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Odd-Even effect in a thiazole based organogelator: Understanding the interplay of non-covalent interactions on property and applications

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Abstract

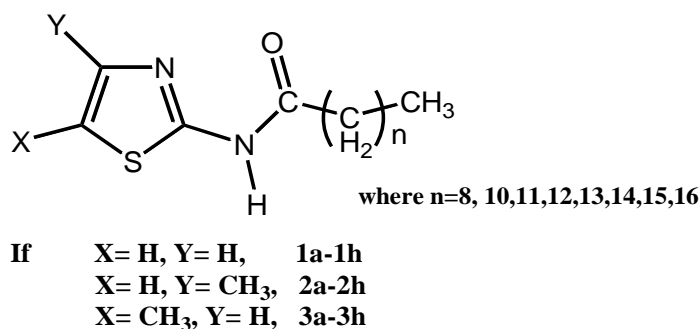
New series of thiazole based amides namely, **1e** [N-(thiazol-2-yl) pentadecamide] to **1h** [N-(thiazol-2-yl)stearamide], **2e** [N-(4-methylthiazol-yl)pentadecamide] to **2h** [N-(4-methylthiazol-yl)stearamide], **3e** [N-(5-methylthiazol-yl)pentadecamide] to **3h** (N-(5-methylthiazol-yl)stearamide) were synthesized, characterized and investigated for their gelation properties. Interestingly, out of three series of thiazole amides synthesized two (**1e-1h** and **3e-3h**) had displayed odd-even effect on gelation property with the increase in the methylene functional group of alkyl chain attached with thiazole moiety. The gelation/non-gelation of solvents was found to be more significant for the series of compounds (**1e-1h**) whereas, the subtle effect was observed in the series of compounds **3e-3h**. A single crystal study of non-gelator (**2d**) highlighted the crucial role of the methyl group and its position on the thiazole moiety in bringing about a change in supramolecular synthon from a robust cyclic N-H...N interaction to the combination of N-H...N and N-H...O interactions. Self-assembly of four molecules of **2d** lead to the formation of zero-dimensional (0-D) hydrogen bonded network instead of one-dimensional hydrogen bonded network observed in gelling compounds mediated by (methyl)C-H...N, C-H...O and van der Waals interaction. Various gelling agents (**3e-3h**) were used for the synthesis of nearly spherical silver and ZnO nanoparticles using sol-gel method, through encapsulation and stabilization of nanoparticles in the gel network. Interestingly, the alkyl chains lengths of thiazole amides were found to affect the size of synthesized Ag and ZnO nanoparticles.

INTRODUCTION

Small organic compounds having a molecular mass typically <3000, which are capable of arresting the flow of liquids (gel formation), are popularly known as low molecular mass organic gelators (LMOGs).¹ LMOGs are attracting much attention due to the structural diversity of gelling compounds and their potential applications in drug release², nanotechnology³, pollution control⁴, oil-spill recovery,⁵ Sensors,⁶ in preparing dye sensitized solar cells,⁷ tissue engineering,⁸ and many more.⁹ Generally, gelling molecules self-assemble into various recognizable shapes-fibres, filaments, tapes, ribbons, tubes, etc., which entangle among themselves to create a three-dimensional (3D) network capable of immobilizing the solvent molecules. Moreover, well-defined supramolecular assemblies of gelator fibres throw an opportunity to design and synthesize one-dimensional inorganic nanomaterials, which is otherwise hard to synthesize, by various physical and chemical methods. Therefore, one of the most explored applications of LMOGs is the template directed synthesis of inorganic nanomaterials of various shapes and sizes. Numerous gelling systems such as cholesterol based, crown ether appended cholesterol compounds, diamines based, sugar based, are well known as structure-directing agent for charged silica and titanium compounds.¹⁰ It is well-accepted that gelators having charge or many H-bond sites would be successful in transcription of silica/titanium compounds(charged precursor) into various shapes and sizes. Unfortunately, no such hypothesis/working rule is available to transcript neutral metal or metal oxide successfully on gelator fibres. Thus, it is required to explore various structural attribute, functional groups, critical balance of hydrophobicity /hydrophilicity of LMOGs required for designing template-directed synthesis of nanomaterial of various shapes and sizes. Moreover, tuning nanomaterial shape and size by systematic variation in gelator structure is also desirable.

Recently, we discovered a new series of LMOGs based on thiazole amide derivatives (**1a-1d**, **2a-2d** and **3a-3d**)¹¹ (Scheme 1), which displayed the importance of position of methyl group on thiazole moiety in inducing gelation of solvent. For example, in the series of 5-methylthiazole amides (**3b** and **3d**) gelation behaviour towards many solvents were observed, but gelation was completely absent in the series of 4-methylthiazole amides (**2a-2b**). Moreover, thiazole amide derivatives without methyl substitution displayed gelation property to lesser extent -fewer number of solvents gellified and the higher concentration of gelator required for gelation, i.e. high critical gelator concentration (cgc). We proposed the crucial role of a methyl group in the formation of weak hydrogen bond, namely, (methyl)C-H...N(thiazole), leading to one dimensional hydrogen bonded network, recognized to be a pre-requisite for organogelation,¹² based on single crystal X-ray study of gelator/non-gelator

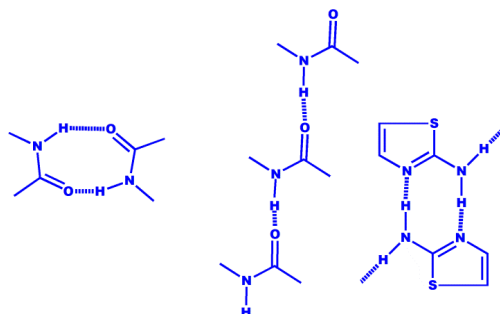
molecules and variable temperature ^1H NMR. Our best efforts to grow crystals of non-gelator (**2a-2d**) failed, which deprived us to provide unequivocal proof of the proposed mechanism of organogelation based on (methyl)C-H...N(thiazole) and van der Waals interaction. Moreover, some of the fundamental questions about mechanism of gelation need to be addressed, such as, i) is it possible to induce gelation property to a non-gelator by systematic increase in the hydrocarbon chain/hydrophobicity; ii) what is the effect of alkyl chain on the gelation behavior of the molecules in polar solvent or non-polar solvents in these series of compounds? ; iii) is the proposed weak hydrogen bond, such as (methyl) C-H...N, robust enough to induce gelation or non-gelation property to a molecule; vi) does the odd-even effect commonly observed in various series of supramolecular gels¹³ play a role in these series of molecules?; v) How predictable is supramolecular synthon of amide in the presence of competitive cyclic N-H...N interaction in thiazole containing amides? (Scheme 2); vi) is it possible gain a control over the shape and size of nanomaterials synthesized by sol-gel method by a methodical change in the alkyl chain length of gelator molecules?



