COMMUNICATION

Novel organogelators based on amine-derived hexaazatrinaphthylene†

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Novel C_3-symmetrical heteroaromatic hexaazatrinaphthylene (HATNA) gelators symmetrically end-substituted with pendant aromatic and aliphatic amines were synthesized. Some of these π-conjugated structures induce self-assembly, forming fibers able to gelate solvents of different polarity at low wt% as demonstrated by spectroscopic and microscopic techniques.

The development of novel structures and materials based on the gelation of solvents by low-molecular weight organic gelators (LMWOGs) is a rapidly expanding area of interdisciplinary research. However, a rational structural design of LMWOGs still remains a major challenge.[1–3] Despite the increasing number of discovered gelation motifs, it is impossible to reliably (*de novo*) predict the gelation capability of a molecule. In our research group there is a high interest to find new gelation motifs from both fundamental and practical standpoints.[4]

LMWOGs with π-conjugated molecular structures represent remarkable examples of stacked molecular self-assemblies, which create one-dimensional nanostructured fibers.[5] Such nanostructured morphology has attracted increasing interest, particularly for applications in nanomaterials and nanodevices.[6] Mostly, a hydrogen bonding function and/or huge planar molecular surfaces need to be incorporated into a gelator molecule to produce fibrous gels.[7,8] Molecular gelation systems are characterized by a strong tendency of the small organic molecules to aggregate in solution into one-dimensional fibrillar architectures. Formation of these elongated structures is mainly governed by solvophilic–solvophobic effects stabilized by unidirectional non-covalent interactions such as hydrogen bonding and π–π stacking. A potential model is based on the concept of AL gelators.[9,10] These compounds consist of a π-conjugated aromatic nucleus (A) connected to an alkyl chain or aromatic group (L). The principal driving force for

gel formation and stabilization of self assembled fibrilar networks (SAFINs) of AL_6 gelators,[11] such as compounds **1** and **2**, is π–π stacking of the aromatic units and London interactions of the alkyl and aromatic chains. Their one-directional circular arrangement facilitates π–π stacking interaction along the C_3 axis to form nanostructured fibers, which act as an organogelator. Recently, other authors have reported that a triphenylene-fused metal trigon conjugate was able to gel organic solvents.[12] So far, only a very limited number of π-conjugated gelators have been reported to be able to gelate a variety of solvents of different polarity. This may lead to an improvement with respect to previous work published in the literature.

Taking advantage of the water solubility of compound **G1**[13] we devised a microwave-assisted methodology to synthesize compounds **1–4** (Fig. 1) consisting of the uncatalysed direct mono-*N*-alkylation of aromatic amines by alkyl halides in water.[14]
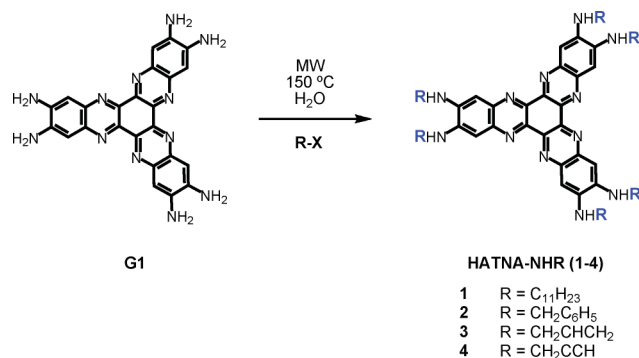

Fig. 1 Synthesis of the C_3-symmetrical HATNA derivates.

1	R = $C_{11}H_{23}$
2	R = $CH_2C_6H_5$
3	R = CH_2CHCH_2
4	R = CH_2CCH

It turned out that the substitution pattern around the hexaazatrinaphthylene (HATNA) core is crucial for the gelation abilities of the formed complexes. Compounds **1** and **2** containing the saturated-chain alkyl and benzyl terminal groups proved to be excellent gelators for a variety of customary solvents as summarized in Table 1 (see ESI†). In fact, they act as "supergelators"[15] with a critical gelation concentration of <1 wt% for dimethylsulfoxide (DMSO), toluene and benzene. Nevertheless, derivates **3** and **4**, possessing double and triple bonds, respectively, did not form organogels. The observed gels (Fig. 2E) were found to be robust, translucent and stable for months. It should be noted that gels have been obtained by a classical heating–cooling process. The gel formation of **1** and **2** was determined by a 'stable to inversion of the

