hour, on gel containing silver nanoparticles displayed color change from pale pink to dark brown.

2.2.3 Analytical data

Salt **1a**: Anal. Calc. for-$C_7H_{10}N_6O_4.H_2O$: C, 32.28; H, 4.61; N, 32.28. Found: C, 32.56; H, 4.34; N, 31.78%. FT-IR (KBr): 3363, 1700, 1670, 1512, 1405, 1307, 1276, 1169, 865, 781,623,530,423cm^{-1}. ^{1}HNMR (400MHz, DMSO, TMS); δ7.530(s, 6H, $3NH_2$), 6.048(s, 2H, CH=CH).

Salt **1b**: Anal. Calc. for-$C_7H_{10}N_6O_4.H_2O$: C, 32.28; H, 4.61; N, 32.28. Found: C, 32.41; H, 4.35; N, 31.84%. FT-IR (KBr): 3589, 3372, 3090, 1697, 1650, 1511, 1373,1278,1228,1194, 1106, 1002,923,781,703,651, 581 cm^{-1}. ^{1}HNMR (400MHz, DMSO, TMS); δ6.606(s, 2H, CH=CH), 6.268(s, 6H, $3NH_2$).

Salt **1c**: Anal. Calc. for-$C_6H_{10}N_6O_4$: C, 31.28; H, 4.34; N, 36.49. Found: C, 31.26; H, 3.90; N, 36.98%. FT-IR (KBr): 3345, 1720, 1670, 545, 1498, 1365, 1254, 1175, 1024, 975,717,653,499.^{1}HNMR (400MHz, DMSO, TMS); δ6.708(s, 6H, $3NH_2$), 3.020(s, 2H, CH_2).

Salt **1d**: Anal. Calc. for- $C_7H_{12}N_6O_4.H_2O$: C, 32.02; H, 5.33; N, 32.02. Found: C, 31.80; H, 5.24; N, 31.95%. FT-IR (KBr): 3363, 3085, 2918, 2849, 1720, 1681, 1537,1413,1303,1158, 1111, 715,582,410 cm^{-1}. ^{1}HNMR (400MHz, DMSO, TMS); δ7.343(s, 6H, $3NH_2$), 2.414-2.188 (t, 4H, CH).

Salt **1e**: Anal. Calc. for- $C_9H_{16}N_6O_4.H_2O$: C, 37.20; H, 6.20; N, 28.93. Found: C, 37.37; H, 5.88; N, 28.86%. FT- IR (KBr):3354, 3083,1708,1670,1571, 1493, 1420, 1326, 1111,983,927, 877, 762,682,621,410 cm^{-1}. ^{1}HNMR (400MHz, DMSO, TMS); δ6.001(s, 6H, $3NH_2$), 2.133-2.188 (t, 4H, CH), 1.507-1.472(m, 4H, CH).

Salt **1f**: Anal. Calc. for- $C_{11}H_{20}N_6O_4.H_2O$: C, 41.46; H, 6.91; N, 26.38.Found: C, 41.32; H, 7.40; N, 26.21%. FT-IR (KBr): 3362,2927,2850,1723, 1680, 1533, 1413, 1290,1231,1156, 1003, 902,710,634,429. ^{1}HNMR (400MHz, DMSO, TMS); δ6.043

(s, 6H, $3NH_2$), 2.203-2.166 (t, 4H, CH), 1.490-1.455(m, 4H, CH), 1.270-1.234 (m, 4H, CH_2).

Salt **1g**: Anal. Calc. for- $C_{13}H_{24}N_6O_4.3H_2O$: C, 40.79; H, 7.84; N, 21.96.Found: C, 40.30; H, 7.39; N, 21.93%. FT-IR (KBr): 3334,3073,1706,1677, 1565, 1489, 1411, 1326, 1111,981,927,858, 769, 674,418 cm^{-1}. ^{1}HNMR (400Mz, DMSO, TMS); δ 6.027 (s, 6H, $3NH_2$), 2.200-2.164 (t, 4H, CH), 1.491-1.458(m, 4H, CH), 1.242(m, 8H, CH_2).

2.3 Results and discussion

2.3.1 Gelation studies

Salts synthesized were subjected to gelation test in various solvents with varied polarity ranging from highly polar solvents such as water, ethanol, methanol to very less polar solvents such as toluene and n-octadecane **(Table 2.1)**.