Scheme 1: List of compounds synthesized

In the present study, we decided to systematically increase the alkyl chain length of gelling and non-gelling molecules having methylene group (CH_2) ranging from (8, 10-16) to see the interplay of weak hydrogen bond (methyl)C-H...N or (thiazole)C-H...N, C-H... π , etc. along with van der Waals interaction in inducing gelation/non-gelation behaviour (Fig.1). The efforts were directed to grow more crystals of gelling/non-gelling compounds in the series to establish structure-property correlation. Fortunately, we are able to grow crystals of non-gelator (**2d**) along with gelator molecules (**1c**, **1d** and **3c**), which helped us to understand the role of weak H-bond interaction and alkyl chain interdigitation on gelation behavior. The potential application of gelators (**3a-3h**) and (**1a-1h**) as a template for the synthesis of silver and zinc oxide (ZnO) nanomaterial were explored. Template direct synthesis of ZnO nanoparticles was undertaken due to ZnO intriguing chemical, electrical, mechanical and optical properties and its potential application in solar cells, hydrogen-storage, gas sensors, liquid crystal

displays, etc.¹⁴ Moreover, the properties and applications of the ZnO nanoparticles strongly dependents upon their structures and morphologies.



Scheme 2: Probable Supramolecular synthons in amide and 2-aminothiazole moiety

RESULTS AND DISCUSSION

Gelation behaviour

The synthesis, characterization, gelation behaviour of thiazole amides (**1a-1d**, **2a-2d** and **3a-3d**) were reported earlier ($n=8, 10-12$).¹¹ In the present study, gelation abilities of **1e-1h**, **2e-2h** and **3e-3h** were examined in a variety of polar and non polar solvents (ESI, Table S1 and S2) by the systematic increase in the alkyl chain length (methylene functional group(n)=13-16). Unsubstituted (**1e-1h**) and 5-methyl substituted (**3e-3h**) thiazole amides displayed excellent gelation properties towards various solvents such as methanol, ethanol, octadecane, etc. with low critical gelation concentration (cgc) (wt %, w/v). A significant enhancement and/or retardation of gelation property in the new series of compounds were observed with the increase in methylene group, which corroborate the role of flexible alkyl chain in effecting organogelation behaviour significantly.¹⁵ Compounds **1a-1h** displayed interesting gelation behaviour with the increase in methylene group in alkyl chain, the compounds having an even number of methylene group (n =even) were outstanding organogelators, whereas compounds having an odd number of methylene group were weak gel or non-gelator(odd-even effect). For example, Compounds **1d** ($n=12$), **1f** ($n=14$) and **1h** ($n=16$) demonstrated organogelation and compounds **1c** ($n=11$), **1e** ($n=13$) and **1g** ($n=15$) showed weak gelation or no-gelation at all (ESI, Fig. S1). The effect of the odd-even number of methylene group of alkyl chain on the gelation behaviour of these series of compounds is quite pronounced.

Similarly, the series of gelators (**3b-3h**) with odd number of methylene units ($n= 11, 13, 15$) in the alkyl tail required large amount of gelling compound to exhibit gelation of solvent (larger cgc value) as compare with compounds having even number of methylene units ($n=10,12,14,16$), suggested the odd-even effect in this series of compounds, even though, less distinct than **1a-1h** series of compounds.

Moreover, the odd-even effect of alkyl chain length becomes more effective after reaching a critical chain length, i.e. $n > 12$ in this series of thiazole amides. A representative graph to show the effect of increase in number of methylene group 'n' in the aliphatic chain length of thiazole amides (**3a-3h**) to critical gelator concentration (cgc) (wt % , w/v) in methanol is shown in Fig. 1a.

Concentration-dependent gelation studies of all the gelators were carried out in ethanol. The dependence of T_{gel} on the concentration of gelator in ethanol is shown in Fig.1b. T_{gel} increases rapidly with concentration up to certain wt % and then showed independence towards the increase in concentration of gelator. Understandably, the increase in concentration of gelator enhances the gel-to-sol transition temperature by actively participating in gelator fibres formation or by improving intermolecular interaction up to certain concentration. After reaching the critical concentration effect on the strength of gelator fibres and its interaction with gelling solvent, as represented by T_{gel} values, reaches a maximum value. The T_{gel} values of compounds **3e-3f** before saturation demonstrated a gradual increase with the increase in the alkyl chain length, which support the function of van der Waals interaction in enhancing the stability of gel network. Furthermore, the gelators having even number of methylene groups (**3f** and **3h**) displayed higher value to gel-sol transition temperature than the gelators having odd number of methylene groups (**3e** and **3g**) in the alkyl chain as seen in the fig.1b at 4% wt. A linear relationship was obtained when semilog graph of the mole fraction of organogelators was plotted against $1/1000T_{gel}$ (K^{-1}) which agreed well with the Schroeder-van Laar equation (eq.1, Fig. 1c).

$$\ln[\text{gelator}] = -(\Delta H_m / RT_{gel}) + \text{constant} \quad (\text{eq. 1})$$

The gel-to-sol transition can be considered a first order transition assuming that the gel melts into an ideal solution and a known amount of gelator is involved in the transition.¹⁶ From the plots, the enthalpy ΔH_m was calculated to be within the range of 71-192 kJ/mol. strikingly, enthalpy of melting of gel network (gel-sol transition) in the series **1e-1h** also showed odd even effect. ΔH_m of gel break down in the case of **3e** and **3g** ($n=\text{odd}$) found to have lower values than **3f** and **3h** ($n=\text{even}$) suggested the extra stability commanded by the gels of **3f** and **3h**.