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Table 1 Physical data for gels of **1** and **2** in various organic solvents (further solvents and details are given in the ESI†)

Compound **1** (green gels)

Solvent	cgc (wt%)[a]	Phase[b]	T_{gel} (°C)[c]
Dimethyl sulfoxide	0.36	G	119
Dimethyl formamide	1.10	G	133
Acetone	1.40	G	51
Toluene	0.50	G	80
n-Hexane	1.78	G	70

Compound **2** (red gels)

Solvent	cgc (wt%)[a]	Phase[b]	T_{gel} (°C)[c]
Benzene	0.50	G	58
Toluene	1.10	G	107

[a] The cgc is the critical gelation concentration at which gelation was observed to restrict the flow of the medium. [b] Abbreviations: G = stable gel (>1 month). [c] Gel–sol transition temperature determined by the dropping ball method.
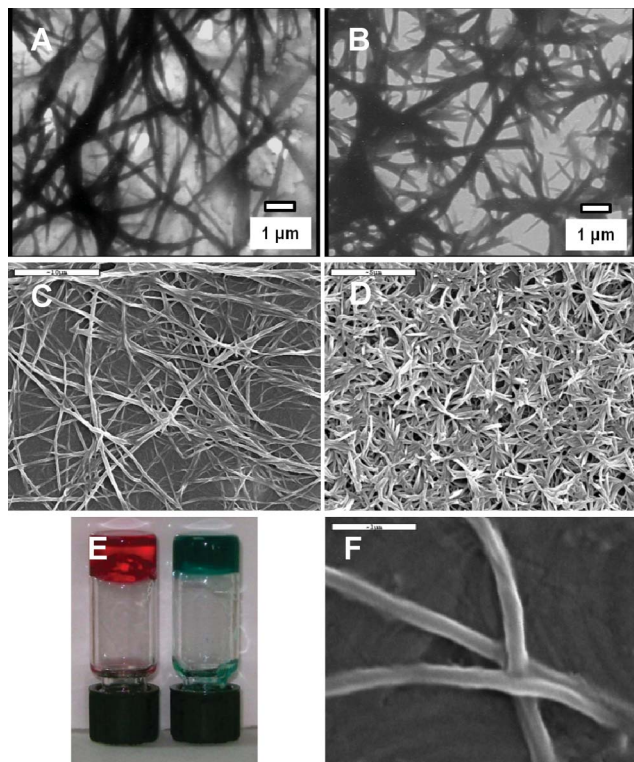
Fig. 2 TEM images of xerogels of **1** (A) and **2** (B) in DMSO and toluene respectively. SEM images of **1** (C, F) and **2** (D). Image E shows digital photographs of the gels **1** (right) and **2** (left) in DMSO (0.36 wt%) and toluene (1.10 wt%) respectively.

test-tube' method and tested for 20 solvents (see ESI†). Gelation using as little as 0.36 wt% of **1** in dimethylsulfoxide was observed within 15 min. All gels displayed high stability over time when stored in sealed glass vials, as no changes in both appearance and melting temperatures, were detected in several weeks.

Formation of amides (HATNA-NHCOR) instead of amines (HATNA-NHCH₂R) results in a complete loss of the gelating ability, which clearly indicates the important role of the α-

methylene moieties linked to nitrogen atoms in the gelation process.[13] This conclusion is strongly supported by the analysis of temperature-dependent ¹H NMR spectra of gels from compound **1**. In DMSO-d_6 at room temperature the experiments display broadened signals of the HATNA moiety and slightly less broadened resonance absorptions for the methylene moieties (see ESI†). All these signals sharpen significantly at increasing temperatures, indicating a partial deaggregation. In addition, hydrogens of the central core suffer an important change in their multiplicity and shifting. However, this temperature dependence is interestingly reversible. Upon cooling, the originally observed spectra were again obtained.

