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ARTICLE

From Helical Supramolecular Arrays to Gel-forming Networks: Lattice-restructuring and Aggregation-control in Peptide-based Sulfamides to Integrate New Functional Attributes

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While supramolecular organisation is central to both crystallization and gelation, the latter is more complex considering its dynamic nature and multifactorial dependence. This makes the rational design of gelators an extremely difficult task. In this report, the assembly preference of a group of peptide-based sulfamides was modulated by making them part of an acid-amine two-component system to drive the tendency from crystallization to gelation. Here, the peptide core directed the assembly while the long-chain amines, introduced through salt-bridges, promoted layering and anisotropic development of primary aggregates. This proved very successful, leading to gelation of a number of solvents. Apart from this, it was possible to fine-tune their aggregation using an amphiphilic polymer like F-127 as additive to get honey-comb-like 3D molecular architectures. These gels also proved to be excellent matrices for entrapping silver nanoparticles with superior emissive properties.

Introduction

Gelation by Low Mol. Wt. organic compounds has captured the attention of scientists both as a platform for new functional systems and also due to the challenge it brings in terms of mechanistic intricacies involved.[1] It is considered as the physical manifestation of secondary interactions between the gelator molecules and the solvent system under consideration, which is complex and dynamic.[2,3] This very fact makes rational design of gelators a difficult task and their properties are largely unpredictable.[4] Recently, we have reported the results of our efforts to design new gelators using crystal lattices of peptide-based sulfamides as starting points.[5] Although ability to undergo 1D-assembly alone was not a sufficient condition, it was possible to improve fibril stability and fibril-fibril interactions by introducing amines through salt bridges to promote gelation as opposed to crystallization. In these designs, the sulfamide core directed the anisotropic assembly which is stabilized by layer of hydrophobic domain from the amine component.

The approach of using conformationally stable peptides for directing the assembly, if generalizable, would make design of functional gelators with predefined properties easier, and is the main theme of the work depicted here. Instead of dipeptide analogs,[5] the present work uses a larger core from their higher homologues (**1**-**9**, Fig. 1) which are characterized by the presence of a 10-membered intramolecular H-bonding that locks the conformation.

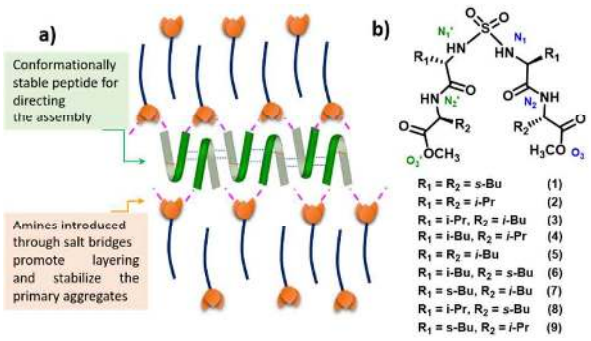

Fig. 1 a) Pictorial representation of folded peptides directing the assembly in gelator network; b) Peptide-based sulfamides selected as core-components in the present work.

Ability of such systems to form helical supramolecular arrays has been reported by us earlier and was originally studied as shortest β-turn mimics.[6] In the present context, this property is utilized for creating entangled three-dimensional networks needed for solvent entrapment. Apart from demonstrating the suitability of these systems to direct fibril growth needed for gelation, we have done some exploratory research to make them functionally useful by fine-tuning their assembly using F-

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127 to get honey-comb like supramolecular architectures, and also have used these gel matrices to modulate the photophysical properties of silver nano particles. Details of these studies are elaborated below.

The first set of sulfamides **1-9** used for preliminary analyses were synthesized by reacting sulfuryl chloride with appropriate dipeptide methyl esters (SI-Scheme 1). These peptides have different combinations of hydrophobic groups at 1, 1' and 2, 2' positions. X-ray quality crystals were secured by slow evaporation of solutions of **5**, **7**, **8**, and **9** from MeOH-H_2O (2:1). Despite having different combination of side-chain groups, the solid-state conformations of these new analogs were similar to those of **1**-**3** studied earlier (Figure 1b).[6] The structures of **5** and **9** are presented in Figures 2-3 as representative examples and those of **7** & **8** are included in SI (Figures S1 and S2). Crystals of both **5** and **9** belonged to monoclinic system under $P2_1$ space group.