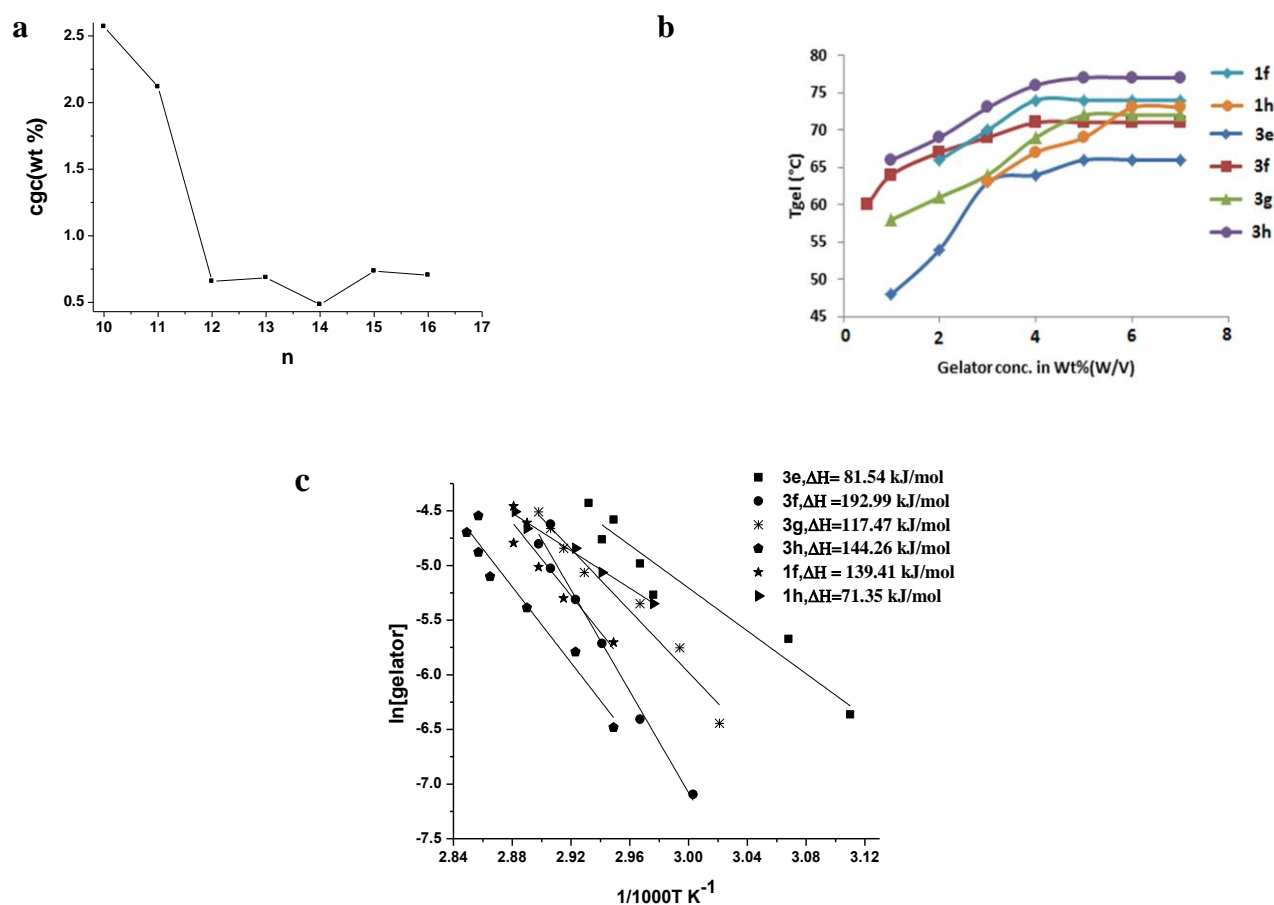


Fig. 1: (a) Critical gelator concentration (wt %, w/v) of **3b-3h** in methanol versus number of methylene groups (n) (b) T_{gel} versus concentration plot of gel in methanol and (c) Semilog plot of the mole fraction of the gelators against $1/1000T(K^{-1})$, where ΔH_m and T_{gel} are the enthalpy of melting and transition temperature of gel-to-sol, respectively. (T_{gel} value of compounds **3b-3d** is taken from ref. 11)

Morphological studies of xerogel

Scanning electron microscopy (SEM) micrographs were recorded for visualizing xerogels morphologies derived from the gelators **1e**, **1h**, **3e**, **3f**, **3g** and **3h** (Fig.2). Understandably, the solvent molecules were immobilized in 3-D network of fibres in the gel state. Dried gelled networks of **1e** and **1h** displayed augmented complexity of arrangement of gelator fibres with increase in methylene group and better entanglement of gelator fibres. The progressive increase in the entanglement of gelator fibres becomes more pronounced in the case of gelators (**3e-3h**). A highly complex network of fibres were visible in the case of xerogel of **3h** (at higher magnification) with highly distinct pores, which might had acted as a reaction chamber for synthesizing nanoparticles stabilized by gelators fibres as discussed later.

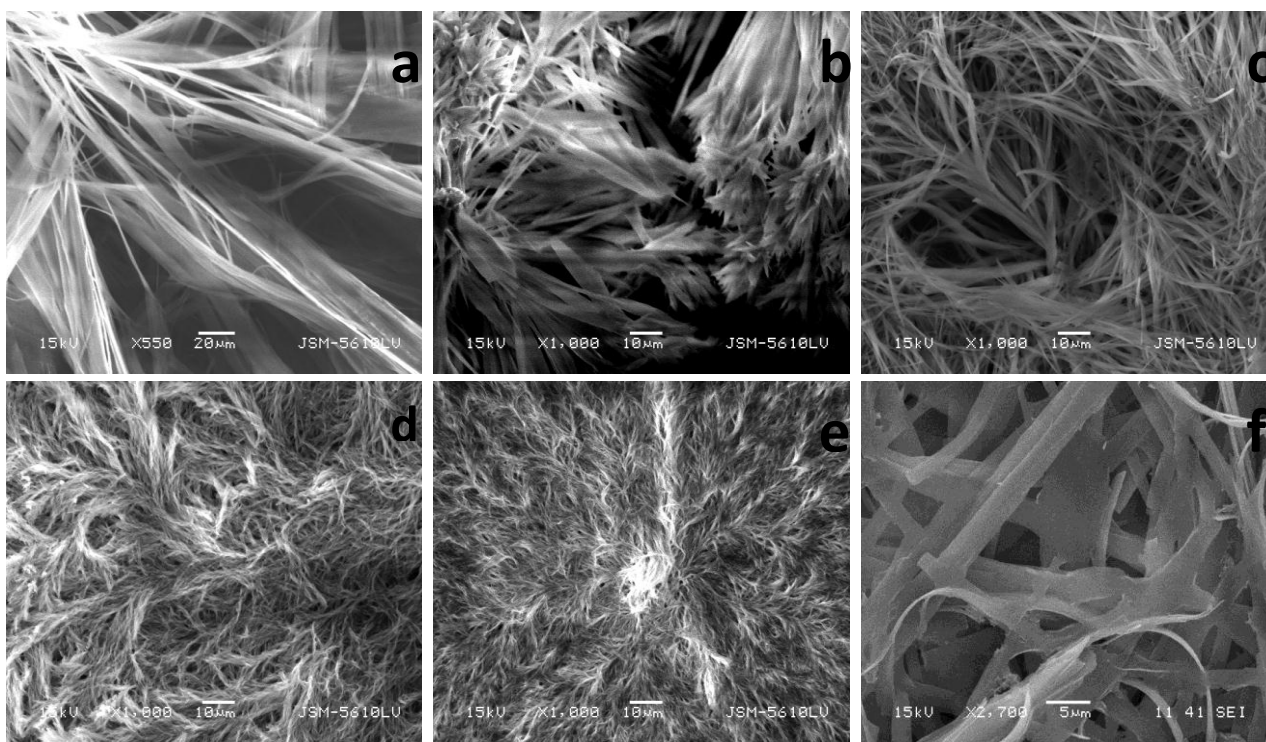


Fig. 2: SEM images of xerogel of (a) **1e**, (b) **1h** (c) **3e** (d) **3f** (e)**3g** and (f) **3h** in methanol at 2 wt% (w/v).