The thermal properties of the gels were examined by differential scanning calorimetry (DSC) and determination of their gel melting temperatures (T_{gel}) were in good agreement with a sharp transition peak in the DSC thermograms. T_{gel} values also increased with the concentration of the LMWOG **1** (see ESI†). In addition, the gels made from compounds **1** and **2** were found to be fully thermoreversible, thus raising the temperature above the T_{gel} induced the gel–sol phase transition, and the solutions changed back to the organogels upon cooling to room temperature. The heating–cooling cycle could in principle be repeated many times without affecting the gelation ability of the compounds.

In order to understand the precise roles of the side-chains and NH- residues of compound **1** in the gelation process, FT-IR studies were carried out (see ESI†). Results pointed out very minor differences between the solid, the solution and the gel phase. In the latter, stretch vibration bands for NH were observed at *ca.* $v = 3276$ cm⁻¹. These results may indicate that the gelator molecules experience intermolecular hydrogen bonding through the amine groups in the nanofibers, which could be one of the key driving forces in promoting the efficient organization of compound **1** into aggregates and fibers.

In order to further ascertain the supramolecular organization of the reported gels, transmission electron microscopy (TEM), scanning electron microscopy (SEM) and atomic force microscopy (AFM) experiments were conducted to obtain images of dried gels from compounds **1** and **2** in dimethylsulfoxide and toluene, respectively.

TEM (Fig. 2A and 2B) and SEM (Fig. 2C and 2D) images revealed that a fibrous network, typical of LMWOG gels, was formed. Nevertheless, the observed networks significantly differed in their shape and dimensions. Thus, twisted cylindrical fibers of several micrometres long with diameters of 150–250 nm wide and 75–150 nm long were obtained in DMSO for compound **1** (Fig. 2A and C). On the other hand, compound **2** in toluene exhibited fibrous lamellar architectures (Fig. 2B and D). These ribbons resulted in considerably shorter but evidently thicker nanofibers (300–600 nm wide), in comparison to those obtained for compound **1**. Fig. 2F shows a loosely entangled higher magnification region of **1**-gel in which well defined fibers are clearly depicted.

Tapping mode AFM imaging of **1** and **2** (Fig. 3) was utilised as a direct method to examine the three-dimensional gel structure. From these measurements, it can be concluded that a noticeable change in the morphology of the assembly may take place when the saturated alkyl chains of **1** were replaced by aromatic rings in **2**. The aggregation of **1** thus formed elongated twisted ropes (Fig. 3A) consisting of intertwined fibers with diameters in the range of 50–80 nm which self-assemble to generate such helical ropes.
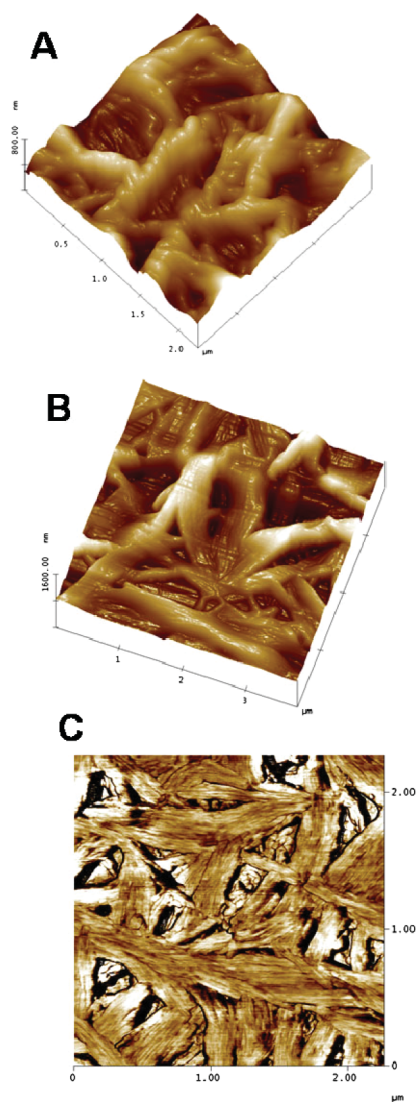
Fig. 3 AFM images of xerogels of **1** (0.36 wt%) and **2** (1.10 wt%) in DMSO and toluene, respectively. 2.25 × 2.25 μm² 3D image of **1** (A) and 4.00 × 4.00 μm² 3D image of **2** (B). (C), 2.25 × 2.25 μm² contrast phase image of the gel **2**, shows the striations inside the ribbons.