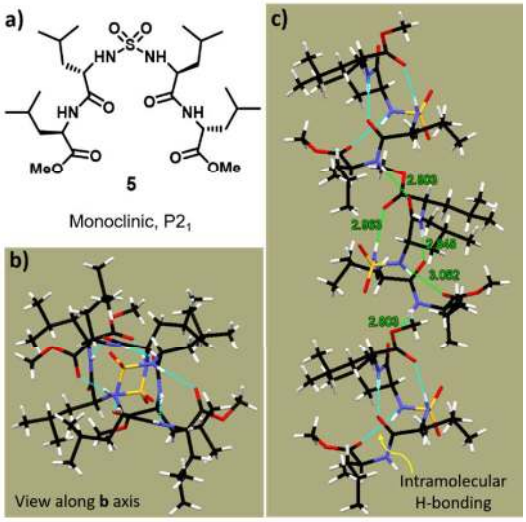

Fig. 2 a) Chemical structure of **5**; b) Lattice assembly - view along b axis; c) Helical array involving extended H-bonds

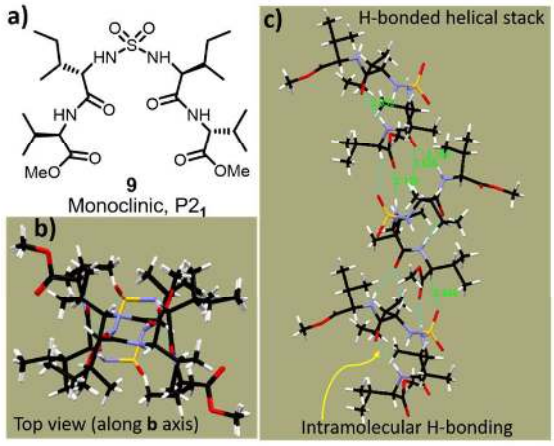

Fig. 3 a) Chemical structure of **9**; b) Lattice assembly - view along b axis; c) Helical array involving extended H-bonds.

A small twist in the orientation of peptide segments with respect to the central sulfamide group allowed them to stack atop one another with NH and CO groups oriented along the axis of the helical array and facilitated continuous H-bonding network (Figures 2c and 3c). Intramolecular H-bonding between N2'H and O1 which stabilizes the conformation is also shown. Notably, there was only a limited number of weak CH…O type of interactions or hydrophobic clustering to pack these columns in the lattice. A similar supramolecular arrangement was seen in the lattices of **7** & **8** as well and the details are included in supporting information (Figures S1 and S2). A peculiarity of the arrangement shown in Figures 2&3 is the radial distribution of amino acid side chains and the ester groups (top views shown in Figure 2b and 3b). The fact that all major sets of secondary interactions in these cases are utilized for one-dimensional assembly makes these lattices suitable for gelator design. To know whether such assembly preference alone is sufficient for gelation, a number of solvents were screened initially but except **4**, others did not show any sign of solvent entrapment (SI-Table 10).

Results

Amine capping approach to drive gelation process:

We hypothesized that a shift from crystallization to gelation is possible if the assembly is made more anisotropic by introducing hydrocarbon chains through salt bridges. As seen in the case of their dipeptide analogs,[5] the hydrophobic groups from amine component were expected to envelope the array of sulfamides which internally directs the assembly. Such layering would not only improve the stability of primary aggregates but also lead to multi-layered sheets; these in turn could roll-over and form fibrillar structures needed for gelation process. With this theme, the esters **1**-**9** were hydrolyzed using LiOH and the resulting diacids **1a**-**9a** were treated with two equivalents of suitable amine (decylamine DA; dodecylamine DDA; tetradecylamine TDA; octadecylamine ODA) in the solvent of interest (SI-Scheme 2). These systems are labelled as **DA1a**, **DA2a** etc. to represent amine and acid components respectively. The contents were warmed initially to make homogeneous solution and then allowed to come to room temperature. Outcome from these gelation studies, summarized in Table 1 clearly show that amine-capping has worked favorably to facilitate supramolecular network needed for solvent entrapment, a complete list showing the gelation profile of all the compounds is given in supporting information (SI-Tables 1-9). A number of these systems formed gels which were stable on vial inversion. Images of gels from some selected salts of **1a**-**9a** are shown in Figure 4 as representative examples, and those of others, are also included in supporting information (Figures S3-S9).