Table 2.1 Gelation studies of **1a-1g** in various solvents

Solvent	1a	1b	1c	1d	1e	1f	1g
Water	**G(2.62)**	C	P	C	**G(1.25)**	C	C
Methanol	S	P	P	S	S	S	S
Ethanol	S	P	P	S	S	S	S
1-pentanol	S	P	P	P	P	S	S
1-Heptanol	S	P	P	P	P	S	S
Iso-octane	S	P	P	P	P	P	S
n-octadecane	S	P	P	P	P	P	P
Toluene	S	P	P	P	P	P	P
Xylene	S	P	P	P	P	P	P

G=gel, P=precipitate, C=crystals, S=solution, values in the parenthesis represent MGC (minimum gelator concentration) in wt %(g/100mL of solvent)

Out of seven salts synthesized, two turned out to be good hydrogelators (**Figure 2.1**). Salts 1a and 1e showed good thermal stability (T_{gel} values lying between 75 and 95 °C) and minimum gelation concentration (MGC) values greater than 1wt%.

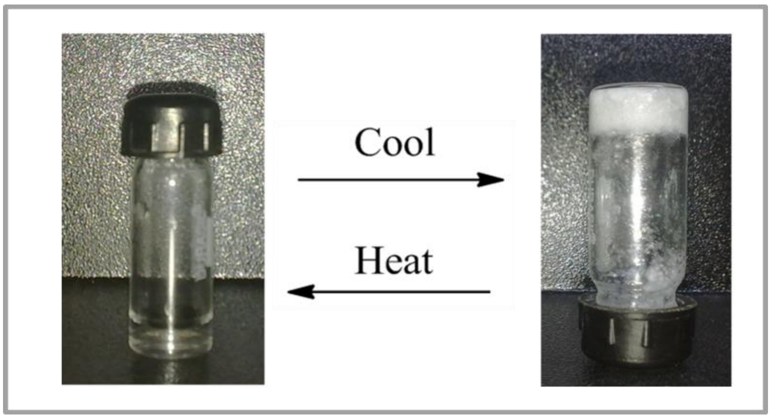


Figure 2.1 Photographic image of sol-gel transition of 1a in water

A graph of T_{gel} versus concentration of gelator molecules in wt% (w/v) showed a gradual increase in T_{gel} up to a certain concentration of gelator then plateau was observed. Understandably, the increase in gelator concentration improves the self-aggregation and stability of supramolecular assembly not beyond certain critical concentration. The nature of the graph for T_{gel} versus concentration of gelator is very frequent for supramolecular gelators **(Figure 2.2)**.

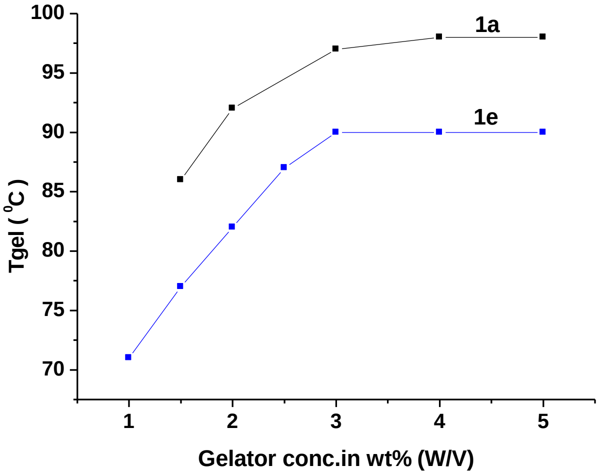


Figure 2.2 Effect of gelators 1a and 1e concentration (in wt %) on sol-to-gel transition Temperature (T_{gel}).

A critical look at the structures of gelator and non-gelators molecules suggested few important observations such as salts made up of molecules having cis and trans orientation of dicarboxylic groups (1a and 1b) is totally dissimilar in gelation behavior towards solvents, and some critical aliphatic carbon chain length was required to induce gelation behaviour through van der Waals/hydrophobic interaction. The spatial orientation of molecules may lead to a different overall packing in three-dimensional network, porous or interpenetrating network, which seems to be a guiding principle for a molecule to show hydrogelation or non-gelation. The salts containing less than four carbon atoms (1c and 1d) in aliphatic back bone turned out inadequate to immobilize solvent through hydrophobic interaction and surface tension. It is also noteworthy that a long carbon chain (1f and 1g) disturbs the delicate balance of hydrophilic and hydrophobic interaction of gelator molecules with solvents and leads to non-gelation of solvents.