Single crystal X-ray studies

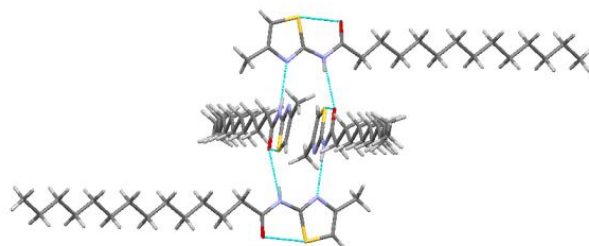
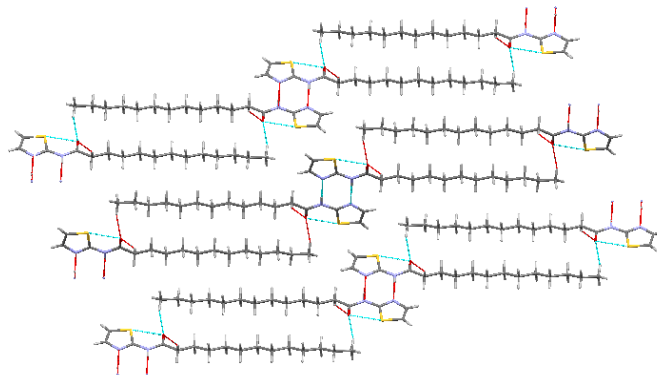
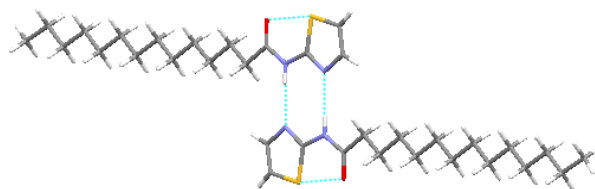
It is well-documented that gelation is a metastable state realized, when crystallization fails.¹ Therefore, gaining information about the packing of gelator molecules in the gel state, is a daunting task. Nevertheless, some information about the packing of gelator molecules in xerogel (dried gel) could be obtained with the comparison of simulated powder X-ray diffraction pattern of single crystal X-ray structure of gelator molecule (if any) and xerogel- a method developed by Weiss et al.¹⁷ Single crystal structure of gelators / non-gelators, if critically analyzed, may throw some light on the structural features and weak non-bonded interactions (supramolecular synthons) required to facilitate aggregation leading to 3D network capable of arresting the flow of liquids (organic/aqueous).

Single crystal of non-gelator **2d** provided an opportunity to understand the probable reason of its non-gelation behavior towards all the solvents employed in the present study. A suitable crystal of **2d** was obtained from methanol-water (80: 20 v/v) by the slow evaporation method. **2d** crystallize out in the monoclinic space group $P2_1/c$ containing two molecules in the asymmetric unit. Four molecules of **2d** were found to self- assembled together to form the 0-D hydrogen bonded network driven by N-H...N [N-H...N = 2.884 Å, \angle N-H...N = 173.84°] and N-H...O interaction [N-H...O = 2.937 Å, \angle N-H...O = 167.09°] (See Fig.3a). A detailed analysis of packing pattern of **2d** showed weak van der

Waals forces between methyl group and alkyl chain, which may be due to packing forces present in the crystalline phase. We ascertain the presence of a 0-D network, the absence of alkyl chain interdigitation and no additional hydrogen bonds such as C-H...N or C-H...O, endowed these sets of molecules (**2a-2h**) incapability to immobilize any solvents. The single crystal study of **2d** supported the proposed mechanism for gelation/non-gelation that the strategic position of the methyl functional group may sustain or obstruct alkyl-alkyl chain interdigitation.¹¹ A suitable single crystal of gelator **1c** was obtained from chloroform having monoclinic ($P2_1/c$) space group. The asymmetric unit displayed a single molecule of **1c** joined together with another molecule through cyclic hydrogen bond N-H...N [N-H... N = 2.942Å, \angle N-H...N = 173.21°] leading to the formation of the 0-D network. The 0-D network was extended to form the 3-D network through multiple C-H...O interaction (Fig.3b). A crystal of **1d** was obtained from chloroform by the slow evaporation method. **1d** crystallized out in the monoclinic space group $P2_1/c$ and showed a robust cyclic (amide) N-H...N (thiazole) [N-H... N = 2.932Å, \angle N-H...N = 174.64°] supramolecular synthon leading to 0-D hydrogen bonded network along with O...S intramolecular interaction (Fig.3c). **3c** crystallize out in a space group Triclinic P-1. H-bonding pattern in the crystal seems to be governed by cyclic (amide)N-H...N (thiazole) synthons [N-H... N = 2.941Å, \angle N-H...N = 173.18°] along with the intramolecular bond between carbonyl oxygen and thiazole sulphur atom, leading to a zero-dimensional (0-D) hydrogen bonded network. A critical examination of the crystal structures demonstrated a weaker hydrogen bond (methyl) C-H...C (thiazole) (distance between C-H... π = 3.224Å, \angle C-H...C = 153.21°) and hydrogen bond (methyl) C-H...C (carbonyl carbon) (distance between C-H...C = 2.879Å, \angle C-H...C = 160.67°) leads to two-dimensional (2-D) hydrogen bonded network (Fig.3d).

One of the major challenges is to understand the cause of gelation/non-gelation behaviour, due to odd/even number of methylene functional group, in these series of molecules. Similar, behaviour by the urea functional groups containing gelators is well known and such behaviour was assigned to favourable anti or syn hydrogen bonded network with the change in alkyl chain length.^{13c} However, no direct proof is available in amide based gelling systems to show such interactions.^{13d} Interestingly, all the gelling/ non-gelling molecules in these series showed robust N-H...N hydrogen bonding between thiazole nitrogen and amide nitrogen instead of an amide-amide functional group interaction (**Scheme 2**). Our observations on the supramolecular assembly of amide containing thiazole compounds are well supported by the observation made by Aakeroy et. al.¹⁸ in the seminal paper on amide functionality as robust synthon and the prospect of amide-amide interactions (0D or ladder type) in the presence of other probable hydrogen bonded supramolecular synthons (amide-amide interaction is less probable in presence of strong N-H...N type cyclic H-bond). Interestingly, the C=O...S (intramolecular) forces

found in all the crystal structures of thiazole amide reported in present as well as in our earlier work¹¹ irrespective of presence/absence or position of methyl functional group. The unusual non-bonded interaction, (carbonyl)C=O...S(thiazole), appeared to force the long alkyl chain to be almost linear orientation with respect to thiazole moiety.¹⁹ Logically, the linearity of alkyl chains would favour interdigitation between alkyl chains along with the opportunity of formation of weaker H-bonds such as C-H...O, C-H...N, etc. On the other hand, the proximity of methyl group to alkyl chains would disturb the overall packing pattern and probably lead to the 0-D dimensional hydrogen bonded network as observed in the structure of non-gelator **2d**. Single crystal structures of **1b** (even, n=10)¹¹ and **1c** (odd, n=11) highlighted additional C-H...O interaction in **1c** leading to 2-D hydrogen bonded network in comparison to **1b**, which is a 0-D network.