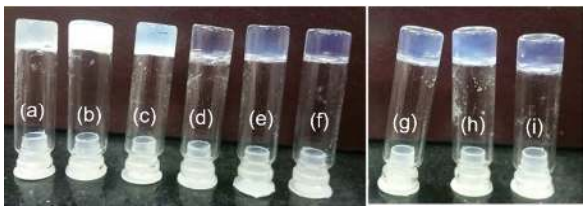

Fig. 4 Gel pictures a) **ODA8a**/Chloroform, b) **ODA8a**/THF, c) **ODA8a** /Cl-benzene, d) **ODA8a** / Xylene, e) **ODA8a** / Mesitylene, f) **ODA8a**/ Toulene, g) **TDA8a** / Xylene, h) **TDA8a** / Mesitylene, i) **TDA8a**/ Toluene; (3 wt % of the diacid and 2 equivalents of appropriate amine in 1 mL of the solvent was used in gelation study)

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Analysis of structures and gelation preferences show that irrespective of the amino acid residues in the sulfamide, the gelation ability improves drastically with the hydrocarbon chain of the amine component. Their major preference is to gel aromatic solvents like mesitylene, xylene, & toluene, followed by THF and $CHCl_3$. Morphological features of xerogels of these two components systems from various solvents were then analysed by SEM and the images of selected examples are presented in Figure 5a-f.

Table 1. Gelation profile of DA, DDA, TDA, ODA salts of **1a**-**9a** [a]

	Gelator/solvent preferences
DA salts	**DA1a**/THF; **DA3a**/Toulene, Mesitylene, Xylene, THF, $CHCl_3$; **DA5a**/2-Butanone; **DA7a**/ Toulene, Mesitylene, Xylene, Cl-benzene; **DA8a**/THF, $CHCl_3$.
DDA salts	**DDA1a**/Toulene, Mesitylene, Xylene; **DDA2a**/Mesitylene, **DDA3a**/Toulene, Mesitylene, Xylene, THF, $CHCl_3$; **DDA5a**/Toulene, Mesitylene, Xylene, **DDA7a**/Toulene, Mesitylene, Xylene, Cl-benzene; **DDA8a**/Toulene, Mesitylene, Xylene, THF.
TDA salts	**TDA1a**/Toulene, Mesitylene, Xylene, THF, 2-Butanone; **TDA2a**/Toulene, Mesitylene, THF; **TDA3a**/Toulene, Mesitylene, Xylene, $CHCl_3$; **TDA4a**/Toulene, Mesitylene, Xylene, THF, $CHCl_3$; **TDA5a**/Toulene, Mesitylene, Xylene, THF, Nitrobenzene; **TDA7a**/Toulene, Mesitylene, Xylene, Cl-benzene, $CHCl_3$; **TDA8a**/Toulene, Mesitylene, Xylene, THF, $CHCl_3$, Cl-benzene; **TDA9a**/ $CHCl_3$.
ODA salts	**ODA1a**/Toulene, Mesitylene, Xylene, THF, 2-Butanone; **ODA2a**/Toulene, Mesitylene, Xylene, THF, Cl-benzene; **ODA3a**/Toulene, Mesitylene, Xylene, *t*-BuOH, THF, $CHCl_3$, Cl-benzene; **ODA4a**/Toulene, Mesitylene, Xylene, THF, $CHCl_3$; **ODA5a**/Toulene, Mesitylene, Xylene, THF, $CHCl_3$, Nitrobenzene; **ODA6a**/Toulene, Mesitylene, Xylene, THF, $CHCl_3$; **ODA7a**/Toulene, Mesitylene, Xylene, $CHCl_3$; **ODA8a**/Toulene, Mesitylene, Xylene, THF, $CHCl_3$, Cl-benzene; **ODA9a**/Toulene, Mesitylene, Xylene.