2.3.2 SEM characterization

To get an insight into the gelator morphology SEM studies were carried out on xerogel (dried gel) of 1a and 1e. Xerogel of both gelators showed entangled fibrous network of molecules which might have immobilized the solvent through various non-covalent interactions **(Figure 2.3)**.

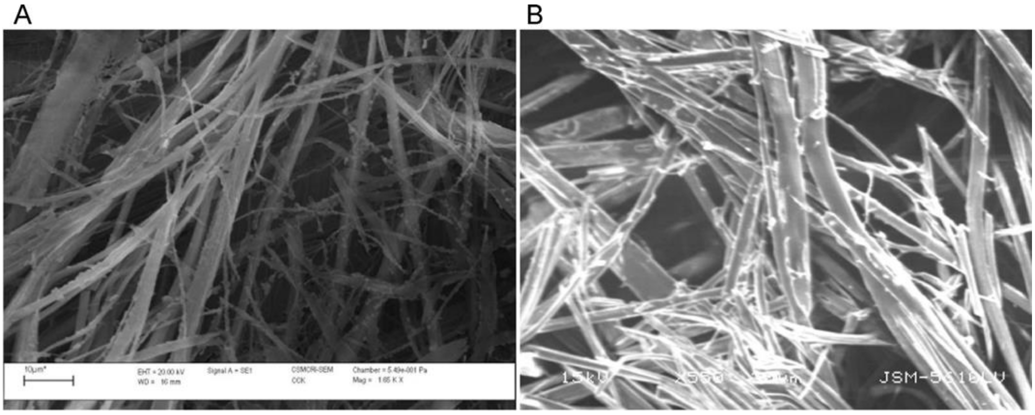


Figure 2.3 SEM images of xerogel of (A) 1a and (B) 1e in water at 2 wt% (w/v).

2.3.3 X-ray diffraction studies

The structure–property correlation between molecules and its gelling behaviour was established by single crystal and powder diffraction studies. 1a gave crystals in water and ethanol as melaminium maleate monohydrate and melaminium maleate respectively. The crystal structure of melaminium maleate monohydrate found to be exactly matching with the known Crystal structure. [19] However, the single crystal of 1a without solvent (crystallographic parameters –**Table 2.2**) turned out to be a new structure, which encouraged us to do a comparative study of gelator molecule interacting with its gelling solvent in the gel state and with xerogel state. Literature search revealed very few incidences to investigate the packing of gelator molecules interacting with its gelling solvent were successful either by single crystal studies [10,22,23] or ab initio crystal structure prediction.[17] We decided to compare the single-crystal structure of melaminium maleate monohydrate structure and melaminium maleate as shown in **Figure 2.4.**The structure reported by Janczak et al.[19] showed a three-dimensional robust network capable of immobilizing water in the void, whereas packing of **1a** without water seems very different from the hydrous structure. The three-dimensional hydrogen bonding pattern of melaminium maleate salt showed no space for any solvent to occupy.

