Supramolecular gelling agents: can they be designed?

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The last two decades have witnessed an upsurge of research activities in the area of supramolecular gelators, especially low molecular mass organic gelators (LMOGs), not only for academic interests but also for their potential applications in materials science. However, most of the gelators are serendipitously obtained; their rational design and synthesis is still a major challenge. Wide structural diversities of the molecules known to act as LMOGs and a dearth of molecular level understanding of gelation mechanisms make it difficult to pin-point a particular strategy to achieve rational design of gelators. Nevertheless, some efforts are being made to achieve this goal. Once a gelling agent is serendipitously obtained, new gelling agents with novel properties may be prepared by modifying the parent gelator molecule following a *molecular engineering* rationale; however, such approach is limited to the same class of gelling agent generated from the parent gelating scaffold. A *crystal engineering* approach wherein the single-crystal structure of a molecule is correlated with its gelling/nongelling behaviour (*structure–property correlation*) allows molecular level understandings of the self-assembly of the gelator and nongelator molecules and therefore, provides new insights into the design aspects of supramolecular gelling agents. This *tutorial review* aims at highlighting some of the developments covering both *molecular* and *crystal engineering* approaches in designing LMOGs.

1. Introduction

Gels are everywhere! Starting from protoplasm to shaving cream, they are fascinating solid-like materials containing mostly liquid. A gel is comprised of two components—gelator(s) and solvent(s). The solid-like appearance of the gel is due to the immobilization of the solvent molecules in the three-dimensional (3D) network formed by the gelator molecules. If chemical bond formation among gelator molecules is responsible for such a 3D network, the resulting gel is called a *chemical gel* (*e.g.*, polyethylene polyester, polyamide, poly-(vinyl alcohol) *etc.*). On the other hand, if the 3D network is formed by a self-assembly process (non-covalent interactions such as hydrogen bonding, π–π stacking, van der Waals interactions *etc.*), the resulting gel is termed a *supramolecular* or *physical* gel.

LMOGs, small organic compounds having molecular mass typically <3000 strictly belong to the supramolecular gelator category and are amazingly powerful in immobilizing organic solvents (organogels) and pure water and/or aqueous solvents (hydrogels) at very low concentration of the gelator.[1] In a typical experiment, when a solution containing a small amount of LMOG in a suitable solvent is heated and cooled below a critical temperature (sol–gel transition or gel formation temperature T_{SG}), the whole volume of the liquid behaves like a solid. The solid-like visco-elastic material thus obtained is a gel. These physical gels obtained from LMOGs are generally thermoreversible (reversible sol–gel transformation upon heating and cooling) and in some rare occasions[2] display thixotropic (reversible sol–gel transformation under mechanical stress followed by rest) behavior. LMOGs which are able to gel organic liquids, generally do not display hydrogelling[3] capability and *vice versa*. However, ambidextrous gelators[4] (capable of gelling both organic and aqueous solvents) are also reported. Recent years have witnessed a surge of research work dedicated to LMOGs because of their various potential applications in sensors,[5] electrooptics/photonics,[6] structure directing agents,[7] cosmetics,[8] conservation of arts,[9] drug delivery and bio-medical applications[10] *etc.*

Gels are materials that are easier to recognize than to define.[11] For all practical purpose, a material is termed a gel

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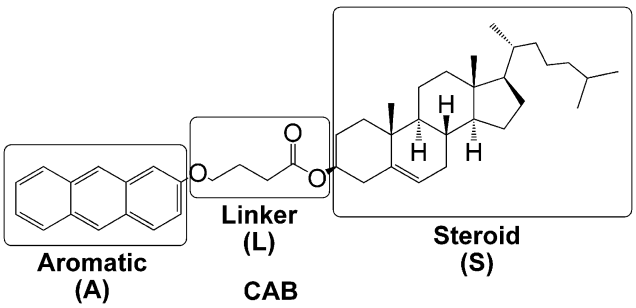
if the whole volume of liquid is completely immobilized as usually tested by the 'tube inversion' method.[12] The gelator molecules form metastable self-assembled fibrilar networks (**SAFIN**s) that can be microscopically (optical microscopy (OM), scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM)) seen. A closer look at these **SAFIN**s reveals various morphological features of which the most noteworthy is the high aspect ratio and branching and/or entanglement of the fibers. During gel formation, it is understood that while cooling the gelator containing solution, the process somehow aborts neat crystallization which would have resulted in phase separation (crystallization or precipitation); instead, it promotes one-dimensional (1D) growth of fibers which by some means manage to self-assemble into complicated three-dimensional (3D) **SAFIN**s within which the solvent molecules are immobilized due to capillary force resulting in gel formation. Molecules having wide structural diversity are known to act as LMOGs (Chart 1). Most of the gelators are serendipitously found. Both structural diversity and lack of molecular level understanding of the gelation mechanism contribute to the low success rate in designing gelators. Nevertheless, there are some conscious attempts aimed at designing LMOGs. This review will cover some such attempts to design LMOGs with special emphasis on crystal engineering as design strategy in organic salt based LMOGs. For the purposes of this review, it will not be possible to cover the pragmatic factors of gelation such T_{SG}, T_{GS} (gel dissociation temperature), MGC (minimum gelator concentration), T_{GS} *vs* MGC plots, DSC, lifetime of gels at room temperature, properties of gels *etc*.; they may be found in the references cited and various reviews.[1]

2. Designing LMOGs

Molecular engineering approach

Serendipity is commonplace in LMOG research. Most of the gelators are obtained by accident and thereafter, new gelators are developed by modifying the molecular structure of the parent gelator molecule. This approach is applicable only in such subclasses of molecules. One of the early examples is 3-β-cholesteryl-4-(2-anthryloxy)butanoate (**CAB**).



About two decades ago, Weiss and Lin serendipitously discovered the gelling ability of **CAB**.[13] Following a 'molecular engineering' approach, the influence of the three structural components (aromatic–linker–steroid (**ALS**)) on the gelation ability was investigated (Chart 2).

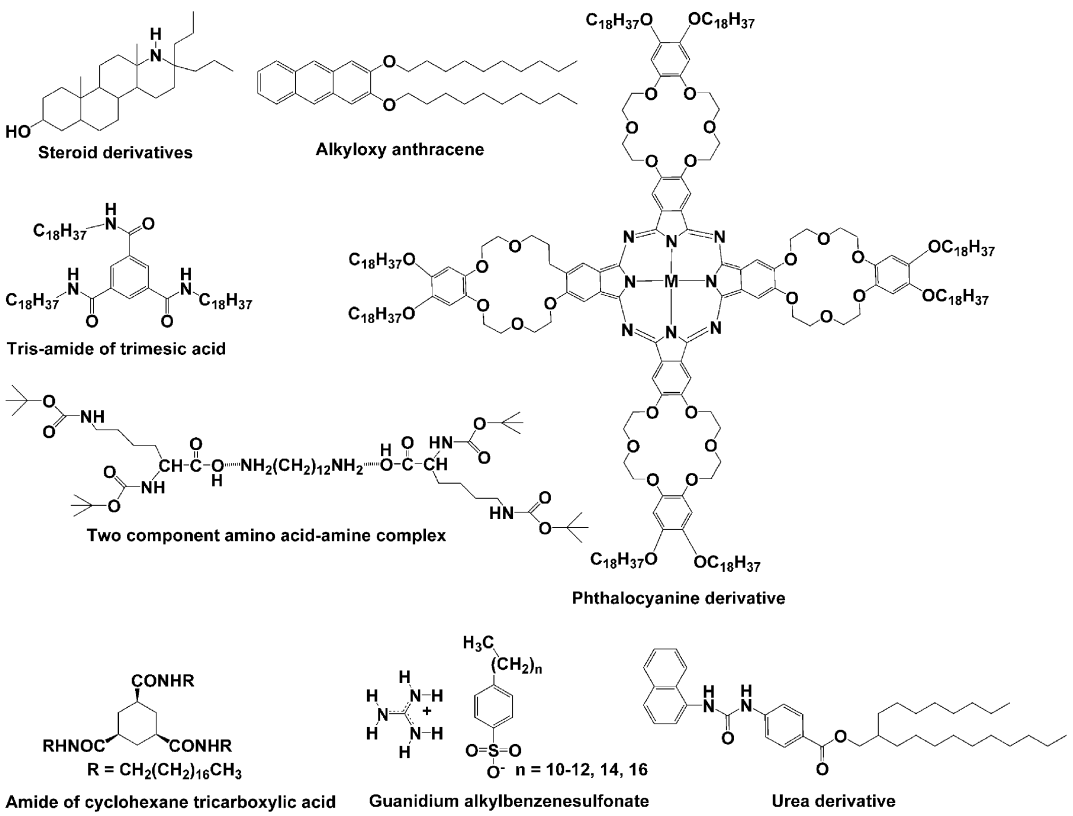


Chart 1 Various types of molecules known to act as LMOGs.

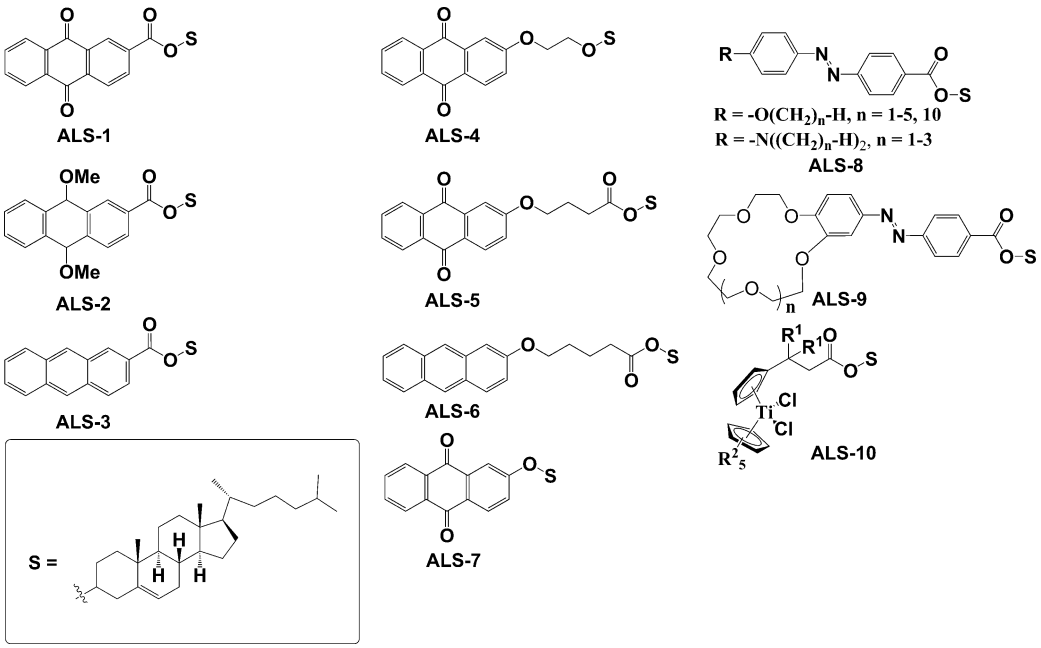


Chart 2 Various **ALS** gelators.