[a] 3 wt % of the diacid and 2 equivalents of appropriate amine in 1 mL of the solvent was used in gelation study

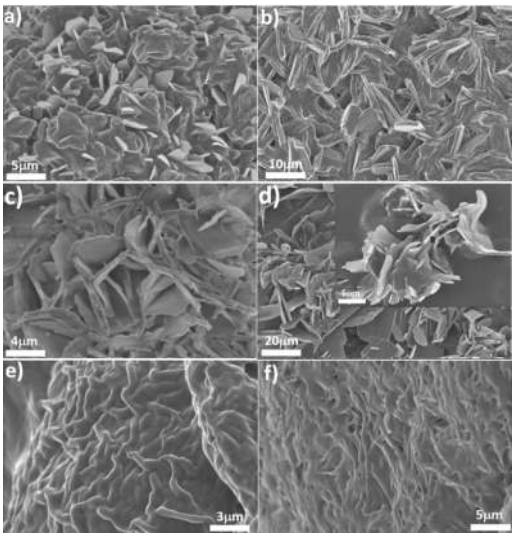

Fig. 5 SEM images of a) **ODA3a**/Mesitylene, b) **TDA3a**/Mesitylene, c) **ODA5a**/$CHCl_3$, d) **ODA5a**/Mesitylene, e) **DA7a**/Mesitylene, f) **ODA3a**/t-BuOH; Samples for SEM imaging were prepared by drop-casting gels prepared from 3 wt % of the diacid and 2 equivalents of appropriate amine in 1 mL of the solvent on a piranha-treated glass plate, followed by drying under ambient condition.

SEM images of the xerogels of **ODA3a**, **TDA3a**, **ODA5a** had either flake- or sheet-like structures as shown in Figure 5a-d. Samples of **DA7a**/mesitylene and **ODA3a**/t-BuOH were however fibrous (Figure 5e-f). Similar images of other samples are included in SI (Figures S10-S13). Although a larger number of publications show the presence of fibrillar networks in xerogels,[7a-j] there are examples of other morphologies like flakes, sheets & ribbons as well, depending upon gelators and the conditions.[7k-p] Understandably, solvent evaporation takes place during sample preparation and hence the final morphologies are not the true reflection of the situation in gel state; there is chance of self-processing as a result of change in concentration during solvent evaporation which would influence the final morphology. To know whether there is a change in morphology in samples prepared at concentration below its cgc, we have carried out SEM experiments with **ODA8a**/THF at lower gelator concentrations (its cgc = 1.2 wt% **8a** with 2 molar equivalents of ODA). Interestingly, more continuous soft supramolecular structures are seen at the concentrations tested (0.1 wt% and 0.01 wt% of **8a** + 2 equiv. each of ODA). These details are included in the SI (Figure S14).

The next task was to get a deeper understanding on molecular packing and then explore the possibility of modulating the assembly process to make the interfaces adaptable for different functions. Continuous salt-bridge formation between diacids and the amine component during gelation process was evident from FT-IR studies. For instance, xerogels of **DA2a**, **TDA2a** and **ODA2a** from mesitylene, xylene, and toluene had NH stretching bands at 3257-3352 cm^{-1} indicative of H-bonding. Further, the band at 1735 cm^{-1} from stretching vibration of –COOH of **2a** disappeared and new absorption bands corresponding to asymmetric and symmetric COO– stretching emerged at 1640 cm^{-1} and 1457 cm^{-1} respectively in confirmation of stable two-component network (SI, Figure S15).

Since efforts to get X-ray quality crystals of these systems were not fruitful, we resorted to PXRD analysis to get useful information about molecular packing. The PXRD spectrum of **ODA1a** xerogel from toluene had peaks at 2θ values of 2.02, 4.47, and 6.0 respectively corresponding to d-spacing of 4.35, 1.97, and 1.47 nm. They were in the ratio of 1:1/2:1/3, suggestive of layered structure (Figure 6a). Since length of the salt (sulfamide unit & alkyl chain) is about 4 nm, the spacing of 4.35 is suggestive of a highly inter-digitated bilayer. A similar arrangement was also seen in the xerogel of **TDA1a** from toluene (2θ values of 2.19, 4.10, 6.41 with