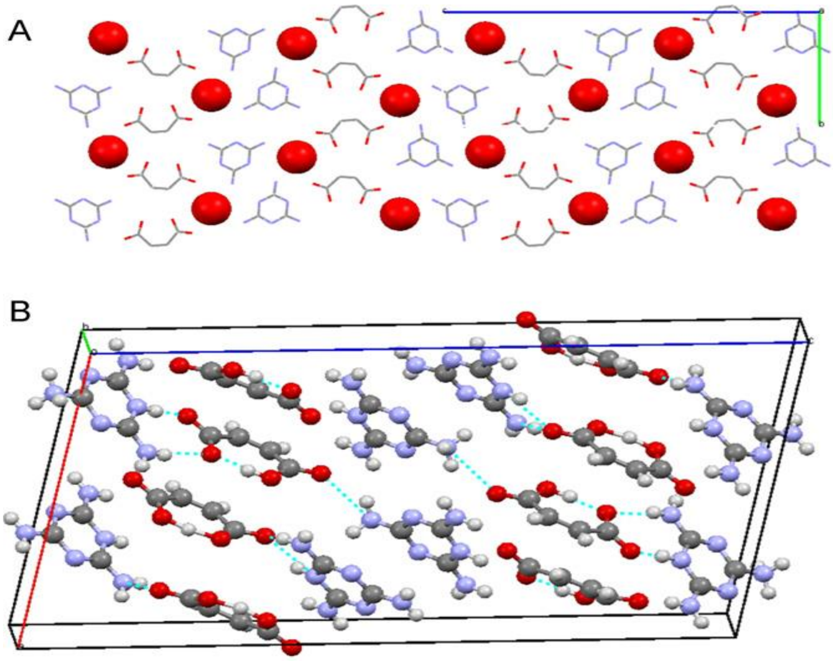


Figure 2.4 Single crystal X-ray structures of 1a (A) with gelling solvent water (regenerated using reference [19]). Red round circle represents water molecules in space fill style and other molecules are shown in wire frame style and (B) without gelling solvent (water). Hydrogen atoms are omitted for clarity in (A).

A detailed study of crystal structure of gelator **1e.H_2O (Figure 2.5)** also provided the similar observation as that of **1a.H_2O**.Single crystals of **1e** was grown from water, which is also a gelling solvent. It crystallized out in a space group Triclinic P-1 (crystallographic parameters-**Table 2.2**).The structure of **1e.H_2O** also showed a three-dimensional robust network capable of immobilizing water in the void **(Figure 2.5B)**.