Aromatic part **A** has a profound effect on the gelation ability of some **ALS** molecules. Making the **A** part more electron rich with steric bulk as in the case of **ALS-2** compared to its electron deficient and less sterically crowded counterpart (**ALS-1**) resulted in nongelation presumably due to less π–π stacking interactions. However, mixing a small amount of **ALS-2** with **ALS-1** resulted in a thixotropic gel with 1-octanol.[1b] Changing from linearly placed 2-anthryl moiety in **ALS-3** to phenanthryl, pyrenyl and 9-anthryl resulted in nongelators.[15] Similarly, **CAB** analogues truncated in the aromatic moiety (naphthyl, phenyl) are not gelators presumably due to less π–π stacking interactions.[14d] Ester, ether, amide, urea or carbamate functionalities are common **L** groups in **ALS** type gelators.[14–16] Odd and even numbers of methylene groups in the **L** part has a profound effect on gelation.[16a] Subtle changes in **S** lead to have marked effects on gelation.[15] The overall shape of the **ALS** molecule appears to be vital. For example, rod-like **ALS** molecules are more efficient gelators than their bent counterparts. Thus, α-anomers of *trans*-**ALS-8** are less efficient gelators than the β-anomers (more rod-like). Similarly, the *cis*-isomers of the azobenzene-**ALS** (**ALS-8** and **-9**) which could be obtained by photo-irradiation are not able to gel the liquids gelled by the *trans*-isomers.[14c] Thus, UV irradiation (light) could be used as a switch between gel and sol phases. Following this 'molecular engineering' approach, an organometallic gelator (**ALS-10**) has also been successfully designed.[17]

The important features that must be present in gelling agents are (i) strong and directional intermolecular interactions that promote supramolecular aggregates, (ii) ability to form intertwined aggregates and (iii) factors preventing neat crystallization of the gelling agents.[18] Thus, as a general strategy, hydrogen bonding functionalities and long alkyl chains were introduced in the target molecules as potential gelling agents. Secondary amides, which are capable of forming complementary hydrogen bonding, are quite often found in numerous gelling agents. Hanabusa *et al*. have developed many intriguing gelling agents based on amide functionalities. For example, Gelling agents **G1** and **G2** derived from a chiral diamine *trans*-1,2-cyclohexyldiamine contain both amide functionality for intermolecular hydrogen bonding and long alkyl chain for preventing neat crystallization. Both these gelling agents not only turned out to be excellent gelators of various organic fluids but also showed intriguing morphological features of the corresponding **SAFIN**s;[18] while the *R*,*R* isomer (**G1**) always showed right-handed helicity, the *S*,*S* isomer (**G2**) displayed left-handed helicity. Molecular modelling studies suggested that an extended molecular tape type of hydrogen bonded assembly (**HB-1**) was possible, which might be responsible for the chiral superstructure observed in TEM images of the **SAFIN**s (Fig. 1).

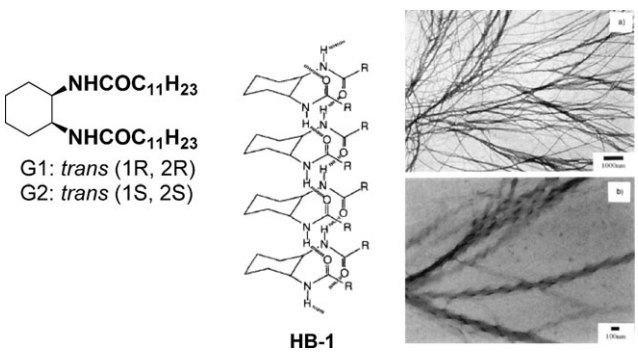


Fig. 1 *Left to right*: Amide based gelators **G1** and **G2**, their plausible hydrogen bonding assembly **HB-1** and TEM images of a loose **G1**-acetonitrile gel (1 mM **G1**) stained by osmic acid (magnification: (a) 7000×; (b) 30000×). Partly reproduced from ref. 18 with permission. Copyright 1996, Wiley-VCH Verlag GmbH & Co. KGaA.

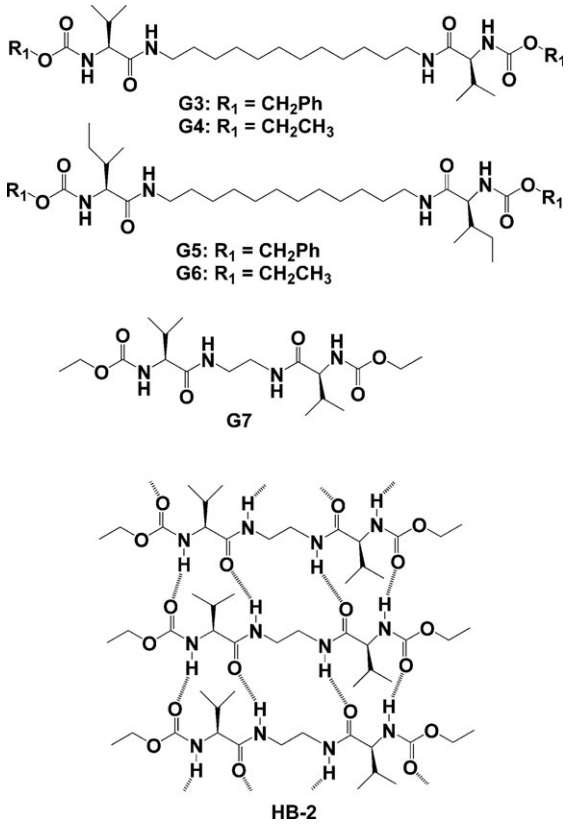


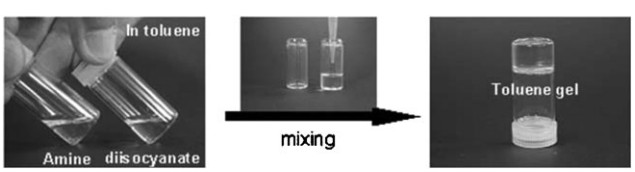
Chart 3 Amino acid derived bolaform amides studied for gelation.

Following a similar strategy, the same group reported[19] gelling agents based on bolaform amides derived from amino acids (**G3–G7**, Chart 3). It was proposed that the gelator molecule formed extended molecular sheets involving hydrogen bonding through urethane and amide groups (**HB-2**).

Heating gelator solutions to effect gelation is obviously disadvantageous for wide ranges of applications. Suzuki *et al*. avoided the heating process in gelation by generating the gelator *in situ* in gelling solvents (Scheme 1).[20]

They have developed bis- and tris-urea based gelators (**G8–G14**, Chart 4) generated *in situ* by reacting the corresponding isocyanates and amines in the targeted solvents (Scheme 2). Extended hydrogen bonding among the urea moieties and van der Waals interactions among the long alkyl chains were proposed to be responsible for the **SAFIN**s and gel formation.

Bommel, Esch and co-workers reported a series of LMOGs (**G15–G18**) capable of gelling water (hydrogel).[21] The design was based on amide derivatives of cyclohexane; the cyclohexane moiety was used as a generic gelating scaffold wherein various important moieties (such as hydrophobic



Scheme 1 Typical procedure of *in situ* gelation. Reproduced from ref. 20 with permission. Copyright 2004, Royal Society of Chemistry.

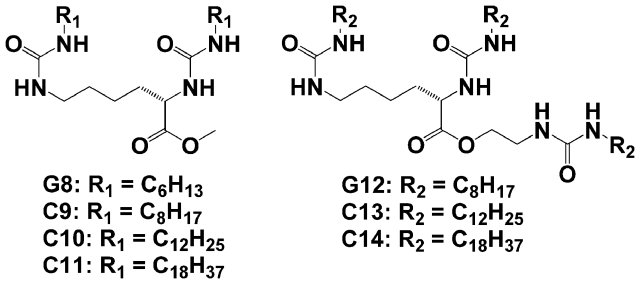
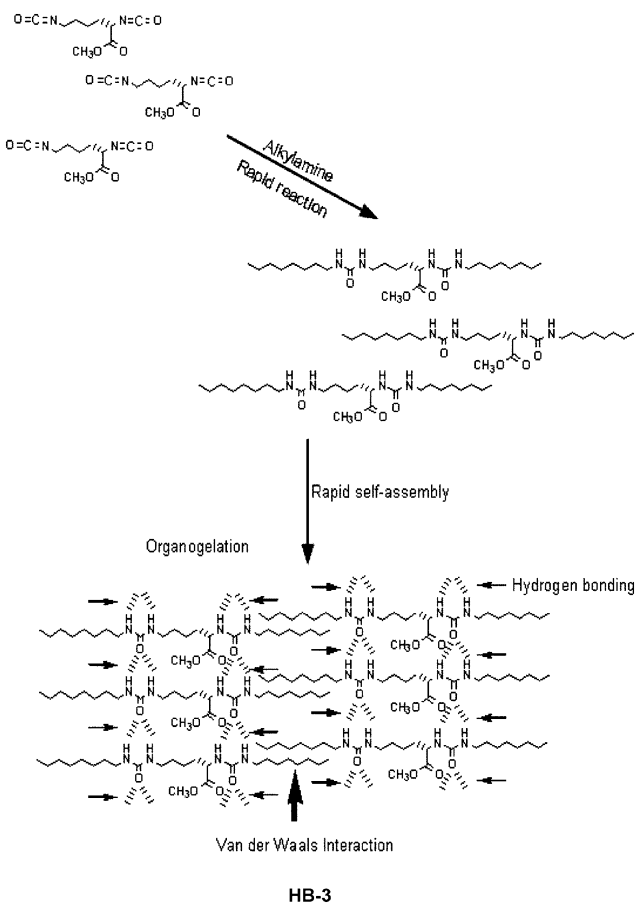


Chart 4 Bis- and tris-urea based gelling agents studied for *in situ* gelation.



Scheme 2 *In situ* gelator synthesis and its plausible aggregation mode. Reproduced from ref. 20 with permission. Copyright 2004, Royal Society of Chemistry.

(hydrophobic amino acids), hydrophilic (acid, ether alcohol, imidazole) thought to promote hydrogelation) was introduced. Hydrophobic amino acid moieties were deliberately used to prevent the interactions of the amide functionalities with water so that they can form highly directional hydrogen bonding interactions among themselves resulting in the formation of a 1D network. The single-crystal structure of a tyrosine-based nongelating model compound revealed the presence of a 1D hydrogen bonded network *via* amide functionality (Fig. 2).

Highly directional hydrogen bonding interactions *via* the urea moiety has been exploited in generating microcellular materials[22] derived from mono- and bis-urea derivatives (for

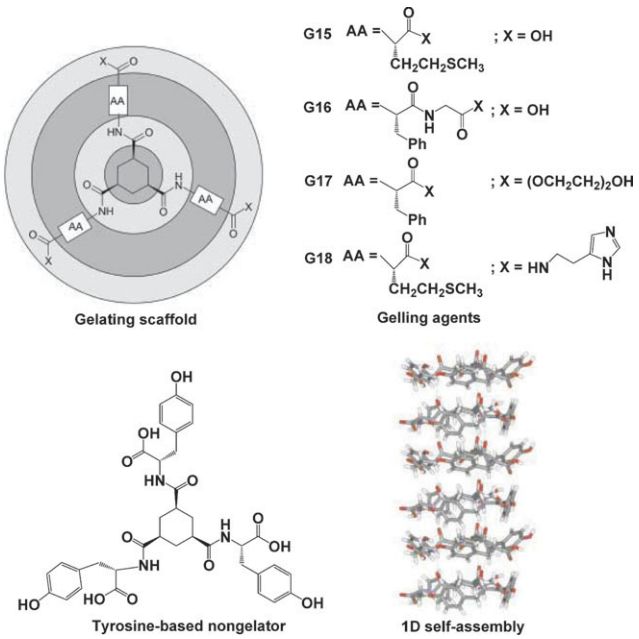


Fig. 2 Upper panel – *left*: schematic representation of the generic gelating scaffold (dark and light grey regions are hydrophobic and hydrophilic respectively); *right*: gelators **G15–G18**; lower panel – *left*: tyrosine-based model nongelator; right: 1D self-assembly in the single-crystal structure of the model nongelator. Reproduced in part from ref. 21 with permission. Copyright 2004, Wiley-VCH Verlag GmbH & Co. KGaA.