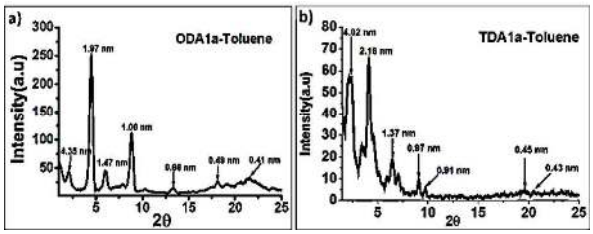

Fig. 6 a) PXRD spectra of **ODA1a** xerogel from Toluene and b) **TDA1a** xerogel from Toluene, showing evidence of layered arrangement (gels were prepared from 3 wt % of the diacid and 2 equivalents of appropriate amine in 1 mL of the solvent)

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d1, d2, d3, of 4.02, 2.16, 1.37 nm; Figure 6b). The PXRD pattern from xerogel of **ODA** salt of **7a** from toluene is included in SI (Figure S16).

F-127 meditated morphology control to get porous networks:

In fact, complexity associated with gelation process increases with the number of components due to different types of secondary interactions possible, but at the same time allows fine-tuning of properties. In order to see whether the networks formed during gelation and their morphological preferences can be modulated using additives, we carried out a set of experiments by including F-127 (Pluronic F-127 M.Wt. ~ 12,500 Da) during gelation process. Ability of such non-ionic surfactants to control the growth of microcrystalline aggregates is well documented in literature.[8] Such amphiphilic block copolymers themselves can aggregate into micelles or their higher order structures depending upon the medium and conditions, and interfere with the development of other aggregates by adsorbing differently onto different crystal planes after nucleation, leading to shape-control. In the present context, we expected that the development of primary aggregates from the gelator molecules could get modulated in a similar way thereby affecting nature of their supramolecular networks. In order to explore this, the gelation of **ODA8a** in THF was carried out in presence of varying amounts of F-127, and the corresponding xerogels were subjected to SEM imaging. As evident from Figure 7a, use of 1 mg/mL of F-127 changed the preference to micro-porous aggregates. Increasing the concentration of this additive to 2 mg/mL resulted in further refinement to get honey-comb like 3D structures (Figure 7b). The fact that F-127 has distinct effect on molecular packing will become evident if we compare the PXRD profiles of samples made in the presence and absence of this additive (Figure 8a and b). For example, xerogel of **ODA8a** (from THF) displayed three peaks at 2θ of 2.36, 4.53, 6.89

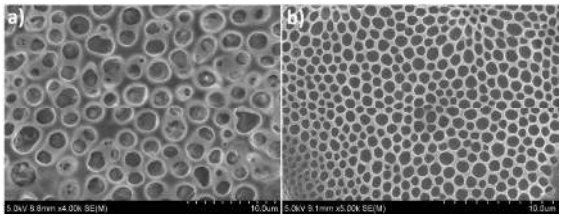

Fig. 7 SEM images of **ODA8a** xerogels when gelation was done in presence of: a) 1 mg of F-127, b) 2 mg of F-127.

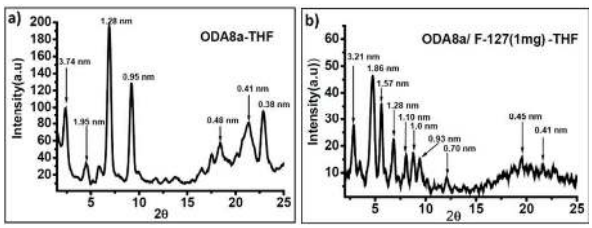

Fig. 8 a) PXRD spectra of **ODA8a** xerogel from THF and b) **ODA8a**+F-127 xerogel from THF, showing evidence of layered and columnar hexagonal arrangements respectively (gels were prepared from 3 wt % of the diacid and 2 equivalents of appropriate amine in 1 mL of the solvent)

corresponding to d-spacing of 3.74, 1.95, 1.28 nm respectively (ratio 1:1/2:1/3) in agreement with a layered structure (Figure 8a). At the same time, xerogel of **ODA8a**+F-127 (from THF) displayed reflections at 2θ values of 2.74, 4.76, and 5.63 respectively corresponding to d-spacing of 3.21, 1.86, and 1.57 nm in the ratio 1:1/√3:1/√4 which support of a hexagonal columnar arrangement (Figure 8b). Increase of F-127 concentration beyond 10 mg/mL had a detrimental effect on fibril development, causing complete dissolution of **ODA8a** preventing gelation (SI, Figure S21).