a**b****c**

d

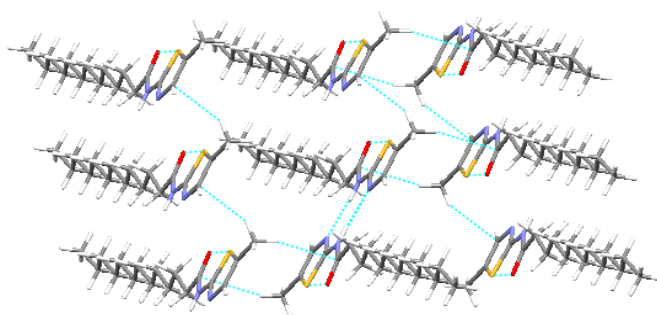


Fig.3: Hydrogen bonded network of (a) **2d** (b) **1c** (c) **1d** and (d) **3c**

A subtle odd-even effect was observed in the series of compounds **3d-3h** which showed an increased or decreased in cgc values with one additional methylene group, which can be attributed to a suitable positioning of alkyl chain over one another and increasing interdigitation (n =even) along with additional C-H...O hydrogen bond. The variable temperature $^1\text{H-NMR}$ of gelling (**1d** and **3d**) and non-gelling compounds (**2d**) supported the retention of H-bonding pattern (no significant chemical shift of protons) in gel and sol phase, whereas non-gelling compounds showed shift of thiazole proton—a mark of its participation in H-bond. The following results corroborated with the IR studies carried out in solid, gel and solution phase of gelling compounds.¹¹

A pronounced effect of increase in alkyl chain length could be observed in the series of compounds **1a-1h** which displayed complete presence (n =even) or absence (n = odd) of gelation property. Structures reported by us displayed additional (methyl)C-H...O bond along with predominant C-H...N interaction with an increase in alkyl chain length from **3c** (n =10) to **3e** (n =12). We proposed an interplay of weak interaction such as C-H...O, C-H...N as driving force for gelation in these series of compounds along with robust supramolecular synthons N-H...N, N-H...O interaction. A favourable presence of alkyl-alkyl chain interdigitation enhances the gelation properties and its absence in the supramolecular assembly of thiazole amides (**2a-2e**) loses its capability to immobilize any of the solvents used in the present study. The powder X-ray diffraction (PXRD) studies of xerogel of gelators/non-gelators are frequently being carried out to get an insight into the packing of gelator fibres. PXRD of xerogel of gelling and non-gelling compounds with even/odd number of methylene functional group was recorded. **3b** (n =12, even) and **1d**, **3d** (n =14, even) showed a periodical high intensity peak position in the lower 2θ angle in the ratio of 1:1/2: 1/3 suggesting lamellar packing such as 21.6034, 11.0243, 7.5231 for **1d**; 22.6578, 11.8392, 7.8609 for **3b**; 21.1379, 11.6241, 7.0921 for **3d** (ESI, Fig.S2). Whereas, in the case of **3c** and **1c** (n =13, odd) such periodical peaks were not observed. Based on these observations we propose that alkyl-alkyl chain interdigitation play a significant role in producing odd-

even effect in the series of compounds **1a-1h** and **3a-3h**.

Template directed synthesis of Ag and ZnO nanoparticles

ZnO nanoparticles loaded gelator samples were prepared by sol-gel method. Thermogravimetric analysis (TGA) of the samples were carried out to verify the removal of the gelator (ESI, Fig. S3) from the synthesized ZnO nanoparticles. TGA analysis of the synthesized samples displayed weight loss of 74.4% corresponding to the complete removal of the gelator molecules at 350 °C. The powders X-Ray diffractograms were recorded to provide the conclusive evidence for the formation silver and ZnO nanoparticles (ESI, Fig.S4). The peaks were observed at 2 theta angles of 31, 39 and 45 corresponding to the (1 0 1), (1 1 1) and (2 0 0) crystalline planes of Ag, respectively.²⁰ Similarly, the peaks were observed at diffraction angles 31, 36, 47, 56, 62 and 67 corresponding to the (1 0 1), (1 0 2), (1 1 0), (1 0 3) and (1 1 2) crystalline planes of ZnO, respectively.²¹

TEM images were used to characterize external morphology of the synthesized Ag and ZnO nanoparticles. TEM imaging of Ag nanoparticles was carried out embedded in gel fibres, which acts as stabilizing and capping agent (Fig. 4). Nearly spherical nanoparticles of Ag were observed in the TEM images suggested successful encapsulation of silver nanoparticles in gel network stabilized by gelator fibres of **3b-3h**. The range of diameters of silver nanoparticles determined using TEM images of silver embedded in the gelled medium of **3b**, **3e**, **3f** and **3h** were found to increase with increase in the alkyl chain length (Table-1). A progressive increase in the nanoparticles size with the increase in alkyl chain length suggested the probable increase in void between 3-D networks of gelator fibres. ZnO nanoparticles were subjected to TEM analysis after calcinations- complete removal of gelator network (Fig. 5). The range of diameters of the series of ZnO nanoparticles based on TEM images of **3b**, **3e**, **3f** and **3h** are shown in Table 1.

Table 1. Particle sizes of synthesized nanoparticles

	Range of diameter(nm) (Ag nanoparticle)	Range of diameter(nm) (ZnO nanoparticle)
3b(n=10)	5-20	10-20
3e(n=13)	18-30	20-30
3f(n=14)	25-37	24-40
3h(n=16)	30-50	28-52

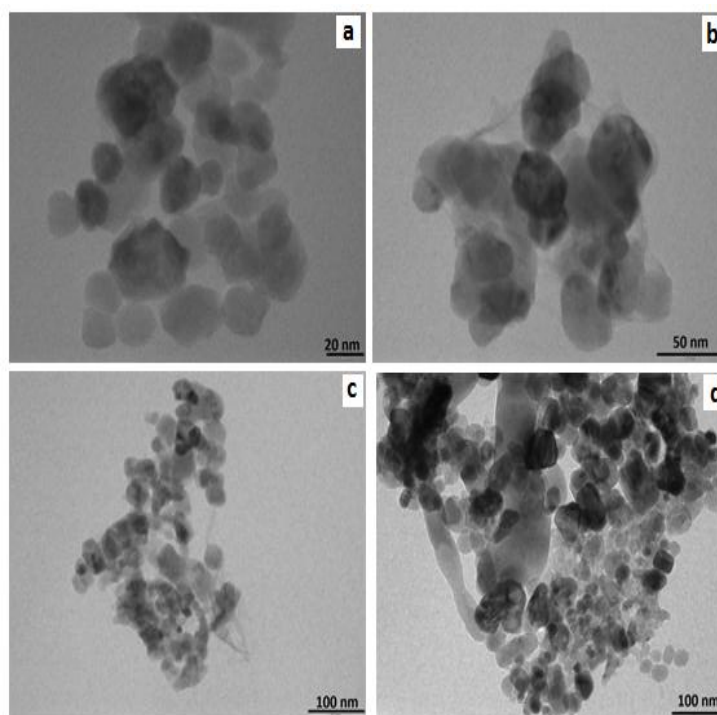


Fig. 4: TEM images of silver nanoparticles formed within the gel network of (a)**3b** (b)**3e** (c)**3f** (d)**3h**