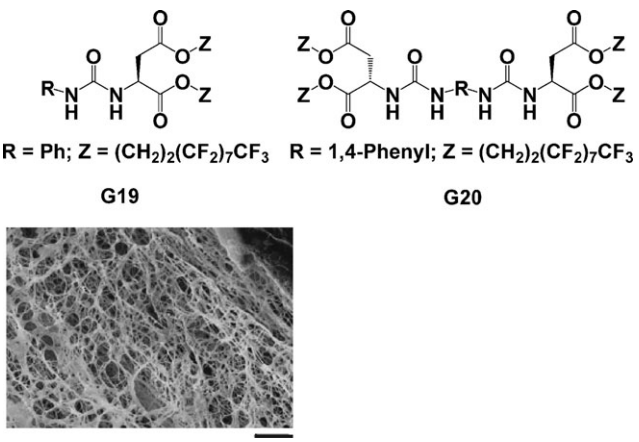


Fig. 3 *Top*: Gelling agents **G19** and **G20** capable of gelling supercritical CO_2; *bottom*: SEM image of the foam produced by **G19** (bar 5 μm). Reproduced in part from ref. 22 with permission, Copyright 1999, AAAS.

example **G19** and **G20**, Fig. 3) having terminal perfluoroalkane groups; while the urea moiety was expected to provide 1D self-assembly *via* hydrogen bonding, the terminal perfluoroalkane groups assured solubility in supercritical CO_2; as a result, these molecules were capable of forming gels with supercritical CO_2 which resulted in microcellular materials simply by the removal of CO_2 (Fig. 3).

Hydrogen bonding involving urea is further reinforced in some geminal bis-urea derivatives (**G21–G27**, Chart 5) having

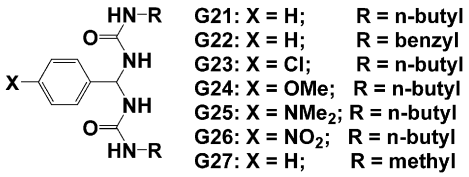


Chart 5 Geminal bis-urea derivatives as gelling agents.

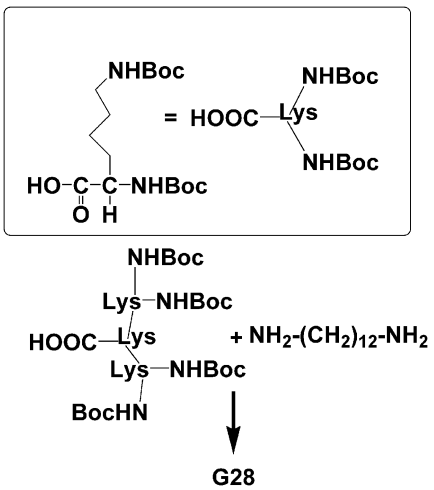


Chart 6 A two-component dendritic gelator.

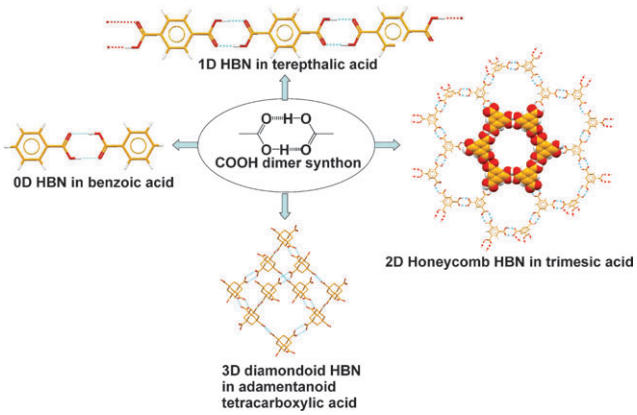
terminal alkyl chains which were found to be excellent gelators of various organic fluids.[23]

The first two-component dendritic gelator (**G28**, Chart 6) reported by Smith and co-workers[24] is comprised of a dendritic part derived from the amino acid lysine and a linear aliphatic diamine. The gelling ability depended heavily on the molar ratio of the gelator components. Any concentration below 1 : 2 (diamine : dendritic component) resulted in difficult gelation. Branching of the dendritic component was also found to be important for gelation. Acid–base hydrogen bonding interactions between the diamines and the COOH moiety of the dendritic part appeared to be crucial for gelation. Smith's group, including others, developed various other dendritic gelators.[25]

Crystal engineering approach

Crystal engineering[26]—a sub-discipline of supramolecular chemistry[27] deals with "the understanding of intermolecular interactions in the context of crystal packing and in the utilization of such understanding in the design of new solids with desired physical and chemical properties."[28] In crystal engineering, it is important to identify supramolecular synthons[28]—spatial arrangements of intermolecular interactions—that are robust enough to ensure generality and predictability of the resulting crystalline solid. The concept of a supramolecular synthon is illustrated with the example of the COOH dimer synthon in Scheme 3.

The frequently occurring COOH dimer hydrogen bonded network (**HBN**) was found to be the key interaction in the zero-dimensional (0D) dimer in benzoic acid,[29] 1D **HBN** in terephthalic acid,[30] two-dimensional (2D) honeycomb **HBN** in



Scheme 3 Illustration of the COOH dimer supramolecular synthon and its application in crystal engineering.

trimesic acid[31] and three-dimensional (3D) diamondoid **HBN** in adamentanoid tetracarboxylic acid.[32] Thus, by exploiting appropriate supramolecular synthons, it might be possible to generate solid-state structures (crystal structures) with some degree of predictability. The concept of supramolecular synthons may be exploited to design new gelling agents which will be unfolded in the following sections. It is beyond the scope of this review to discuss various aspects of crystal engineering with specific examples. Further information on this subject may be obtained from some excellent reviews[26,28] and references cited therein.

Determination of molecular packing within gel fibers

SAFINs that can often be seen by various microscopic techniques do have definite crystal structure (in most of the cases) as evident from the corresponding X-ray powder diffraction (XRPD) patterns. Thus elucidation of crystal structure of **SAFIN**s in native (gel) form would help understand various non-bonded supramolecular interactions responsible for self-assembly of gelator molecules in the gel state which would eventually lead to designing of gelators. Thus, obtaining molecular level information about the various nonbonded interactions (supramolecular synthon) responsible for **SAFIN** formation is indispensable for gelator design. However, it is virtually impossible to determine the single-crystal structure of a gel fiber because single crystals of a gel fiber are too small for diffraction measurements. Weiss and co-workers reported for the first time an interesting methodology to discern packing of molecules within gel fibers.[33] In this method, the XRPD of the gel fibers in its native state is compared with the simulated pattern obtained from its single-crystal data. An excellent match of these XRPDs indirectly determines the molecular packing within gel fibers. To get a simulated XRPD, the single-crystal structure of the gelator is a must. However, growing single crystals of a gelator molecule is extremely difficult and also, recording good quality XRPD data of the gel fibers in the native form (gel) generally suffers from the scattering contribution of the solvent molecules and less crystalline nature of the gel fibers and therefore, in most cases, attempts to record XRPD of gel fibers turn out to be a major disappointment. The other possibility of solving the single-crystal structure of gel fibers *ab initio* from its polycrystalline XRPD data is not routine yet and requires sophisticated and not-so-accessible synchrotron beam line.[34]

Structure–property correlation

Since **SAFIN**s are made of 1D fibers (in most cases) with very high aspect ratio, it is reasonable to believe that there must be some anisotropic interactions of the gelator molecules that allows growth in one direction and lack of such interactions in other two dimensions prevents lateral growth resulting in 1D fibers. Thus, if a molecule has self-complementary, reasonably strong and directional hydrogen bonding site(s) so that it can self-assemble in one direction, it is quite possible that such a molecule would grow as fibers with high aspect ratio under suitable condition. The tendency for the molecules to grow as 1D fibers may favor **SAFIN** formation resulting in a gel. Thus, it is logical to correlate supramolecular self-assembly patterns of a molecule obtained from its single-crystal data with its gelling/nongelling behaviour.

Structure–property correlation in sugar based gelators

Shinkai and co-workers attempted a structure–property correlation by comparing the single-crystal structures of few structurally isomeric sugar molecules **G29–NG32** (Chart 7) among which only **G29** is a gelator.[35]

Single-crystal structures displayed 1D hydrogen bonded networks in both **G29** and **NG30**; while a 1D network in **G29** is sustained by two intermolecular hydrogen bonding involving two OH groups, only one intermolecular hydrogen bonding involving an OH group is responsible for the network in **NG30**. Thus, it was argued that more intermolecular hydrogen bonding contributes to the stability of the 1D network in **G29** compared to that in **NG30** resulting in gel formation by the former. On the other hand, **NG31** and **NG32** showed 2D and 0D hydrogen bonding networks, respectively, thereby being unable to produce 1D fibers so resulting in nongelators (Fig. 4).

The question may, however, arise that the crystal structures of the neat gelator and the gel fibers in native (gel) state need not necessarily be identical and therefore, such a correlation between the neat crystal structure and gelation ability may not be that relevant. However, it is not uncommon to find different crystal structures having identical primary supramolecular interactions (in the present context, the anisotropic self-complementary hydrogen bonding interactions).

Thus, the role of anisotropic interactions cannot be ruled out in **SAFIN** formation. The fact that all the molecules having

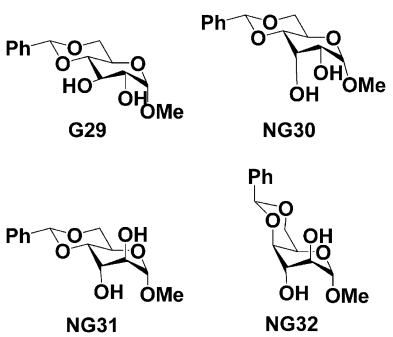


Chart 7 Isomeric sugar molecules studied for gelation.