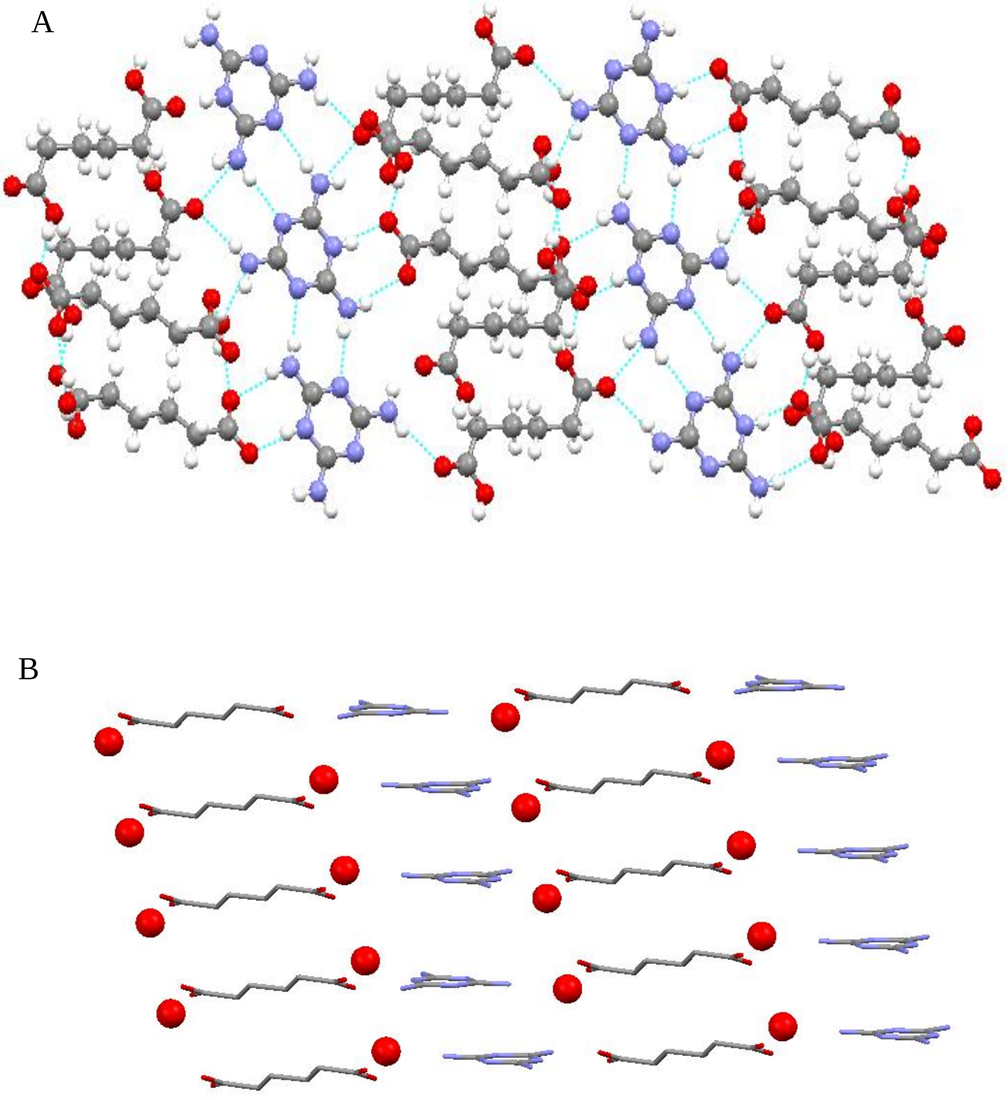


Figure 2.5 Single crystal X-ray structures of 1e with gelling solvent (water) (A) in ball and stick style (B) Red round circle represents water molecules in ball and stick style and other molecules are shown in capped stick style. Hydrogen atoms are omitted for clarity in B.

Table 2.2 Crystallographic parameters for Salt **1a** and **1e**

Crystal data	**1a**	**1e**
CCDC	877950	996386
Empirical formula	$C_{14} H_{21} N_{12} O_8$	$C_{18}H_{36} N_{12} O_{10}$
FW	485.43	580.56
Crystal size (mm)	0.30 x 0.12 x 0.07	0.13 x 0.11 x 0.08
Crystal system	Monoclinic	Triclinic
Space group	P 2_1/n	P-1
a/Å	13.7740(15)	4.7235(6)
b/Å	5.5313(6)	9.6516(13)
c/Å	26.786(3)	15.6618(18)
$\alpha/^0$	90.00	105.133(11)
$\beta/^0$	101.864(2)	92.763(10)
$\gamma/^0$	90.00	99.323(11)
Volume / $Å^{-3}$	1997.2(4)	677.08(15)
Z	4	1
$D_{calc.}$	1.614	1.4237
F(000)	1012	309.1743
μ (mm^{-1})	0.134	0.998
Temperature (K)	293(2)	293
Observed reflections [I > 2 σ(I)]	4636	4339
Parameters refined	316	187
Goodness of fit	1.079	1.5231
Final R_1 on observed data	0.0515	0.1020
Final wR_2 on observe data	0.1464	0.2724

A detailed study of packing of 1a in a gelling solvent (gel state), pure crystalline state (bulk solid) and xerogel state was carried out using powder X-ray diffraction method, which was further compared with simulated powder X-ray pattern of $1a\cdot H_2O$ and 1a single crystal data as shown in **Figure 2.6**.The XRD Pattern of gel of 1a in water showed peaks at 2θ= 9.37, 10.86, 12.68, 15.28, 17.63, 20.73, which matched well with the peaks in simulated hydrated single crystal. XRD peaks of 1a in gel state at a higher angle were difficult to identify due to strong scattering from water molecules. An important peak in all the powder XRD pattern of 1a at 2θ equal to 27.7Corresponds to "d" spacing of 3.2 A^o, is representing π-π interaction between melamine molecules.[17]

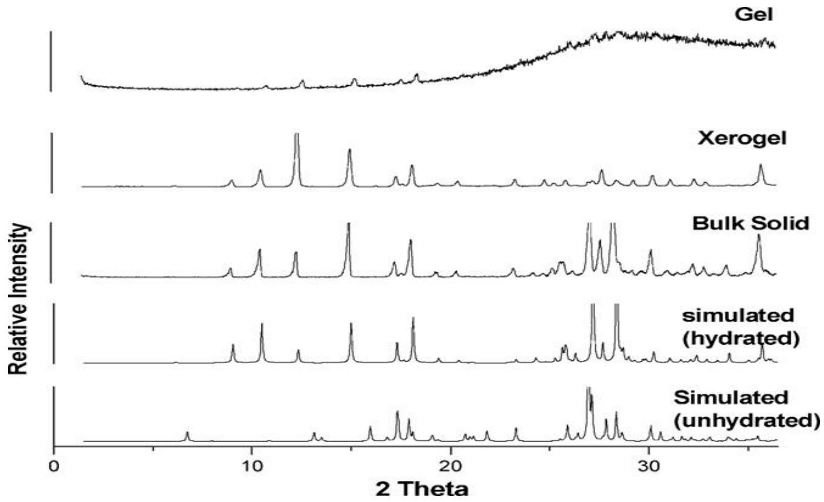


Figure 2.6 Powder XRD pattern of salt 1a in gel state, dried gel (xerogel), bulk solid and simulated powder pattern obtained from single crystal X-ray data.