The synthesized ZnO nanoparticles also displayed a gradual increase in size with one additional methylene functional groups change, which corroborate the hypothesis that nanoparticles were synthesized in the well-defined void created by gelator fibres

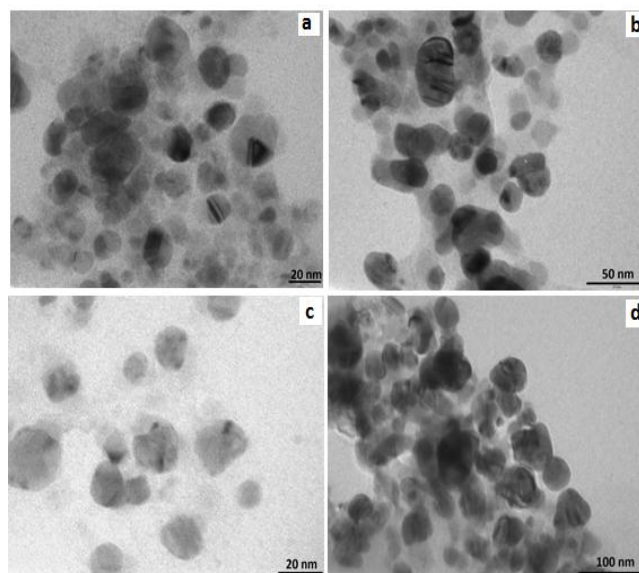
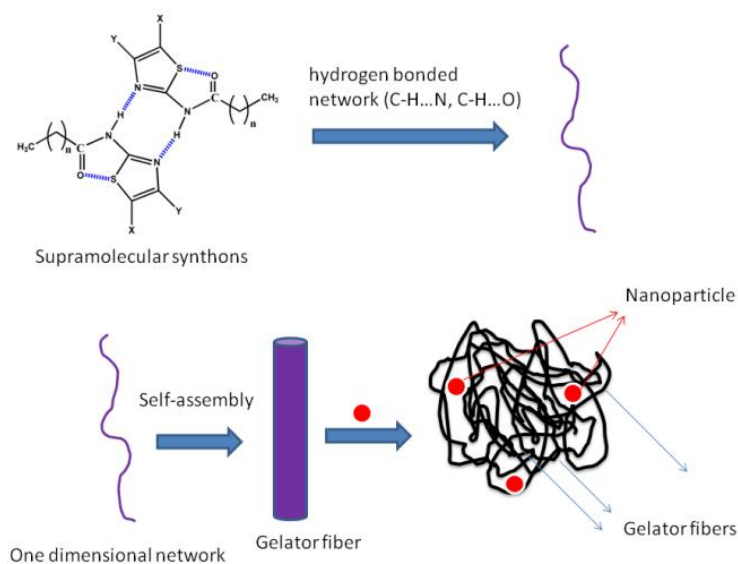


Fig. 5: TEM image of ZnO nanoparticles formed within the gel network of (a)**3b** (b)**3e** (c)**3f** (d)**3h**

A probable mechanism of nanoparticle synthesis is proposed in Scheme 3 based on single crystal studies of gelator/non-gelator and various physico-chemical analysis of thiazole based amide, and

synthesized nanoparticles.



Scheme 3 : Proposed mechanism of template directed synthesis of nanoparticles in thiazole amide based gelator

CONCLUSION

In conclusion, we have synthesized and characterized new series of compounds **1e-1h**, **2e-2h** and **3e-3h** by systematically changing the alkyl chain length. A significant odd-even effect was observed in the series of compounds **1a-1h** and **3a-3h** beyond a certain critical chain length i.e. $n=8$ for **1 (3a)** and $n=11$ for **1 (1c)**. The odd-even effect of gelling molecules were attributed to the interplay between numerous hydrogen bonds such as C-H...O, C-H...N, etc. and van der Waals interaction between alkyl chains (interdigitation). The series of unsubstituted thiazole amide seems to induce gelation of organic solvents through a hydrogen bonded network supported by weak van der Waals interaction. The alkyl-alkyl chain interdigitation is conducive in the case of even number of methylene group, which supported gelation, whereas awkward packing of alkyl chain in the case of odd number of methylene groups of the series (**1a-1h**) leads to complete non-gelation behaviour. A less prominent odd-even effect of methylene group on organogelation properties of **3a-3h** may be attributed to the synergistic effect of (methyl)C-H...N(weak) and N-H...N(strong) H-bond capable of formation of 3-D network sufficient to immobilize a solvent in presence and/or absence of alkyl-alkyl interdigitation. A low c_{gc} values and better efficiency of organgelators **3b-3h**, when 'n' is even, may be assigned to the extra stability gifted by favourable alkyl-alkyl chain interaction. The present study establishes the weak H-bond (methyl) C-H...N as crucial interaction leading to 1-D network in 5-methylthiazole amide derivatives, whereas 4-methyl thiazole amide derivatives formed a 0-D network in the absence of such

interactions. Our observations match with known fact that 1D network favours organogelation, whereas 2D/3D network leads to weak gel or no gel at all.¹² Nearly spherical Ag and ZnO nanoparticles synthesis were successfully carried out in gelator assembly of the series **3b-3h**. In the absence of anisotropic nanoparticle such as nanorods, ribbons, tubes, etc. which is frequently observed in the case of template directed synthesis using LMOGs, we believe that the nanoparticle synthesis takes place in the core of supramolecular gel assembly in agreement with the earlier known cases of *in situ* silver nanoparticles synthesis in the supramolecular gels.²² The gelator fibres play a role of encapsulation and stabilization of synthesized nanoparticles in the gel phase. The size of nanoparticles of Ag and ZnO were found to be dependent on the alkyl chain length of thiazole amides (**3b-3h**), signifying variation in the complexity of gelator network and tunability of pore size between fibres, due to systematic increase in the van der Waals interaction and interdigitation of alkyl chains.

EXPERIMENTAL SECTION

Materials

2-Aminothiazole (97%), 2-Amino-5-Methylthiazole (98%), 2-Amino-4-methylthiazole (98%), Octadecanoic acid (97%), Heptadecanoic acid (>98%), Hexadecanoic acid (98%), Pentadecanoic acid (99%) (All from Aldrich) were used as received. The other chemicals were of the highest commercial grade available and were used without further purification. The solvents used for the preparation of gels were reagent grade. All solvents used in the synthesis were purified, dried and distilled as required.

All thiazole based amide derivatives were synthesized by reacting the acid chloride of various aliphatic acids (pentane carboxylic acid to octadecane carboxylic acid) with thiazole derivatives (fig. 1) using a modified synthetic procedure.²³ A detailed synthesis, characterization and gelation properties of compounds **1a-d**, **2a-d** and **3a-d** was reported by us.¹¹ All new compounds synthesized in the present study **1e-1h**, **2e-2h** and **3e-3h**, were characterized by IR, ¹H-NMR, and MS analysis.