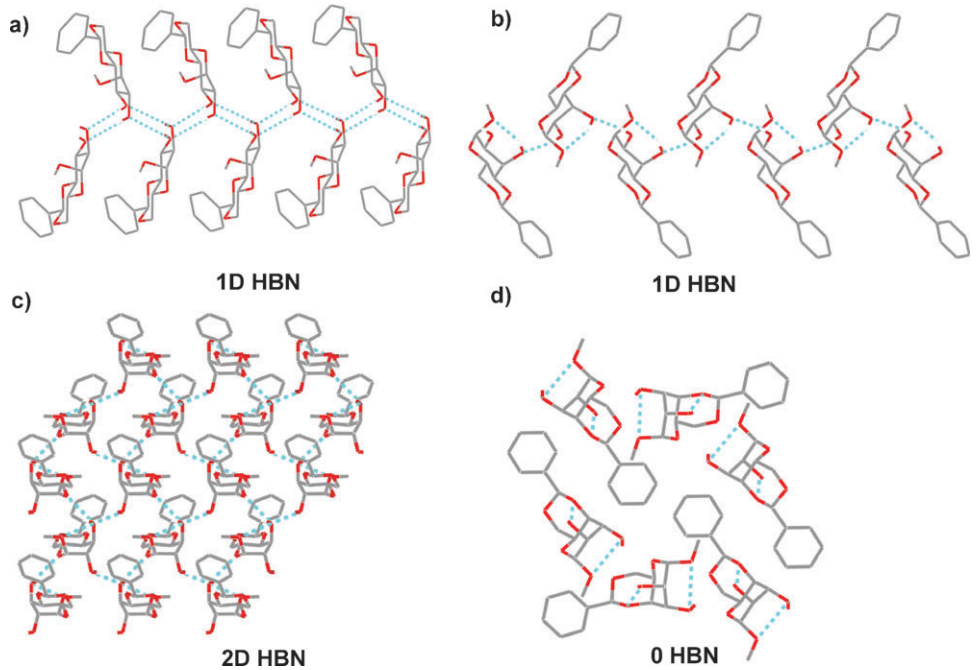


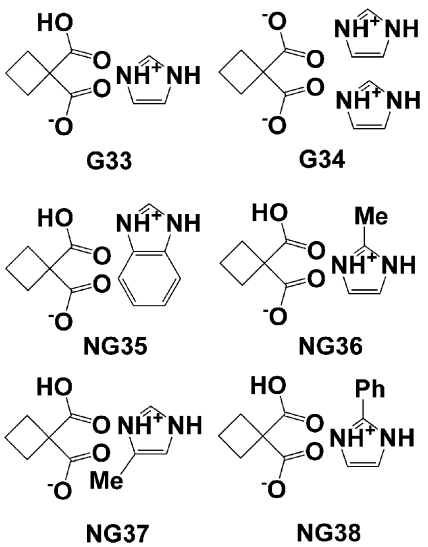
Fig. 4 Hydrogen bonding network in the crystal structures of (a) **G29**, (b) **NG30**, (c) **NG31** and (d) **NG32**. Figures are generated using CIF files retrieved from CSD 5.28, November 2006.

such anisotropic interactions do not display gelation ability and a gelator cannot gel all possible solvents clearly indicates the importance of other factors yet to be understood completely. Thus, the requirement for a molecule to self-assemble in one direction in order to be a gelator is an *indispensable* rather than a *sufficient* condition. The importance of being one-dimensional in gelation was also pointed out by Hanabusa *et al.*[36] and by Esch and Ferringa.[37] A working hypothesis that a 1D hydrogen bonded network favours **SAFIN** and thus, gel formation, can become quite handy in designing LMOGs. Direct correlation between single-crystal structures of molecules and their gelling/nongelling properties must be established in as many examples as possible before it can be accepted as a reasonable basis for designing new gelators. However, efforts with such a focus are indeed limited. This could be because of the difficulty in getting X-ray quality single crystals of gelators.

Structure–property correlation in organic salt based gelators imidazolium cyclobutane carboxylate salts

While working on the crystal engineering aspects of organic salt based compounds,[38] attempts were being made to get single crystals of a salt, namely imidazolium hydrogen cyclobutane-1,1-dicarboxylate **G33** (Scheme 4).

One such attempt to crystallize **G33** from nitrobenzene solvent resulted in a gel.[39] Optical micrographs of the gel and SEM of the xerogel of **G33** in nitrobenzene clearly displayed the presence of several micrometer long entangled fibers (Fig. 5). Interestingly, salt **G34** produced a weak and unstable gel with nitrobenzene and its SEM of xerogel was also quite different from that seen in the xerogel of **G33** (Fig. 5c). These results suggested that free COOH was important for gelation. It was also observed that the 1 : 1 acid–base salt of cyclobutane-1,1-dicarboxylic acid generated



Scheme 4 Imidazolium salts studied for gelation.

from other derivatives of imidazole did not produce a gel (Scheme 4).

While gelator **G33**[39] showed a 3D **HBN**, both the non-gelators **NG35**[39] and **NG38**[40] displayed a 2D **HBN** (Fig. 6) in their single-crystal structures. Detailed X-ray powder diffraction (XRPD) studies revealed that the crystalline morph of the gel fibers in its native environment (gel form) was different from that present in the neat crystal, bulk solid and xerogel (Fig. 7).

A closer look at the single-crystal structure of **G33** revealed the presence of 1D primary supramolecular **HBN** comprised of alternating cations and anions held by hydrogen bonding interactions involving imidazole N–H and COO^- (Fig. 6(a))

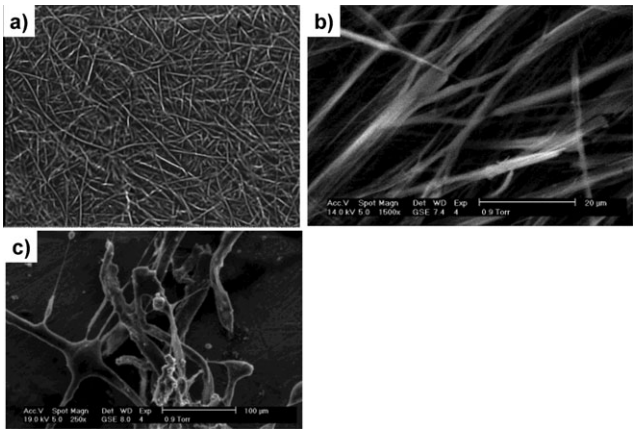


Fig. 5 (a) Optical micrograph (400×) of the gel of **G33** (in nitrobenzene); SEM images of the xerogels of (b) **G33** (1 wt%, nitrobenzene), (c) **G34** (nitrobenzene). Adapted from ref. 39 with permission. Copyright 2003, American Chemical Society.

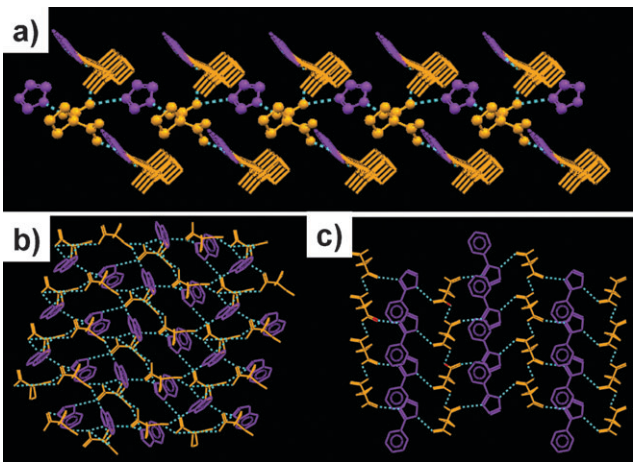


Fig. 6 Crystal structure illustrations; (a) 3D **HBN** in **G33**; 1D primary supramolecular **HBN** involving alternating acid and imidazole moieties are depicted in a ball-and-stick model; 2D **HBN** in (b) nongelators **NG35** and (c) **NG38**; orange = carboxylate; purple = imidazolium. Figures are generated using crystallographic coordinates retrieved from CSD 5.28, November 2006.

whose presence could not be ruled out in the gelled state. It was, therefore, reasonable to assume that the 1D primary supramolecular network was responsible for the **SAFIN** formation and free COOH might have played an important role in establishing the 'junction zone'[41] to effect gelation.

Supramolecular synthons that ensure 1D hydrogen bonded network formation in organic salts

This accidental discovery of imidazolium carboxylate salt based gelators (see above) led to the realization that organic salt based gelators have a number of advantages; (a) organic salt formation is probably the easiest reaction to carry out in chemistry; just mixing acid and base would result in the corresponding salt with quantitative or near quantitative yield in most cases; thus within a short period of time many salts can be prepared and screened for gelation behavior, (b) while the energy of normal hydrogen bond is within the range of

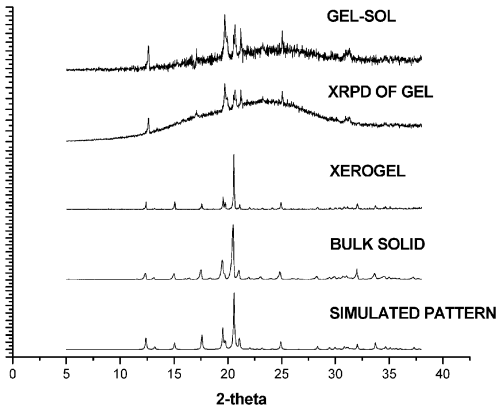


Fig. 7 XRPD patterns of gelator **G33** under various conditions; XRPD pattern GEL-SOL was obtained by subtracting the XRPD of the gel and the diffraction pattern of the neat solvent. Reprinted from ref. 39 with permission. Copyright 2003, American Chemical Society.

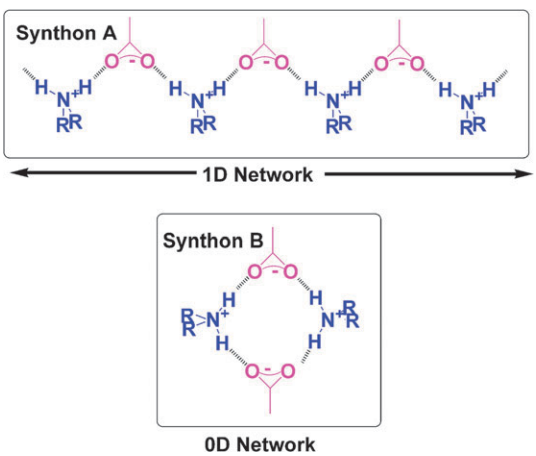
10–65 kJ mol^{-1}, the charge assisted hydrogen bond has energy within 40–190 kJ mol^{-1} which often surpasses some covalent bonds (146–563 kJ mol^{-1});[42] thus, charge assisted hydrogen bonds as in the case of organic salts are stronger and also directional making the product more robust which is often a criterion for real-life applications, (c) the commercial availability of a virtually infinite number of acids and bases opens up an opportunity to explore a combinatorial library approach in the quest for new LMOGs.

Secondary ammonium monocarboxylate (SAM) synthon

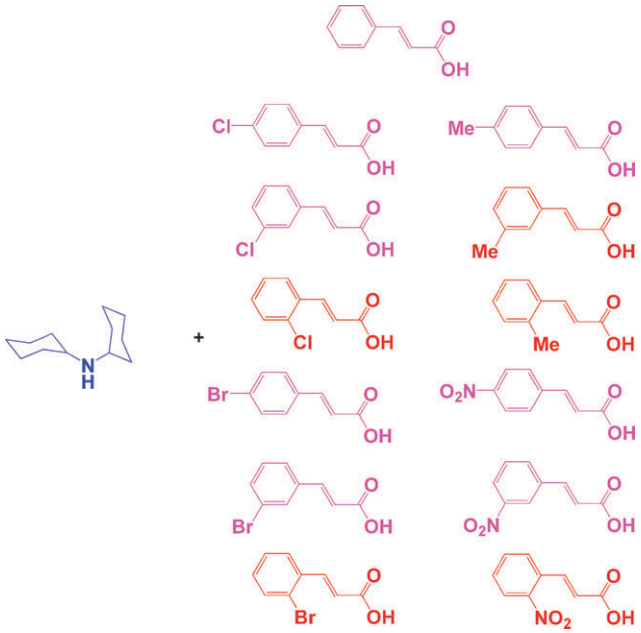
The ion pairs in secondary ammonium monocarboxylate (**SAM**) salts can display two types of supramolecular synthons as depicted in Scheme 5.[43] While synthon A is 1D, synthon B is discrete or 0D.

Thus, a series of **SAM** salt derived from variously substituted cinnamic acid and dicyclohexylamine was screened (Scheme 6)[44] for gelation behavior owing to the possibility of having 1D supramolecular synthon A and consequently gelation.

Substitution at the 2-position of cinnamate moiety resulted in nongelators whereas most of the 4- and 3-substituted cinnamate salts (except 3-methylcinnamate) displayed excellent



Scheme 5 Two types of plausible **HBN** in **SAM** salt.