2.3.4 Synthesis and characterization of silver nano-particles

Organogelators or hydrogelators could be employed as template for nano-materials synthesis due to well-defined supramolecular assembly of gelator molecules in a Solvent such as fibres, rods and tubes.[24] We used gelator 1a as structure directing agent for the synthesis of silver nano material. Silver salt loaded gel was subjected to UV treatment and formation of silver nanoparticle was visibly evident as seen in **Figure 2.7**. The formation of silver nano-particles was confirmed by various physicochemical techniques such as UV-Visible spectroscopy, powder X-ray diffraction and TEM.

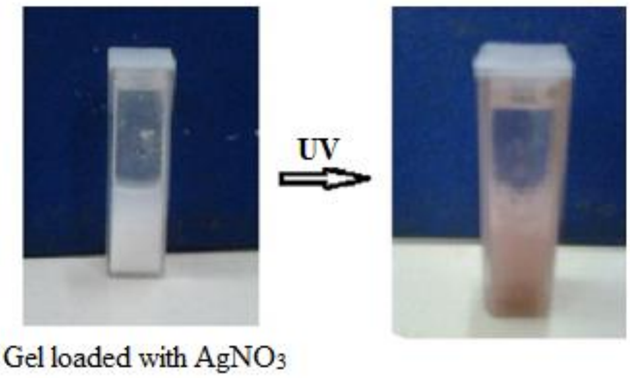


Figure 2.7 Photographic image of silver nano-particles synthesis within the gel.

UV-Vis spectra **(Figure 2.8a)** showed the plasma absorption with a peak maximum at 428 nm indicating the formation of silver nanoparticles. [25, 26]

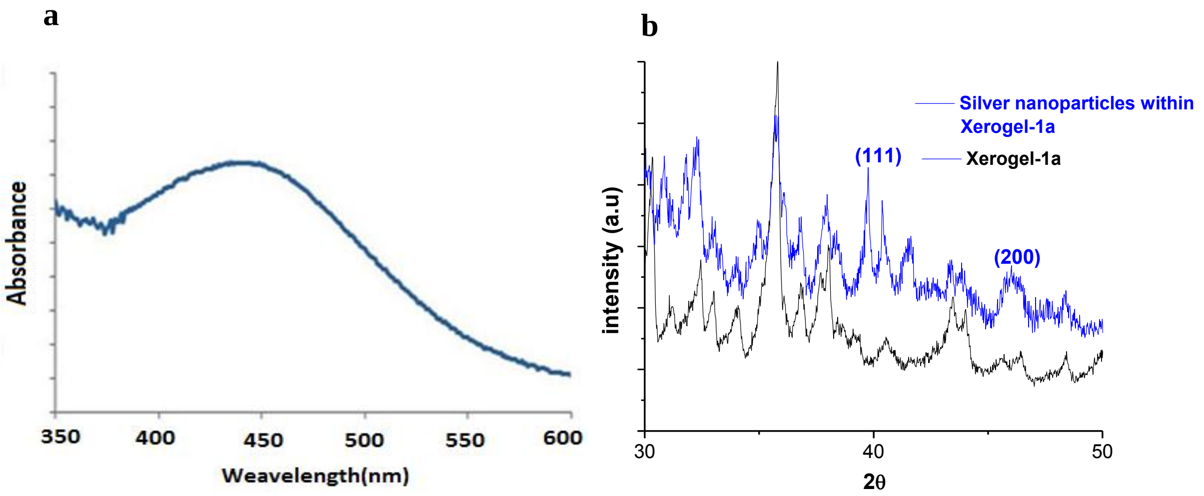


Figure 2.8(a) UV-Vis spectra of the silver nano-particles and (b) Powder XRD pattern of silver nanoparticles.

The structure of silver nano-particle was further investigated by powder XRD analysis. A typical XRD pattern of the silver nano-particle is shown in **Figure 2.8b**. Two distinct diffraction peaks were observed at 2θ values of 39.5 and 45.6, corresponding to the (1 1 1) and (2 0 0) crystalline planes of Ag, respectively.[27] Moreover, the broad nature of the XRD peaks could be attributed to the nano-size of the particles.