General Synthesis methodology

Oxalyl chloride (2ml, 20 mmol) was added slowly to a stirred solution of Monocarboxylic Acids (2 mmol) in dry dichloromethane (10 ml) under a nitrogen atmosphere, and stirring was continued under a nitrogen atmosphere for 12 h. Excess oxalyl chloride and solvent were removed by distillation under reduced pressure. The acid chloride obtained was dissolved in dry dichloromethane (10 ml) and added to the aminothiazole (2 mmol) in triethylamine (0.3 ml, 2.15mmol). The mixture was stirred under a nitrogen atmosphere for overnight. The reaction mixture was then added to dilute hydrochloric acid (5%), and extracted with chloroform. The product residue after removing chloroform was purified

by repeated crystallization from ethyl acetate/pet. ether mixture.

1e: Yield 85%, m.p. 105 °C, ^1H NMR (400 MHz, CDCl_3 , TMS): δ 12.165(s,1H,NH),7.457 (d, 1H; CH), 7.023(d, 1H; CH), 2.590-2.553(t, 2H; CH_2), 1.827-1.752(m, 2H, CH_2), 1.424-1.264 (m, 22H, CH_2), 0.910(t, 3H; CH_3). MS(EI): m/z 324.53 $[\text{M}]^+$. FTIR (KBr): 3171, 2916, 2849,1688,1577,1468,1321, 1279,1166, 1065, 959, 874, 805, 778, 624, 520 cm^{-1} .

1f: Yield 80%, m.p. 121 °C, ^1H NMR (400 MHz, CDCl_3 , TMS): δ 12.053(s,1H,NH),7.458 (d, 1H; CH), 7.026(d, 1H; CH), 2.585-2.547(t, 2H; CH_2), 1.888-1.771(m, 2H, CH_2), 1.424-1.265 (m, 24H, CH_2), 0.911-0.876(t, 3H; CH_3). MS (EI): m/z 338.31 $[\text{M}]^+$. FTIR(KBr): 3174, 2917, 2849, 1686, 1581, 1468, 1380, 1322, 1288, 1110,1067, 959, 873, 777, 718, 625, 520 cm^{-1} .

1g: Yield 83%, m.p. 117 °C, ^1H NMR (400 MHz CDCl_3 , TMS): δ 11.9855(s,1H,NH),7.462 (d, 1H; CH), 7.032(d, 1H; CH), 2.590-2.365(t, 2H; CH_2), 1.827-1.752(m, 2H, CH_2), 1.437-1.264(m, 26H, CH_2), 0.911-0.877(t, 3H; CH_3).MS (EI): m/z 351.84 $[\text{M}]^+$. FTIR(KBr): 3170, 2917, 2849, 1685, 1576, 1469, 1379, 1321, 1272, 1168, 1064, 959, 875, 778, 718, 624, 520 cm^{-1} .

1h: Yield 79%, m.p. 102 °C, ^1H -NMR (400 MHz, CDCl_3 , TMS): δ 11.865(s,1H,NH),7.458 (d, 1H; CH), 7.024(d, 1H; CH), 2.581-2.544(t, 2H; CH_2), 1.828-1.753(m, 2H, CH_2), 1.430-1.265 (m, 28H, CH_2), 0.912-0.878(t, 3H; CH_3). MS(EI): m/z 366.18 $[\text{M}]^+$. FTIR(KBr): 3176, 2924, 2851, 1683, 1580, 1465, 1379, 1323, 1275, 1169, 1065, 962, 872, 774, 718, 623, 520 cm^{-1} .

2e: Yield 72%, m.p.100 °C, ^1H NMR (400 MHz, CDCl_3 , TMS): δ 12.165(s,1H,NH),6.506 (s, 1H; CH), 2.507-2.478(t,2H; CH_2), 2.346(s,3H; CH_3),1.768-1.712 (m,2H; CH_2), 1.330-1.266 (m,22H; CH_2), 0.911-0.880(t,3H; CH_3). MS (EI): m/z 338.39 $[\text{M}]^+$. FTIR (KBr): 3358, 3164, 2928, 2854, 1672, 1553, 1469, 1314, 1235, 1115,1079, 974, 772, 564 cm^{-1} .

2f: Yield 70%, m.p.83°C, ^1H NMR (400MHz, CDCl_3 , TMS); δ 13.360(s,1H,NH),6.652(s, 1H; CH) 2.698-2.660(t,2H; CH_2), 2.511(s,3H; CH_3), 1.801-1.765 (m, 2H; CH_2), 1.377-1.311(m,24H; CH_2), 0.908-0.874(t,3H; CH_3). MS (EI): m/z 352.29 $[\text{M}]^+$. FTIR (KBr): 3348, 3152, 2914, 2849, 1670, 1552, 1461, 1317, 1233, 1117, 1085, 976, 778, 561 cm^{-1} .

2g: Yield 74%, m.p.89°C, ^1H NMR (400 MHz, CDCl_3 , TMS); δ 13.345(s,1H,NH),6.526(s, 1H; CH), 2.557-2.422(t,2H; CH_2), 2.262(s,3H; CH_3), 1.777-1.642 (m, 2H; CH_2), 1.331-1.208(m,26H; CH_2), 0.911-0.877(t,3H; CH_3).MS (EI): m/z 366.40 $[\text{M}]^+$. FTIR (KBr): 3359, 3160, 2923, 2859, 1675, 1559, 1463, 1329, 1239, 1121, 1090, 982, 770, 569 cm^{-1} .

2h: Yield 71%, m.p.96°C, ^1H NMR (400 MHz, CDCl_3 , TMS): δ 13.178(s,1H,NH),6.559(s, 1H; CH), 2.501-2.463(t,2H; CH_2), 2.238(s,3H; CH_3), 1.756-1.720 (m, 2H; CH_2), 1.331-1.267(m,28H; CH_2), 0.912-0.896(t,3H; CH_3). MS (EI): m/z 380.20 $[\text{M}]^+$. FTIR (KBr): 3355, 3154, 2918, 2851, 1678, 1552, 1468,

1311, 1233, 1111, 1089, 976, 777, 560 cm^{-1} .

3e: Yield 78%, m.p.105 °C, ^1H NMR (400MHz, CDCl_3 , TMS): δ 12.191(s,1H,NH),7.085(s, 1H; CH), 2.546-2.526 (t,2H; CH_2), 2.451(s,3H; CH_3), 1.772-1.767 (m, 2H; CH_2), 1.278-1.266 (m,22H; CH_2), 0.912-0.878 (t,3H; CH_3). MS (EI): m/z 338.19[M] $^+$. FTIR (KBr): 3179, 3060, 2912, 2847, 1682, 1589, 1466, 1418, 1381, 1303, 1279, 1181, 958, 719, 526 cm^{-1} .