Scheme 6 Salts of pink and red acids are gelators and nongelators, respectively.

gelation abilities (Scheme 6). Interestingly, the 4-chloro salt displayed novel selective gelation of petrol from a petrol/water mixture[44a,b] (Fig. 8) suggesting a possible application in oil spill problems.[45]

Dicyclohexylammonium cinnamate salt itself was able to gel only 5 out of 29 solvents tested for gelation indicating the importance of the position of substituents in gelation process. On the other hand, the corresponding dicyclohexylammonium salts of hydrocinnamic and benzoic acids were nongelators indicating the influence of the unsaturated backbone on the gelation behavior (Scheme 7).[44]

Single-crystal structures of six gelators displayed synthon A (Fig. 9) whereas 16 nongelators showed either 2D or 0D (synthon B) networks (Fig. 10). These results clearly and most explicitly demonstrated the importance of 1D **HBN** in gelation process.[44b]

XRPD studies revealed that the gel fibers in the xerogel state of most of the gelators had identical crystalline morph with that of the bulk solid as well as the neat crystals (Fig. 11). Interestingly, SEM of the xerogels revealed the presence of fibers having high aspect ratio, often branched and entangled

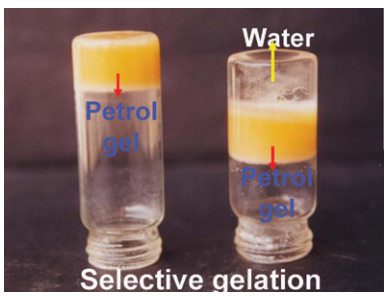
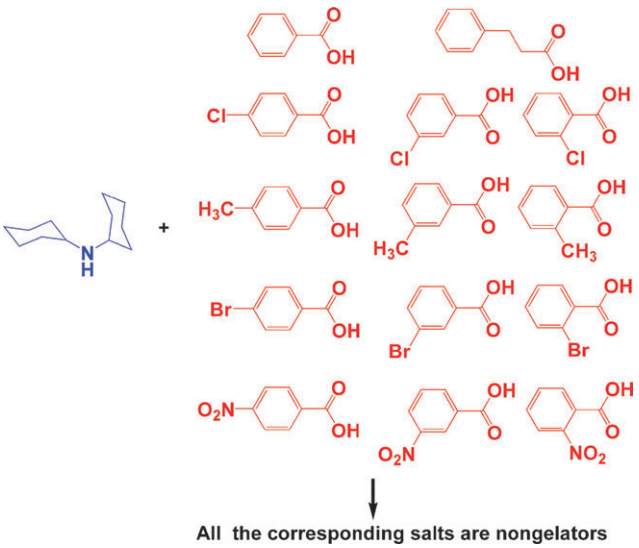


Fig. 8 Selective gelation of petrol by dicyclohexylammonium 4-chlorocinnamate.



Scheme 7 Hydrocinnamate and various benzoate salts as nongelators.

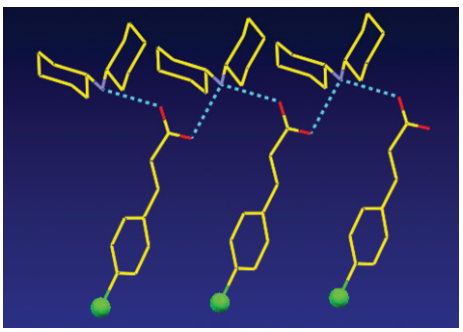


Fig. 9 1D **HBN** (synthon A) found in the single-crystal structures of the gelator salt dicyclohexylammonium 4-chlorocinnamate (Scheme 6). The figure is generated using crystallographic coordinates retrieved from CSD 5.28, November 2006.

to form a 3D fibrilar network within which the solvent molecules were immobilized to form a gel (Fig. 12).

Conformationally more flexible aromatic analogue of dicyclohexylammonium cation, namely dibenzylammonium cation, appeared to have a profound effect on the hydrogen bonding network and consequently gelation in a series of dibenzylammonium salts of cinnamic and benzoic acids (Scheme 8).[46] Out of 27 salts prepared, 9 cinnamates and 10 benzoate salts were moderate to good organo-gelators.

All the salts (6 cinnamates—**2-ClCIN**, **2-BrCIN**, **4-**, **3-**, **2-MeCIN**, **3-NitCIN**; 12 benzoates—**4-**, **3-** and **2-ClBEN**, **4-**, **3-** and **2-BrBEN**, **4-** and **3-MeBEN**, **4-**, **3-** and **2-NitBEN**, **BEN** as listed in Scheme 8) for which single-crystal structures could be determined showed a 1D **HBN** (synthon A) (Fig. 13) except for **2-ClCIN** wherein a solvate water molecule participated in the **HBN** resulting in a different supramolecular architecture; 12 of them (3 cinnamate and 9 benzoate) were gelators, emphasizing the importance of a 1D **HBN** for gel formation. It is interesting to note that all the dicyclohexylammonium benzoate salts displayed synthon B and were nongelators (see above)[44b] whereas the dibenzylammonium benzoate salts displayed 1D **HBN** and many of them were

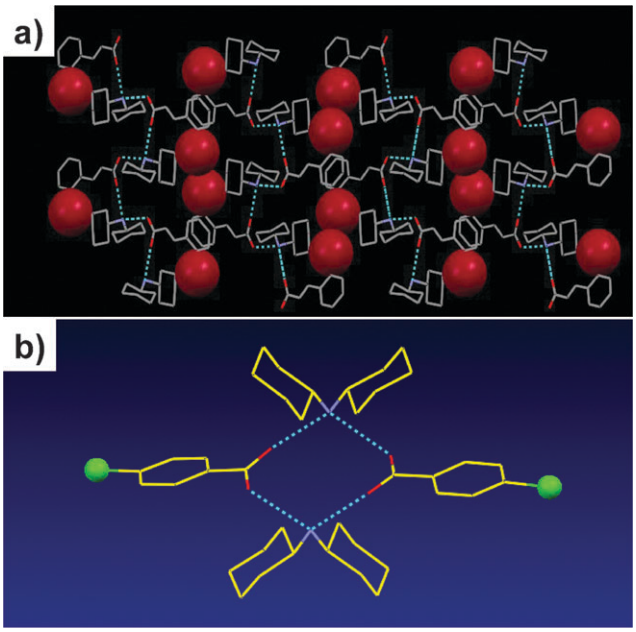


Fig. 10 (a) 2D network in dicyclohexylammonium 2-bromocinnamate salt (Scheme 6); (b) 0D (synthon B) observed in dicyclohexylammonium 4-chlorobenzoate (Scheme 7). Figures are generated using crystallographic coordinates retrieved from CSD 5.28, November 2006.

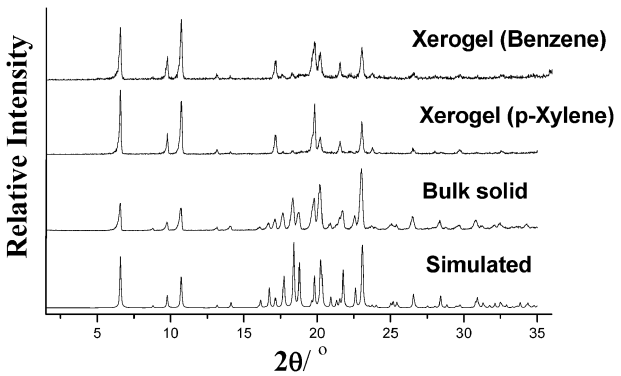


Fig. 11 XRPD patterns under various conditions for the gelator salt dicyclohexylammonium 4-nitrocinnamate (Scheme 6). Reprinted from ref. 44*c* with permission. Copyright 2005, The Royal Society of Chemistry.

gelators. Thus, by changing the cation from dicyclohexylammonium to dibenzylammonium, a hydrogen bond isomerism could be imposed to obtain 1D **HBN** in benzoate salts, which appeared to have direct influence on their gelling properties. Influence of weaker interactions such as C–H$\cdots\pi$[47] was attributed as one of the contributing factors of such a dramatic shift of supramolecular architecture.

Long chain alkyl groups that self-assemble *via* van der Waals interactions as observed in many hierarchical structures such as micelles,[48] vesicles[49] *etc*. were found to influence the hydrogen bonded network in SAM salts derived from dicyclohexylamine and alkyl monocarboxylic acids (Scheme 9).[50]

Single-crystal structural analyses of 9 out of 17 salts studied revealed interesting structural features; salts having n = 1–4, 6, 8–9 displayed synthon B (OD) whereas with sufficiently longer alkyl chain length (n = 14–15), synthon A (1D) was observed.

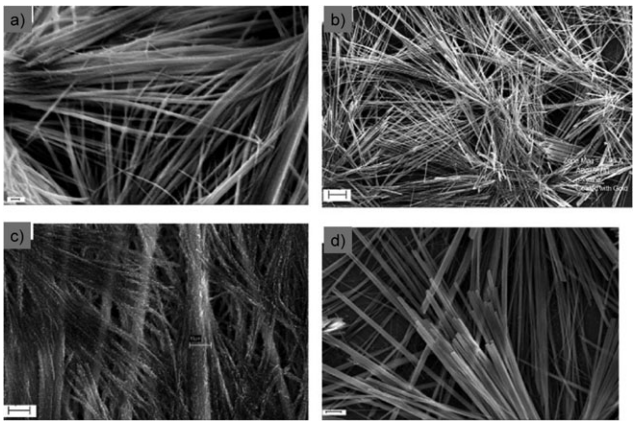


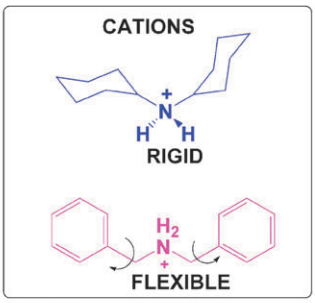
Fig. 12 SEM of the xerogel of the gelators listed in Scheme 6; (a) 4-bromocinnamate/*p*-xylene (2.5 wt%), bar = 2 mm, (b) 3-bromocinnamate/*p*-xylene (2.5 wt%), bar = 100 mm, (c) 4-methylcinnamate/nitrobenzene (2.5 wt%), bar = 10 mm and (d) cinnamate/cyclohexane (1.3 wt%), bar = 10 mm. Reprinted from ref. 44*b* with permission. Copyright 2004, Wiley-VCH Verlag GmbH & Co. KGaA.

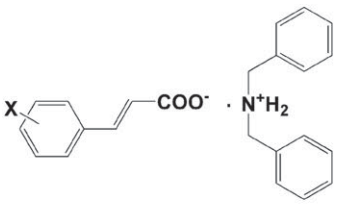
It was clearly observed that because of the long alkyl–alkyl chain interactions, synthon A was stabilized in salts having longer alkyl chain (n = 14–15) (Fig. 14). Based on the resemblance of XRPD patterns, it was concluded that salts with n = 10 onwards up to n = 17 most probably had similar supramolecular architecture *i.e*. synthon A (Fig. 15). Unfortunately none of these salts showed any gelation properties with the solvents studied. These results emphasized the importance of solvent–network interactions compatibilities for gel formation. However, upon changing the cation from dicyclohexylammonium to dibenzylammonium in salt (n = 15), it was possible to impart gelation with nitrobenzene as well as diesel. The gel fibers in the xerogel state were found to be of various morphologies (Fig. 16).

Secondary ammonium dicarboxylate (SAD) synthon: ascertaining the 1D HBN

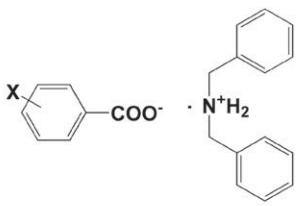
1D hydrogen bonded networks can be envisaged in secondary ammonium dicarboxylate (SAD) salts wherein synthon B is propagated in one dimension virtually due to the presence of two COO^- moieties (Scheme 10); A series of SAD salts (Scheme 11)[51] derived from dicarboxylic acids having either linear or angular functional topology, and dicyclohexylamine displayed 1D **HBN** as envisaged in Scheme 10 (Fig. 17).