Subsequently, rheological experiments were carried to understand the viscoelastic behaviour and gel strength. The storage modulus G', loss modulus G'' and the yield stress (σ_y) are useful parameters to assess their rigidity and ability to store energy.[9] To know the effect of F-127, gel from **ODA8a** in THF was taken for rheological studies. In the case of sample prepared without the additive, G' was greater than G'' between 0.1-20% strain and then crossed each other giving a % yield strain value of 20.11% (Figure 9a). In the frequency sweep experiment with this sample (done at 1% strain), G' and G'' remained steady over the frequency range of 1-100 rad/s (Figure 9b). Interestingly, there was not much change in the viscoelastic behaviour of the sample prepared in presence of F-127. Here again, G' was above G'' during 0.1-20% strain and crossed each other at 19.79% yield stain (Figure 9c-d). Thus, it was possible to fine tune the gelator network by including an optimum amount of F-127 without compromising the gel strength and rheological properties. Similar results from studies involving **TDA5a** and **ODA5a** are presented in SI (Figure S17-18)

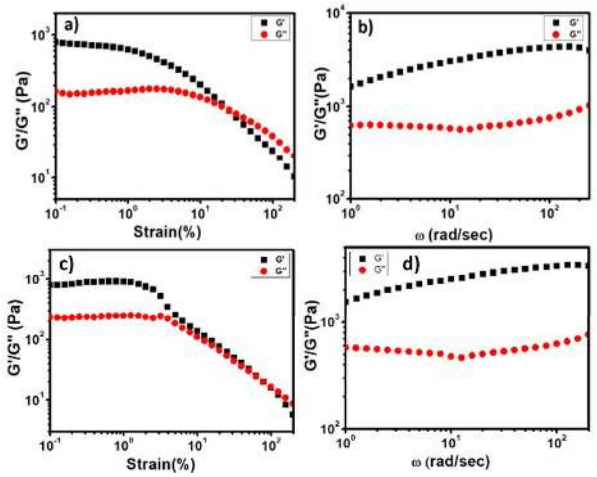

Fig. 9 a) Strain sweep experiment with **ODA8a** gel in THF; b) Result from Frequency sweep experiment (1-100 rad/s). Corresponding data from the gel prepared with **ODA8a** in presence of 2 mg F-127 are shown in c&d; These gels were prepared by adding 2 equivalents of ODA to solution of **8a** (5 wt%) in 1 mL of THF.

Thus, the results discussed above show the generalizability of 'amine-capping approach' in gelator design [5] which employs a

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suitable core moiety to direct the assembly and use the second component to shift the tendency from crystallization to gelation. Studies involving F-127 also show that the use of non-ionic surfactant to modulate the assembly process is not just restricted to the area of crystal engineering but can also be used to control the network formation during gelation. Since the honey-comb-like aggregates have well-defined interiors, they represent a new class of micro-porous organic materials. Fabrication of such ordered porous structures are receiving tremendous attention in recent times as they offer promise in catalysis, sensor design, templating, micro-fabrication, biomaterials etc.[10] Possible use of sulfamide-based gel matrices presented here in one or more of these areas will be investigated and communicated in due course. As the immediate next step, compatibility of this system with silver nano-particles, and the 'matrix effect' on their photo-physical behaviour was investigated and the results are summarized below.