3f: Yield 82%, m.p.121°C, ^1H NMR (400 MHz, CDCl_3 , TMS): δ 11.986(s,1H,NH),7.062 (S, 1H; CH), 2.532-2.494(t,2H; CH_2), 2.431(s,3H; CH_3), 1.808-1.739 (m, 2H; CH_2), 1.267-1.224 (m,24H; CH_2), 0.913-0.897(t,3H; CH_3).MS(EI):m/z 352.20[M] $^+$. FTIR(KBr): 3427, 3180, 3080, 2919, 2850, 1697, 1585, 1462, 1409, 1381, 1311, 1280, 1111, 953, 832, 723, 527 cm^{-1} .

3g: Yield 80%, m.p.111 °C, ^1H NMR (400 MHz, CDCl_3 , TMS): δ 12.005(s,1H,NH),7.075(s, 1H; CH) 2.531 -2.494(t,2H; CH_2), 2.437(s,3H; CH_3), 1.806-1.752 (m, 2H; CH_2), 1.398-1.266(m,26H; CH_2),0.912-0.893(t,3H; CH_3).MS(EI):m/z 366.63[M] $^+$. FTIR(KBr): 3432, 3181, 2919, 2850, 2274, 1697, 1588, 1472, 1380, 1312, 1166, 1112, 1067, 962, 831,782 , 622 cm^{-1} .

3h: Yield 79%, m.p.108 °C, ^1H NMR (400 MHz, CDCl_3 , TMS): δ 12.173(s,1H,NH),7.088(s, 1H; CH), 2.533 -2.515(t,2H; CH_2), 2.497(s,3H; CH_3), 1.787-1.752 (m, 2H; CH_2), 1.331-1.266(m,28H; CH_2), 0.912-0.878(t,3H; CH_3).MS(EI):m/z 380.35[M] $^+$. FTIR (KBr): 3428, 3179, 2919, 2850, 1696, 1583, 1465, 1411, 1380, 1311, 1278, 1168, 1108, 793, 722 cm^{-1} .

Characterization

FTIR Spectra were recorded on a Perkin Elmer –RX FTIR instrument. Solid samples were recorded as an intimate mixture with powdered KBr. The ^1H - NMR spectra were measured by using a Bruker AVANCE, 400MHZ with TMS as internal standard. Morphologies of all reported xerogel (dried gel) were investigated by using scanning electron microscopy (SEM) (JEOL JSM5610 LV microscope). For SEM study, the hot sample gel, liquid was placed over the SEM sample holder and allowed to form the gel. Then, the sample was subjected to dryness under normal room temperature and pressure and coated with carbon (**1e**, **1h**, **3e-3g**) and gold sputtering (**3h**). The morphologies of synthesized Ag and ZnO nanoparticles were investigated using transmission electron microscope (TEM) (Philips CM 200) in the working voltage of 20-200kV. TEM studies were carried out by placing a small amount of the corresponding compound dispersed in Ethanol/water on carbon-coated copper grids and dried by slow evaporation. The range of diameter of the synthesized nanoparticles were determined by measuring the diameters of <100 nanoparticles (from smallest to biggest) using TEM images. Powder diffraction patterns of neat xerogel **1e** (methanol, slowly evaporated) and xerogel loaded with silver nanoparticles was recorded on XPERT Philips ($\text{CuK}\alpha$ radiation). The silver nano-particles loaded on

gelator fibres was subjected to powder diffraction studies using Bruker D8 (CuK α radiation) diffractometer. Single crystal X-ray study of compounds **1c**, **1d**, **2d** and **3c** was carried out on Single Crystal X-ray diffractometer (Xcalibur, EOS, Gemini diffractometer). All structures were solved using Olex1.2 software²⁴ and refined using ShelXL refinement package.²⁵

Gelation Test

A weighted amount of potential gelator (10mg) and a measured volume (1mL) of selected pure organic solvent/water were placed into a capped test tube (outer diameter -10mm and length- 75 mm), and the system was heated in an oil or water bath, till the dissolution of solid materials. The solution was cooled to room temperature and finally, the test tube was turned upside down to observe if the solution inside, could still flow or not(test-tube inversion method). No flow of the solvent was designated as Gelation of the solvent. Gel-to-sol transition temperatures (T_{gel}) were determined by using a conventional “dropping ball” method. In this test, a small glass ball (63mg) was carefully placed on the top of the gel to be tested, which was produced in a test tube. The tube was slowly heated in a thermostated oil bath until the ball fell to the bottom of the test tube. The temperature at which the ball reaches at the bottom of the test tube is taken as T_{gel} of that system.

Synthesis of Silver nanoparticle

To load the organogels with AgNO₃ for the synthesis of silver nanostructure, AgNO₃ (2 mg) and the gelator (2 wt %) was dissolved in ethanol (2ml) by heating. The solution was allowed to stand to form a colourless gel. The gel was irradiated with a mercury vapour UV lamp. On irradiation, there was visually observable change to the gel, the colour rapidly changed from colourless to pale pink within 15 minutes of irradiation and it changes to reddish brown over a period of an hour.

Synthesis of ZnO nanoparticle

To prepare ZnO particles, 35 mg zinc acetate was mixed with 10 mg KOH in 1 ml ethanol. This was added to a solution containing 20 mg gelator in 1.0 ml Ethanol. This mixture was heated and finally allowed to cool. A white gel thus obtained was allowed to stand for a day at ambient temperature and then dried in a vacuum. In order to remove the template, the sample was heated to 400°C for 4 hr.²⁶

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Diffraction facility at the Faculty of Science, The Maharaja Sayajirao University of Baroda, Vadodara, Gujarat (India).

NOTES AND REFERENCES

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†Electronic Supplementary Information (ESI) available: Gelation behaviour of compounds **1a-1h**, **2a-2h** and **3a-3h**, TGA thermogram, photographic image of **1c-1h**, crystallographic table of **1c**, **1d**, **2d** and **3c** and .CIF files of **1c**, **1d**, **2d** and **3c**. See DOI: 10.1039/b000000x/

‡(CCDC Nos. of **1c**, **1d**, **2d** and **3c** are 958233, 966725, 957407 and 965887 respectively)

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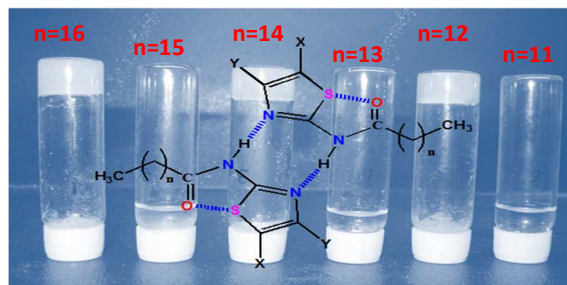
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Table of contents (TOC)**Odd-Even effect in a thiazole based organogelator: Understanding the interplay of non-covalent interactions on property and applications**Priyanka Yadav^a and Amar Ballabh^{a*}

Research Highlights- The effect of systematic change in alkyl chain appended to thiazole moiety on supramolecular gelation and nanoparticle synthesis were investigated.