However, none were found to be gelators. Interestingly, when the concept was applied to **SAD** salts derived from cyclobutane-1,1-dicarboxylic acid, dicyclohexylamine and dibenzylamine, a new class of gelator was discovered.[52] The **SAD** synthon has also been exploited to get an easy access to an organometallic supramolecular gelling agent, namely dicyclohexylammonium ferrocene-1,1′-dicarboxylate, the single-crystal structure of which displayed a 1D SAD synthon as envisaged in Scheme 10.[53]

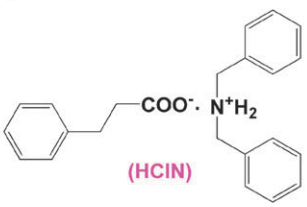




(4-ClCIN), X = 4-Cl; (3-ClCIN), X = 3-Cl;
(2-ClCIN), X = 2-Cl (4-BrCIN), X = 4-Br;
(3-BrCIN), X = 3-Br; (2-BrCIN), X = 2-Br
(4-MeCIN), X = 4-Me; (3-MeCIN), X = 3-Me;
(2-MeCIN), X = 2-Me, (4-NitCIN), X = 4-NO_2;
(3-NitCIN), X = 3-NO_2; (2-NitCIN), X = 2-NO_2,
(CIN), X = H



(4-ClBEN), X = 4-Cl; (3-ClBEN), X = 3-Cl;
(2-ClBEN), X = 2-Cl; (4-BrBEN), X = 4-Br;
(3-BrBEN), X = 3-Br; (2-BrBEN), X = 2-Br;
(4-MeBEN), X = 4-Me; (3-MeBEN), X= 3-Me;
(2-MeBEN), X = 2-Me; (4-NitBEN), X = 4-NO_2;
(3-NitBEN), X = 3-NO_2; (2-NitBEN), X = 2-NO_2;
(BEN), X = H



Scheme 8 Dibenzyl salts studied for gelation. Salts in pink and red are gelators and nongelators, respectively.

Primary ammonium monocarboxylate (PAM) synthon

Primary ammonium monocarboxylate (PAM) salts display 1D columnar **HBN** in the majority of the cases; it also shows 2D hydrogen bonded sheet type structure (Scheme 12) only in few examples. PAM salts are, therefore, expected to display 1D columnar network in a majority of cases and could be potential LMOGs.

Studies on a series of PAM salts derived from various cinnamic acids and benzylamine gave intriguing results; 8 salts out of 14 (Scheme 13) prepared showed gelation abilities.[54] Single-crystal structures of 6 gelators (**3-ClCIN**, **3-BrCIN**, **4-** and **3-MeCIN**, **3-NitCIN** and **CIN**) and 2 nongelators (**2-BrCIN** and **2-MeCIN**) as listed in Scheme 13 displayed

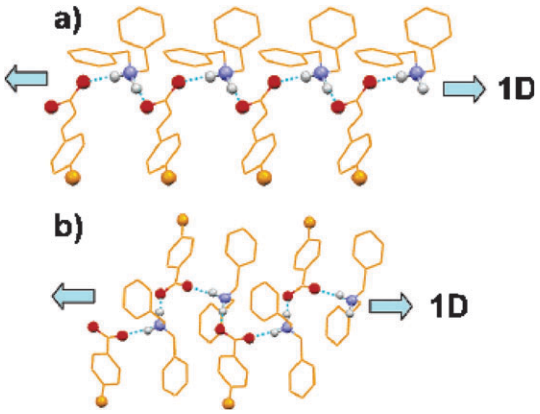
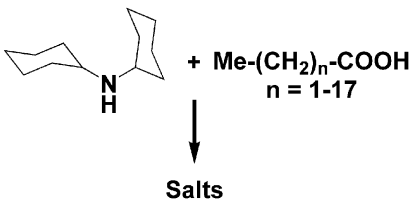


Fig. 13 1D **HBN**s in (a) **4-MeCIN** and (b) **4-MeBEN** as listed in Scheme 8. Reprinted from ref. 46 with permission. Copyright 2006, American Chemical Society.



Scheme 9 **SAM** salts derived from *n*-alkyl acid of varying chain length studied for gelation.

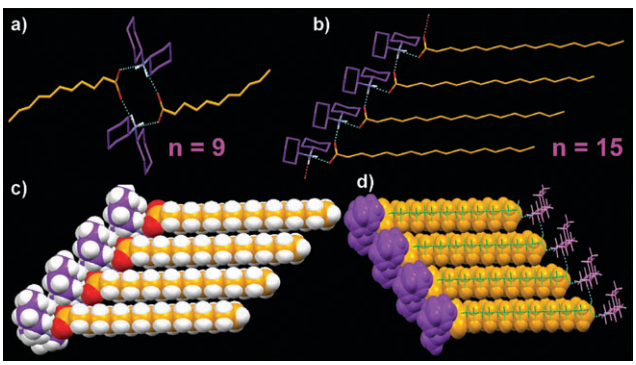


Fig. 14 (a) Synthon B or 0D **HBN** in salt with $n = 9$ (Scheme 9); (b) Synthon A or 1D **HBN** in salt with $n = 15$; (c) space-filling model of 1D **HBN** in salt with $n = 15$ depicting long alkyl–alkyl chain interactions; (d) long alkyl–alkyl chain interactions further reinforced as a result of layered packing in the crystal structure of salt with $n = 15$ as listed in Scheme 9. Figures are generated using crystallographic coordinates retrieved from CSD 5.28, November 2006.

1D columnar **HBN** having different supramolecular connectivities (Fig. 18) emphasizing once again the role of 1D **HBN** in gel formation.

The most intriguing event was the sound induced instant gelation of petrol and other solvents by the salt **CIN** (Scheme 13). Instant gelation[20,55] is important in real-life material applications since in this process what is avoided is the heating which is understandably one of the main impediments in real-life applications such as in an oil spill in the present case. It is also quite interesting to note that **CIN** is not able to gel petrol by following the usual heating–cooling

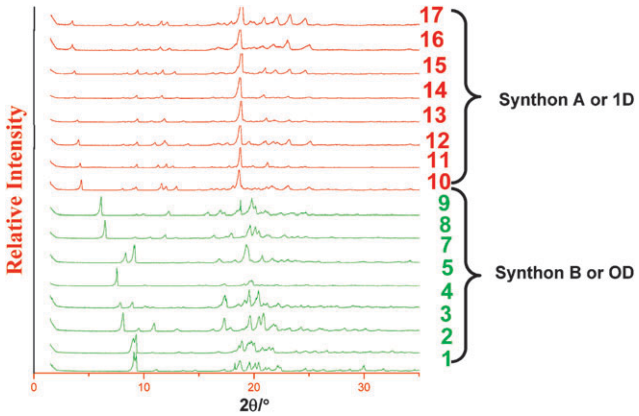


Fig. 15 XRPDs of salts having n = 1–17 (Scheme 9); remarkable resemblance of the XRPDs of salts with n = 10–13, 16 and 17 with those of salts having n = 14 and 15 can be recognized. XRPDs of salts having n = 1–9 are distinctly different from those of salts having $n > 9$; the XRPD of salt having n = 6 could not be recorded due to its semi-solid nature. Adapted from ref. 50 with permission. Copyright 2006, American Chemical Society.

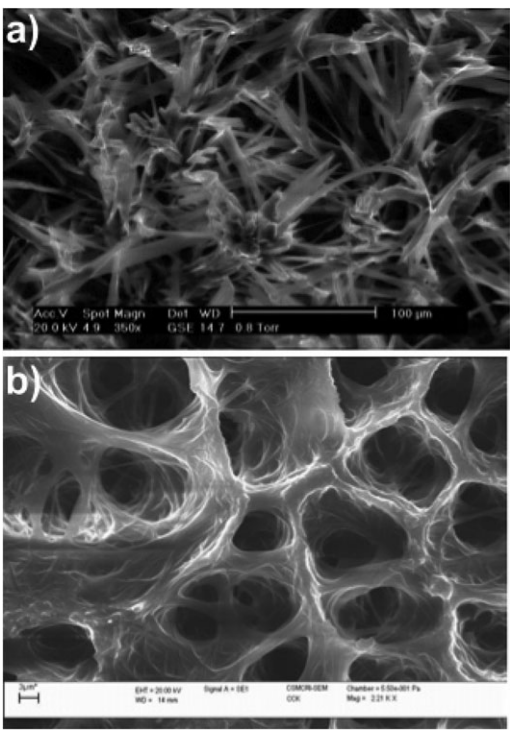
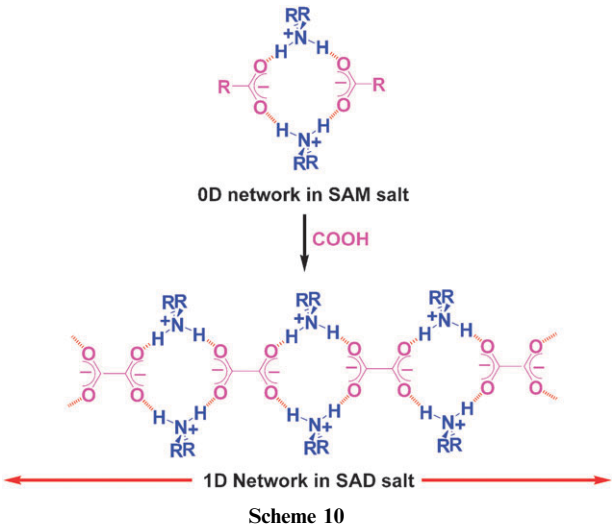


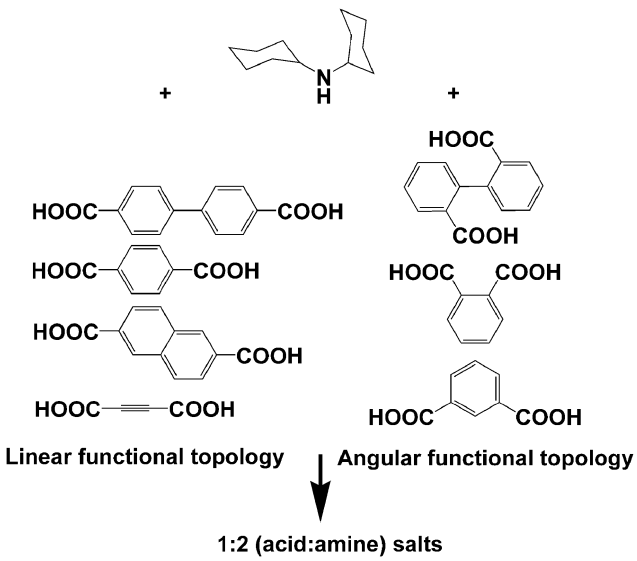
Fig. 16 SEM picture of the xerogel of dibenzylammonium salt with n = 15 (Scheme 9) derived from (a) nitrobenzene solvent (bar 100 μm) and (b) diesel (bar 3 μm). Reprinted from ref. 50 with permission. Copyright 2006, American Chemical Society.

process (conventional way). Detailed XRPD studies on a benzene gel of **CIN** revealed that the crystalline morph of the gel fibers of xerogel obtained by instant gelation is identical with that of the bulk solid and neat crystal structure of **CIN** whereas the xerogel fibers obtained by the conventional gelation showed different crystalline morph (Fig. 19).