In contrast, the AFM images of **2** showed entangled lamellar ribbons (Fig. 3B) with straight narrow striations ranging from 20–30 nm thick (Fig. 3C). It is worth noting that the striations observed on the ribbons could be considered as individual fibers that aggregate into a parallel columnar packing to form bundles.

Taking into account the microscopic analysis carried out, we can suggest that the gel generation might arise from the self-assembly of **1** and **2** molecules into 1D fibrillar architectures though π–π interactions and further hydrogen bonding and van der Waals forces between the side chains of these columnar structures to form bundles of fibers. These interactions are somehow hinted by FT-IR spectra (ESI†) as well as by the reactive points of the structure of compounds **1** and **2**. Subsequently, these bundles could aggregate to give rise to a randomly connected network of long ropes (**1**) or lamellar ribbons (**2**) as well.

A spectroscopic characterisation of the gels was also performed to complete all characterisation results. Fluorescence emission spectra of compounds **1** and **2** in DMF are shown in Fig. 4
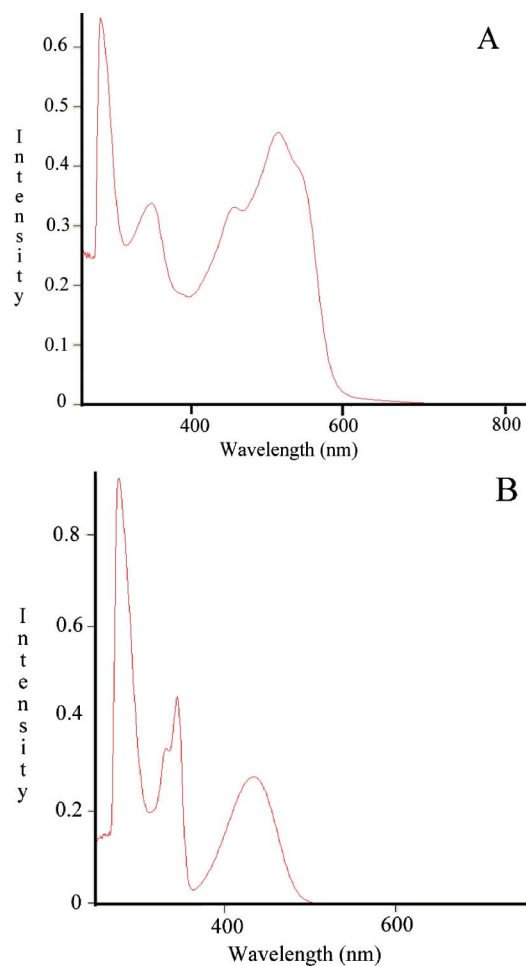

Fig. 4 Fluorescent emission of (A) compound **1** in DMF (λ_{ex} = 360 nm) and (B) compound **2** in DMF (λ_{ex} = 360 nm) at 25 °C.

and provided more information on the stacking pattern of such compounds. No remarkable changes in the profiles obtained for compounds **1** and **2** were observed apart from an important shift of the bands at lower wavelengths for compound **2** (Fig. 4B). The fluorescence of compound **2** under UV light (365 nm) in benzene at high dilution (see ESI†, page S29) was also indicative of the remarkable properties of these molecules.

The aggregation of compounds **1** and **2** was also studied by UV–vis spectroscopy as shown in Fig. 5 for compound **1**. Firstly, concentration-dependent UV–vis spectra of the compound **1** in solution and gel state were recorded. As shown in Fig. 5A, the π–π* transition bands of **1** in the dilute DMF solution appeared at 380 nm, which shifted to 362 nm in the gel state. The blue shift of the UV absorption indicated the formation of the π–π stacking by hexaazatrinaphthylene cores during the gelation, which were forced to adopt a face-to-face mode.