The formation of nano-particles of silver can be visually observed through a continuous color change from colourless to pale brown within15 min, and finally to dark brown within 60min. The TEM images of the silver nano-particles within the gel network of 1a are shown in **Figure 2.9**.The size of silver nano-particles attached with gelator fibres was found to be in the range of 10–20nm.In the present case, the gelators fibres are made up of charged species such as melaminium and mono-carboxylate; the overall supramolecular assemblies may have some charge, which might be responsible for attracting some silver ion towards itself. The silver ion anchored with gelator fibres should be acting as nucleating site where the growth of silver nano-particles were taking place after UV irradiation.

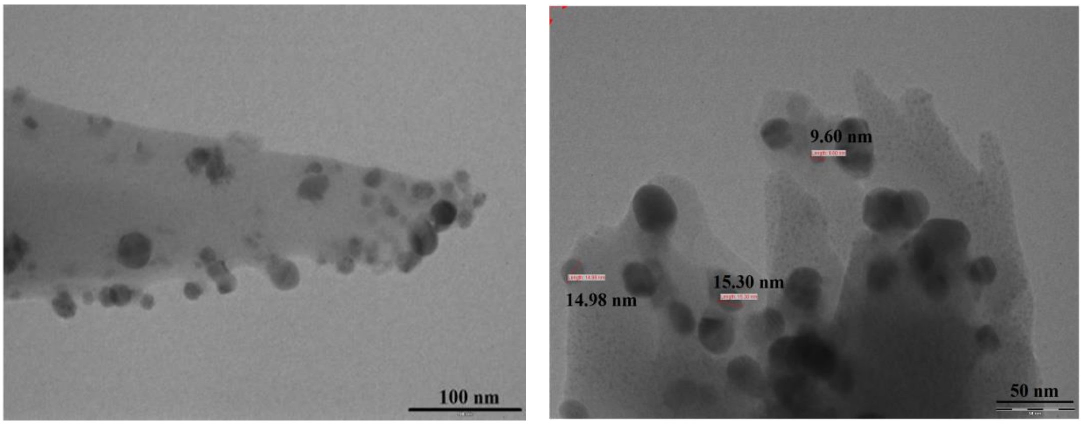


Figure 2.9 TEM image of silver nano-particles formed within the xerogel fibre.

2.4 Conclusions

We have demonstrated two new LMOGs salts, melaminium hydrogen maleate (1a) and melaminium hydrogen adipate (1e) as a novel class of non-polymeric hydrogelator. The ease of synthesis of these salts in almost quantitative yield gives an advantage over other classes of melamine-based hydrogelator/organogelators [6–9, 28, 29] which may require tedious multi-step synthesis. To the best of our knowledge, these salts are the lowest molecular weight Melamine based bi-component gelators. Furthermore, the formation of porous hydrogen bonded network in hydrated structure of 1a seems to be one of the prerequisites for hydrogelation and this observation matches well with the observation made by various research groups. [17, 22, 23] Powder XRD pattern of gelator 1a matches remarkably well with bulk crystalline, xerogel and hydrated single crystal (simulated) recognizes a similar morph and porous network in all these states. However, position and intensity of few peaks in the XRD of 1a in the gel state suggest that the packing of gelator molecules may be similar to its xerogel and crystalline state but not necessary be identical. On the other hand, simulated XRD pattern of unhydrated single crystal showed a different diffractogram than simulated XRD of hydrated single crystal of 1a, prompted us to believe that the excessive heating and drying of gel may lead to irreversible breakdown of the porous network and formation of new hydrogen bonded three-dimensional system represented by single crystal of 1a (without solvent).We propose molecules capable of forming three-dimensional supramolecular assembly with void may act as a potent hydrogelator. A designing of supramolecular synthesis of porous network may lead to the discovery of new aqueous gelling agent with tunable and predictable property. The success of salt 1a as a structure directing agent for spherical silver nano-particles in the range of 10–20 nm, may be attributed to the overall charged supramolecular assembly of 1a as also demonstrated by Weiss et al. [30] The colloidal suspension of silver nano-particles stabilized by the charged supramolecular assembly of 1a in water was found to be stable for few months at room temperature.

2.5 References

(1)P. Terech, R.G. Weiss, *Chem.Rev.*, **1997**,97,3133.