Nanometal entrapment and emission-control:

Metal nanoparticles embedded in gel matrix are considered as a new class of soft composite materials with applications in diverse areas.[11] Although conceptually simple, the fact that nano-metals are often capped with stabilizing ligands necessitates good compatibility between this outer surface and gelator network. To explore the usefulness of sulfamide-based gelators developed here for making such hybrid materials, the entrapment and emission behaviour of silver nanoparticles were systematically studied. At first, silver nanoparticles capped with reduced glutathione was prepared by reported procedure and extracted to chloroform layer.[12] To 1 mL of this solution was added the gelator (**ODA8a**, 3 wt% 8a with 2 equiv. of ODA) and the mixture made homogeneous by gentle heating. This on standing transformed into a gel with enhanced emission compared to that of free solution. The images of free NP solution and that in the gel matrix are shown in Figure 10a(i) and Figure 10a(iv) respectively. Figure 10c gives a quantitative comparison of the emission intensity from free nanoparticle solution and that in the immobilized state (i vs. iii). The study was also repeated by including F-127 (2 mg) during gelation process to know whether the change in fine-structure of the supramolecular network would affect the photo-physical behaviour. As evident from Figure 10c(ii), a noticeable emission enhancement was seen in this case as well but the extent was slightly less in comparison with the sample containing NPs and gelator alone. The corresponding image of the gel is shown in Figure 10a(iii). The variation in fluorescence intensity with respect to gelator concentration was also systematically studied to follow the 'matrix effect' closely. Towards this, the emission intensity of nanoparticle solutions in $CHCl_3$ containing 0.4, 0.8, 1.2, 1.6 and 3.0 wt% of **8a** with 2 equivalents each of ODA were prepared and their emission spectra recorded. The results presented in Figure 11 clearly show that there is a steady increase of intensity till 1.2 wt% is reached and a weakening afterwards. Interestingly, the CGC of this system was also found to be 1.2 wt% which suggest that the best emission enhancement is reached at CGC, beyond which the emission reaching the detector decreases likely because of scattering effects.[13]

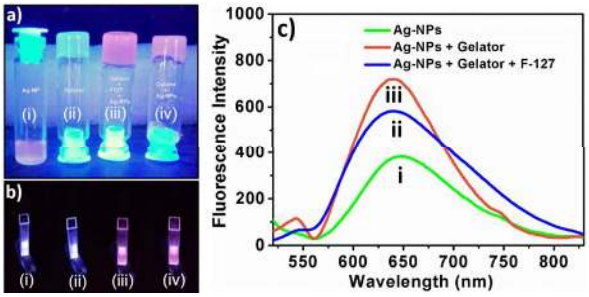

Fig. 10 a) Photographs (taken in a UV chamber with 365 nm lamp) of (i) AgNPs in $CHCl_3$, (ii) **ODA8a** (3 wt%) alone in $CHCl_3$, (iii) Gelator+F127+NPs in the gel state, (iv) **ODA8a** (3 wt%) and NPs in the gel state; b) The corresponding samples photographed in a spectrofluorometer with excitation of 365 nm; c) Spectra showing the fluorescence enhancement from nanoparticles in the gel matrix (λex = 480 nm, slit: 5 nm/ 5 nm).

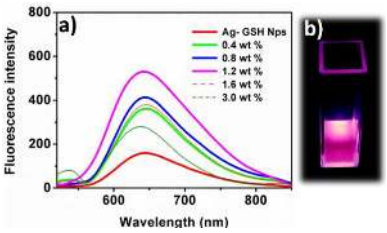

Fig. 11 a) Changes in fluorescence intensity of Ag nanoparticles with different concentrations of **ODA8a**, (λex = 480 nm, slit: 5 nm/ 2.5 nm), b) Image shows the emissive nature under spectrofluorometer with 1.2 wt% of gelator (λex = 365 nm).

The effect of temperature on the emission profile was subsequently compared in order to know how well the matrix is able to shield quenching otherwise possible in the solution state.[14] In the case of nanoparticle solution, there was drastic reduction in intensity on increasing the temperature from 10 °C to 60 °C (Figure 12a) whereas a much better tolerance was seen in the gel state where it was emissive even at 60 °C (Figure 12b). In order to see the effect of gelator concentration on this temperature dependence, similar experiments were repeated with samples made from 0.5 wt% (lower than cgc) and 2 wt% of **8a** (higher than cgc). Among these, the trend in the case of 0.5 wt% was similar to that from 1.2 wt% but the response from the sample containing 2 wt% of 8a was poor (SI, Figure S19). Although not in gel state, good network of supramolecular structures from the gelator could exist even at 0.5 wt% which is entrapping the nanoparticles, causing the emission enhancement. In principle, a matrix that can confine nanoparticles and decrease the pathways of non-radiative decay of excited systems without causing scattering should be