Oscillatory rheological measurements confirmed the viscoelastic, rigid and brittle nature of the obtained gels (Table 2). G' was uniformly found to be of greater magnitude than G''. The gels were stable over a wide frequency range (0.1–100 rad s⁻¹), and dynamic strain sweep measurements showed that they break at less than 0.5% strain.

In conclusion, we have reported for the first time the gelation ability of two HATNA compounds **1** and **2** as well as the formation
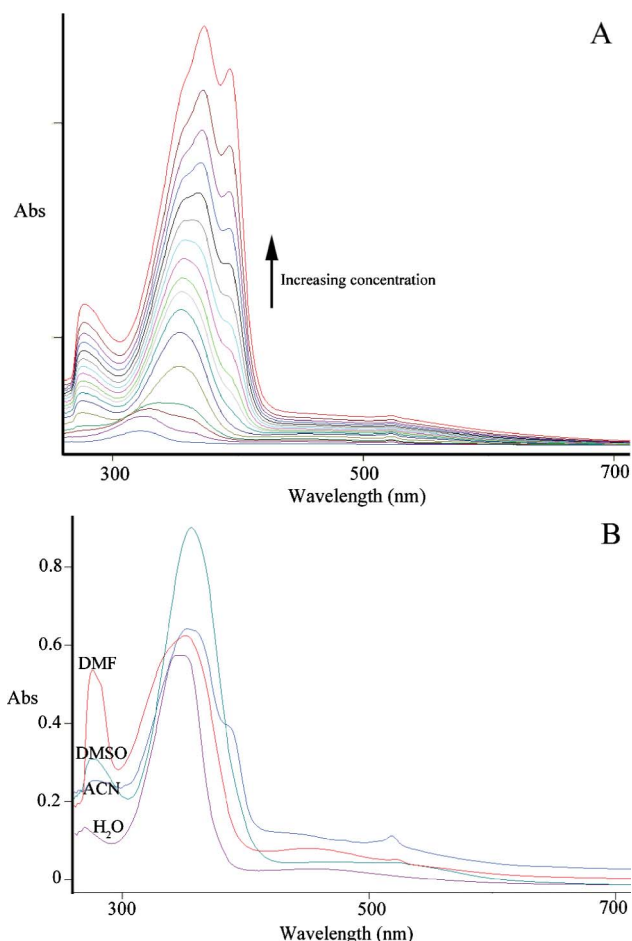
Fig. 5 UV–vis spectra of compound **1**; (A) in solution and gel-state at different concentrations ($10^{-5}–10^{-3}$ M) and (B) in dilute solutions (10^{-5} mM) of solvents with different polarity (DMF, DMSO, acetonitrile-ACN, and H_2O) at 25 °C.

Table 2 Rheological data for gels[a] of **1** and **2** in DMSO and toluene, respectively

Compound	Solvent	cgc[b] (wt%)	G'^c (×10^3 Pa)	G''^d (×10^3 Pa)
1	DMSO	0.50	10 ± 0.6	1.0 ± 0.80
2	Toluene	1.20	70 ± 1.3	7.2 ± 0.90

[a] Gels (1 mL) were prepared upon warming the cool isotropic solutions to 25 °C. [b] Critical gelation concentration. [c] G' = average storage modulus. [d] G'' = average loss modulus.

of their stable organogels, which was studied by FT-IR, DSC, TEM, SEM and AFM images. A variety of solvents can be gelated, providing robust and translucent gels stable for months. Furthermore, very subtle structural changes were shown to potentially have a dramatic effect on supramolecular aggregation.

The results obtained from spectroscopic and microscopic techniques reveal the occurrence of self-assembly and auto-aggregation within the gel, induced by the terminal groups present in the periphery of the HATNA core. With this surprising discovery, studies are ongoing in our laboratories to design new LMWOGs based on this core for fine-tuning the range of solvents to be gelated and determine the influence of the terminal groups in the self-assembly and in the gel formation.

Additionally, the present gels have a significant potential for further development and a range of applications are envisaged in the near future. Based on preliminary computational studies on their HOMO–LUMO gap, these materials have promising properties to act as n-type semiconductors. Several studies are currently ongoing in our laboratories and in collaboration with other groups in this regard.

Acknowledgements

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