The difference was also evident from the corresponding SEM micrographs of the xerogels (Fig. 20).



Scheme 10



Scheme 11 SAD salts studied for gelation.

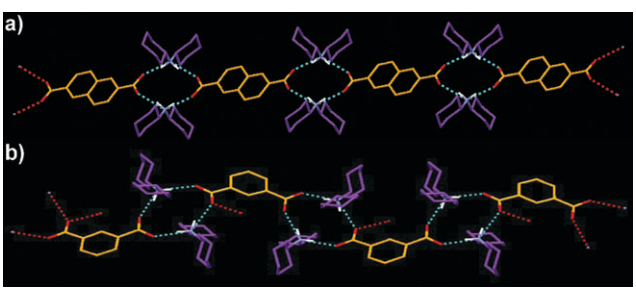
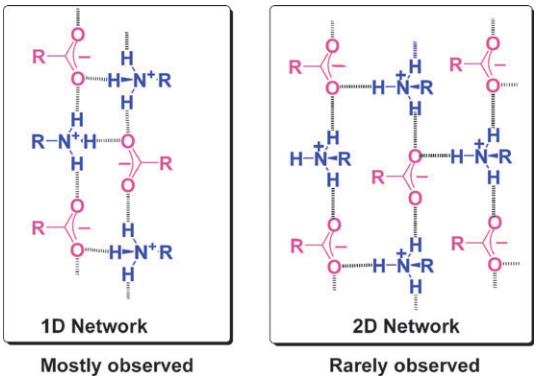


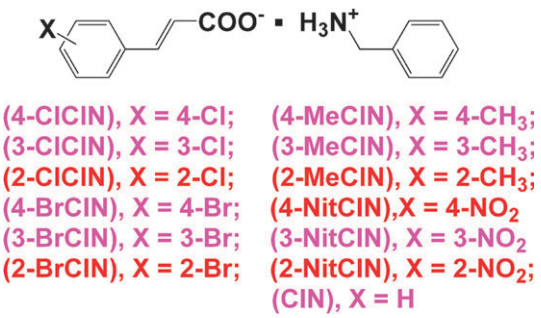
Fig. 17 1D **HBN** in (a) bis-dicyclohexylammonium 2,6-naphthalene-dicarboxylate) and (b) bis-dicyclohexylammonium isophthalate (Scheme 11). Figures are generated using crystallographic coordinates retrieved from CSD 5.28, November 2006.

Frequently occurring 1D columnar **HBN** observed in PAM salt (Scheme 12) can be envisaged to produce 2D sheet type **HBN** in bis-alkylammonium dicarboxylate salts (Scheme 14).

A systematic study[56] on a series of bis-alkylammonium dicarboxylate salts derived from cyclobutane-1,1-dicarboxylic



Scheme 12



Scheme 13 Salts in pink and red are gelators and nongelators, respectively.

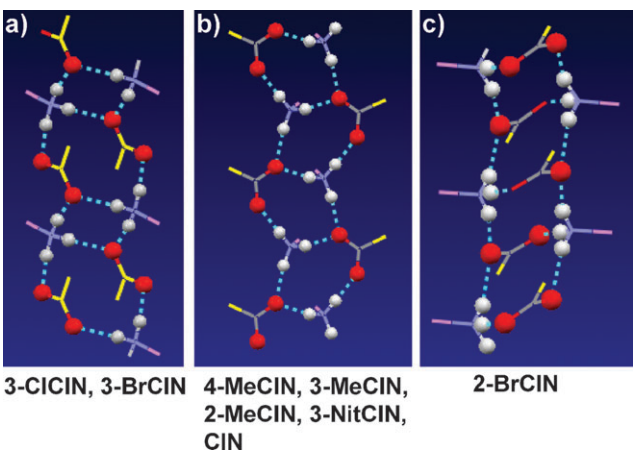


Fig. 18 Various supramolecular connectivities in the 1D columnar **HBN** observed in the single-crystal structures of the **SAD** salts (Scheme 13). Figures are generated using crystallographic coordinates retrieved from CSD 5.28, November 2006.

acids and primary alkyl amines having various alkyl chain lengths (Scheme 14) revealed the following:

All the salts with $n < 11$ showed no gelation ability with the solvents studied whereas salts with $n > 10$ were capable of gelling various organic fluids including commercial fuels such as petrol, diesel and kerosene. Single-crystal structures of the salt ($n = 5$) showed 2D **HBN** as envisaged in Scheme 14 (Fig. 21).

Interestingly, both the structures of salt ($n = 11, 12$) displayed a 1D nanotubular **HBN** instead of a 2D lamellar structures as observed in the case of salt ($n = 5$). In the crystal

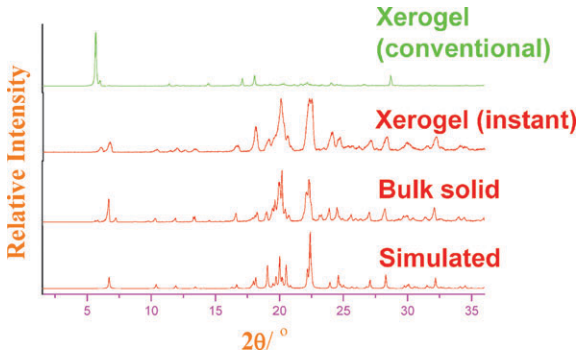


Fig. 19 XRPD of salt **CIN** (Scheme 13) under various conditions. Adapted from ref. 54 with permission. Copyright 2006 American Chemical Society.

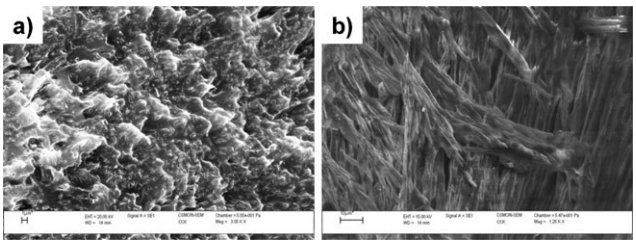
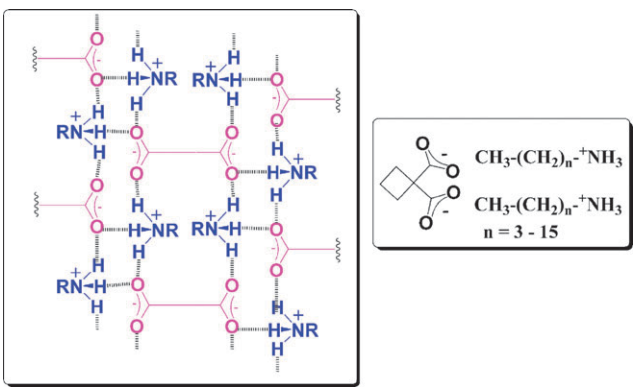


Fig. 20 SEM micrographs of xerogels of **CIN** (Scheme 13); (a) **CIN** in benzene (2.5 wt%, conventional; (b) **CIN** in benzene (2.5 wt%, instant). Adapted from ref. 54 with permission. Copyright 2006, American Chemical Society.



Scheme 14 Left—plausible 2D **HBN** in primary ammonium dicarboxylate salts; right—dicarboxylate salts of *n*-alkylamines studied for gelation.

structures of salts ($n = 11, 12$), various N–H···O interactions lead to the formation of 1D infinite tape architecture having curved surface presumably due to the angular topology of the acid moiety. A 1D nanotubular **HBN** is thus formed by dimerization of two such identical curved tapes *via* complimentary N–H···O interactions (Fig. 21). Careful analyses of the structures revealed that long alkyl–alkyl interactions were mainly responsible for such a hydrogen bonding isomerism from 2D nonfunctional (nongelling) lamellar **HBN** (salt with $n = 5$) to 1D functional (gelling) nanotubular **HBN** in salts ($n = 11, 12$) (Fig. 21). Remarkable similarities of the XRPD patterns (not shown here) of the salts ($n = 13, 14, 15$) with that of the salts ($n = 11, 12$) indicated the presence of similar 1D

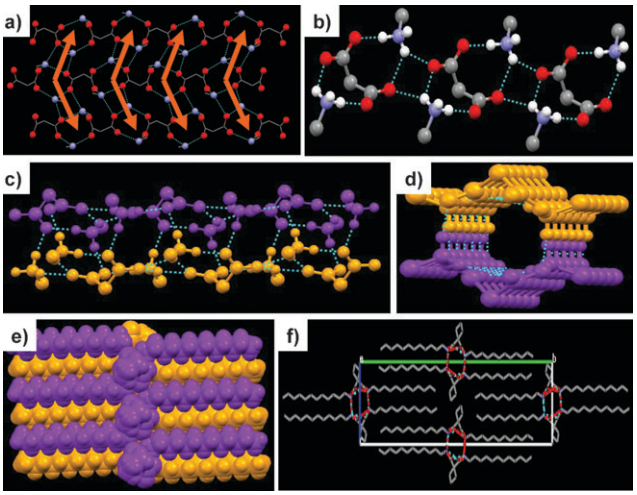


Fig. 21 (a) 2D **HBN** in salt (n = 5); (b) 1D tape **HBN** having curved surface; (c) recognition of two identical 1D tape to produce nanotubular construct; (d) tilted axis view of the nanotube; (e) side view of the nanotubular construct demonstrating intra-network alkyl–alkyl interactions; (f) packing of nonotubular construct demonstrating inter-network alkyl–alkyl interactions in salt (n = 11) (Scheme 14). Figures are generated using crystallographic coordinates retrieved from CSD 5.28, November 2006.

nanotubular **HBN** in the former salts which was further corroborated by their gelation abilities.

Combinatorial library approach

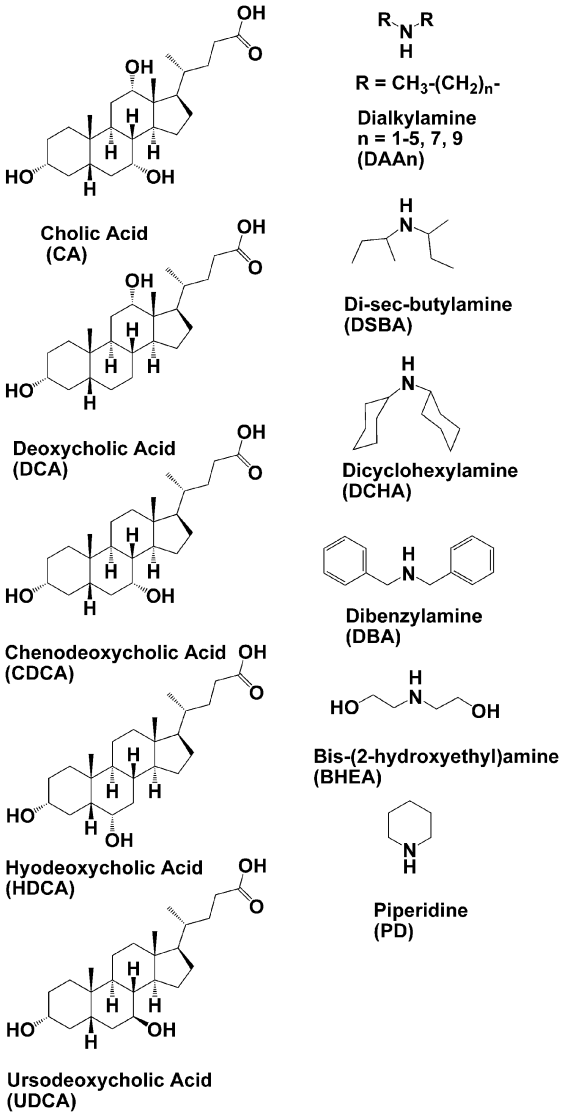
Since synthesis of organic salts are much easier and less time consuming than that of covalent organic synthesis of a molecule and combination of commercially available acids and amines in preparing the corresponding salts are virtually endless, it is sensible to prepare combinatorial libraries for potential gelators using the crystal engineering rationale. Such libraries may then be screened for identifying potential gelators which may be studied in detail and developed for material applications.