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able to show similar effect. In order to see whether the nature of gel matrix is having any significance in the emission enhancement, we have done additional experiments with gel created from the lower homologue of the sulfamides studied here (SI, Figure S20). Interestingly, gel from this dipeptide analog was not efficient in fluorescence enhancement which suggests that good compatibility of gel network with the capped nanoparticle system at the microscopic level is important. Since silver nanoparticles and their emission properties are being made use of in applications like sensing, imaging, optoelectronics etc.,[15] gel matrices like this provides an excellent opportunity to improve the sensitivity profile and application scope.

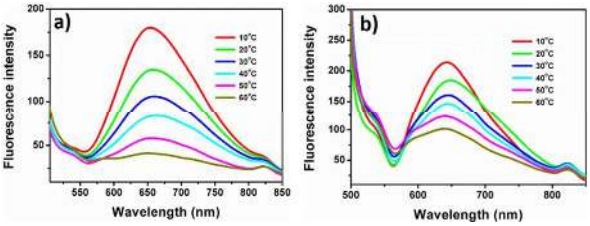

Fig. 12 a) Changes in fluorescence intensity of Ag nanoparticles in $CHCl_3$ solution; b) Corresponding changes in NPs entrapped in the gel state, with respect to temperature; 1.2 wt% of 8a with 2 equiv. of ODA was used (slit: 5 nm/ 2.5 nm).

Laboratories of Shinkai,[16] Terech,[17] Hanabusa,[18] Weiss,[3,19] Feringa,[20] Smith,[21] Ajayaghosh,[7a,22] Dastidar,[5a,c,g] etc. have contributed significantly to the area of supramolecular functional materials. In the case of gelator design, the number of rational approaches are relatively less, and the reports have come mainly from the laboratories of Shinkai, Hanabusa and Dastidar. The results presented here demonstrates a useful strategy to design functionally important supramolecular networks and involve selecting a conformationally well-defined self-assembling core to direct the assembly process with an additional component to modulate solubility characteristics and anisotropic assembly. This strategy is expected to have generality and would help in incorporation of groups with specific chemical properties for developing new functional systems.[23] Vast variety of crystal lattices of organic compounds that are availabe would allow us to choose the right combination to optimise the properties.

Conclusions

A series of peptide-based sulfamides having high tendency to form supramolecular helical arrays in the solid state was selected for the design of gel-forming systems. This preference for 1D-assembly alone was not sufficient to induce gelation in the solvents examined but their di-acids in combination with long-chain amines proved effective in entrapping various solvents, especially the aromatic ones. In this rational approach, the peptide based sulfamide was chosen to direct the assembly process while the amines introduced through salt bridges caused layering through clustering of their hydrocarbon chains. This led to anisotropic assembly required for gelation which was studied by spectroscopic, electron-microscopic and rheological methods. By including an amphiphilic polymer like F-127 during gelation process, it was possible to change the morphology and nature of xerogels from flakes to honey-comb like 3D-network with potential use in areas like micro-fabrication, biomaterials etc. In addition, these gels also turned out to be very good matrices for entrapping silver nanoparticles to improve their emissive properties.

"There are no conflicts to declare".

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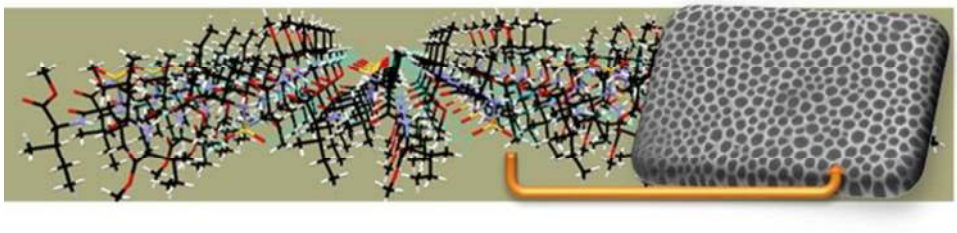

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