(2) L.A. Estroff, A.D. Hamilton, *Chem.Rev.*, **2004**,104, 1201.

(3)P. Dastidar, *Chem. Soc.Rev.*, **2008**, 37,2699.

(4) E. Ostuni, P. Kamaras, R.G. Weiss, *Angew.Chem.Int.Ed.*,**1996**, 35, 1324.

(5) K. Hanabusa, T. Miki, Y. Taguchi, T. Koyama, H. Shirai, J. Chem. Soc., *Chem. Commun.*, **1993**, 1382.

(6) S. Yagai, M. Higashi, T. Karatsu, A. Kitamura, *Chem. Mater.*, **2004**, 16, 3582.

(7) S.Yagai, T.Nakjima,K.Kishikawa,S.Kohmota,T.Karatsu,A.Kitamura, J.*Am.Chem. Soc.*, **2005**,127,11134.

(8) F.J.M. Hoeben, M.J. Pouderoijen, A.P.H.J. Schenning, E.W. Meijer, *Org. Biomol. Chem.*, **2006**, 4, 4460.

(9)S. Yagai, H. Aonuma, Y. Kikkawa, S. Kubota, T. Karatsu, A. Kitamura, S. Mahesh,A. Ajayaghosh, *Chem. Eur. J.*,**2010**,16,8652.

(10)O.Lebel, M.-E. Perron, T. Maris, S.Y. Zalzal, A. Nanci, J.D. Wuest, *Chem. Mater.*, **2006**, 18, 3616.

(11) S. Manna, A. Saha, A.K. Nandi, *Chem.Commun.*, **2006**, 4285.

(12) A. Saha, S. Manna, A.K. Nandi, *Langmuir*, **2007**, 23, 13126.

(13) A. Saha, B. Roy, A. Garai, A.K. Nandi, *Langmuir*, **2009**, 25, 8457.

(14)A. Saha, S. Manna, A.K. Nandi, *Chem. Commun.*, **2008**, 3732.

(15) B.Roy, A. Saha, A. Esterrani, A.K. Nandi, *Soft Matter.*,**2010**, 6, 3337.

(16) P. Bairi, B. Roy, A.K. Nandi, *J. Phys. Chem.* ,**2010**,114,11454.

(17)K.M. Anderson, G.M. Day, M.J. Paterson, P. Byrne, N. Clarke, J.W. Steed, *Angew. Chem.Int.Ed.*, **2008**, 47, 1058.

(18)G.M. hitesides, E.E.Simanek,J.P.Mathias,C.T.Seto,D.N.Chin,M.Mammen,D.M. Gordon, *Acc.Chem.Res.*, **1995**, 28, 37.

(19) J.Janczak,J.P.Genivaldo, *ActaCryst.*,**2004**,C60,211.

(20) C.S. Love, V. Chechik, D.K. Smith, K. Wilson, I. Ashworth, C. Brennan, *Chem. Commun.*,**2005**, 1971.

(21) K.Esumi, A. Suzuki, N. Aihara, K. Usui, K. Torigoe, *Langmuir*, **1998**,14,3157.

(22) K.D. Kumar, D.A. Jose, A. Das, P. Dastidar, *Chem. Commun.*, **2005**, 4059.

(23)J. Cui, Z. Shen, X. Wan, Langmuir, 2010, 26, 97.

(24) K.J.C. van Bommel, A. Friggeri, S. Shinkai, *Angew. Chem. Int. Ed.*, **2003**, 42, 980.

(25) J.J. Mock, M. Barbic, D.R. Smith, D.A. Schultz, S. Schultz, *J.Chem.Phys*., **2002** , 116, 6755.

(26) I.O. Sosa, C. Noguez, R.G. Barrera, *J. Phys. Chem. B*., **2003**,107,6269.

(27)A. Mantion, A.G. Guex, A. Foelske, L. Mirolo, K.M. Fromm, M. Painsid, A. Taubert, *Soft Matter*.,**2008**,4,606.

(28) W. Zhang, S.O. Gonzalez, E.E. Simanek, *Macromolecules*, **2002**, 35, 9015.

(29) S. Yagai, T. Karatsu, A. Kitamura, *Langmuir*, **2005**, 21, 11048.

(30) X.Huang, R.G. Weiss, *Langmuir*, **2006**, 22, 8542.