A combinatorial library using SAM synthon

A combinatorial library of 60 salts was prepared by reacting 5 bile acids and 12 secondary amines to exploit the SAM synthon (synthon A) as the possible driving force for gelation (Scheme 15).[57]

The rationale behind choosing secondary ammonium bile acid salts as potential gelators are the following: bile acids are monocarboxylic acids having a unique bent geometry with hydrophobic and hydrophilic surface and display interesting lattice inclusion properties.[58] The plausible hierarchical supramolecular self-assembly of the ion pair in such salts may be envisaged as a 1D network irrespective of their primary supramolecular aggregates (either 0D or 1D) as depicted in Scheme 16, which would hopefully ensure their gelation properties. 16 salts of the combinatorial library were found to be supramolecular gelators of which 6 were ambidextrous.

Among the gelator salts, bis-decylammonium cholate (**CA.DAA9**) turned out to be the best gelator and further studies were carried out on this gelator salt in order to get more insights. Optical and atomic force microscopy (OM and



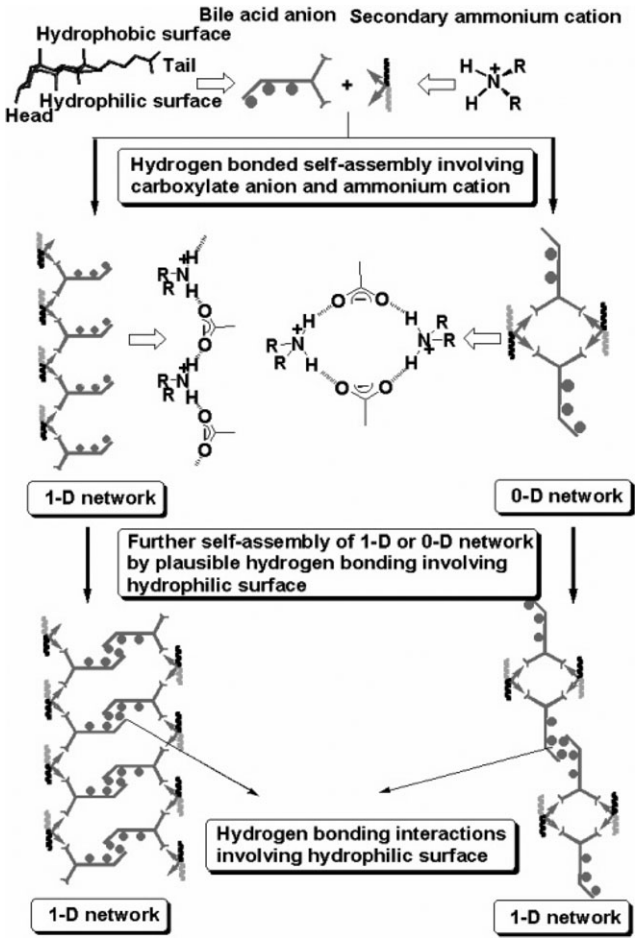
Scheme 15 Various bile acids and secondary amines used for generating combinatorial library of salts studied for gelation.

AFM, respectively) revealed intriguing morphological features; while OM displayed the presence of several micrometer long intertwined fibers, AFM showed the presence of entangled fibers having helical twist (Fig. 22).

A combinatorial library using PAM synthon

Scanning a combinatorial library of 40 PAM salts derived from 10 variously substituted cinnamic acids and 4 n-alkyl primary amines having varying alkyl chain lengths (Scheme 17) resulted in 3 new gelators, namely hexadecylammonium 4-chloro, 4-methyl and 4-bromocinnamate (**C1A15**, **C4A15** and **C7A15**, respectively, Scheme 17).[59] Interestingly **C7A15** had the rare ability to gel various commercial fuels such as petrol, kerosene and diesel selectively from the corresponding oil/water mixtures (Fig. 23).

Systematic study on 4-bromocinnamic acid salt of n-alkyl amines with varying chain length revealed that salts **C7A*n*** (n = 3–6) were nongelators whereas salt **C7A*n*** (n = 7–15) were gelators of which salts **C7A*n*** (n = 11–15) were better



Scheme 16 Plausible hierarchical supramolecular self-assembly of the ion pairs in secondary ammonium bile acid salts. Reprinted from ref. 57 with permission. Copyright 2006, American Chemical Society.

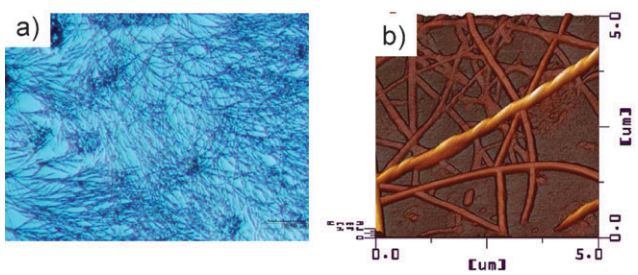
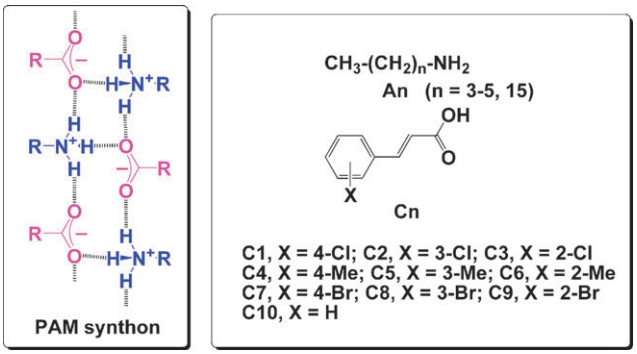


Fig. 22 (a) Optical micrographs of gel fibers of **CA.DAA9** (5 wt% in 1 : 1 DMSO–water, v/v) (bar 1 μm); (b) AFM micrographs of xerogel fibers of **CA.DAA9** (5 wt% in DMSO–water, 1 : 1, v/v). Reprinted in part from ref. 57 with permission. Copyright 2005, American Chemical Society.

gelators indicating the significant role of long alkyl chains in gelling properties. Single-crystal structures of 11 nongelators and 4 gelators confirmed the presence of 1D columnar networks having two types of supramolecular connectivity (Fig. 24).

However, intra-network arrangements of the ion pairs were distinctly different in nongelators and gelators; while the alkyl chains could not interact with each other within the network due the centrosymmetric arrangement of the cationic and



Scheme 17 *Left*: 1D **HBN** in PAM salts; *right*: *n*-alkylammonium cinnamate salts studied for gelation.

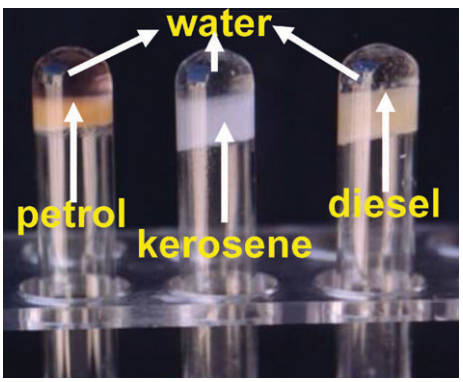


Fig. 23 Selective gelation of oil from oil/water mixtures by **C7A15** (Scheme 17): (a) petrol; (b) kerosene and (c) diesel. It can be seen that the top water layers remain unaffected. Adapted from ref. 59 with permission. Copyright 2006, American Chemical Society.

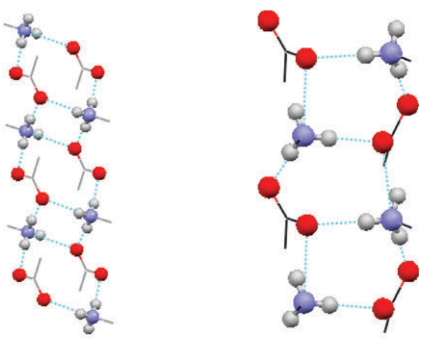


Fig. 24 Supramolecular connectivities observed within the 1D **HBN** in the salts. Figures are generated using crystallographic coordinates retrieved from CSD 5.28, November 2006.

anionic species along the network in the nongelator salts, the opposite was the case in the gelator salts except for salt **C7A10** which displayed a similar arrangement of ionic species as observed in nongelator salts (Fig. 25).

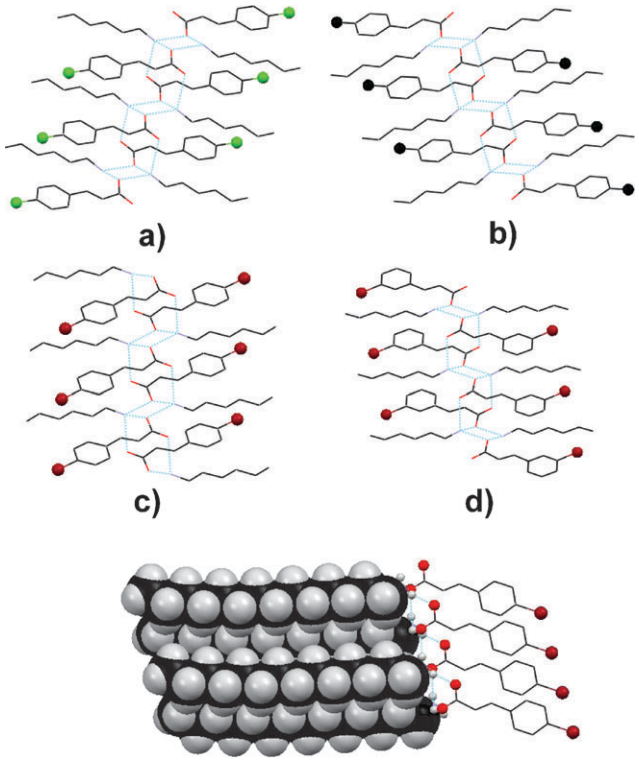


Fig. 25 1D **HBN**s and the relative arrangement of the ionic moieties along the network as observed in the nongelator salts (a) **C1A5**, (b) **C4A5**, (c) **C7A5**, (d) **C8A5** and gelator salts (e) **C7A13** (salts **C7A9** and **C7A11** display an identical network) (Scheme 17); Adapted from ref. 59 with permission. Copyright 2006, American Chemical Society.

3. Concluding remarks

This review has highlighted recent developments in designing LMOGs which is a challenging task. Both *molecular* and *crystal engineering* approaches are useful tools to design new LMOGs. The *crystal engineering* approach can make a significant contribution in designing new LMOGs as demonstrated in organic salt based LMOGs which are more attractive in terms of their synthetic simplicity and various possibilities. However, it might be possible to exploit the *crystal engineering* approach in discovering new LMOGs other than salt-based LMOGs. Obtaining a 1D network in the gel fiber, however, is not enough to ensure gelation. It is important to understand the detailed mechanism of gel formation; what are the parameters that start nucleation of fibers, how the fibers self-assemble to form **SAFIN**, how the **SAFIN** interact with solvent leading to gel are some of the important questions which need be addressed with great detail before a better strategy for designing LMOGs can be found. We believe that this review will attract the attention of researchers to address some of these seemingly difficult problems so that the current model of understanding 'gels' is improved, which will help incorporate crucial features in the targeted molecules to achieve better success rate in future design.

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