# Self-organization of gelator molecules inside an organogel

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## Abstract

Low-molecular-weight organic gelling agents are currently subject of increasing attention, not only
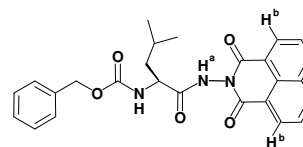
## Introduction

Low-molecular-weight organic gelling agents are currently subject of increasing attention, not only because of the numerous applications of gels, but also because understanding the detailed structural information of molecular assemblies is important for the rational design of those materials.[1-5] Spectroscopic techniques such as nuclear magnetic resonance (NMR), infra-red (IR), fluorescence emission and circular dichroism (CD) are commonly employed with the aim at elucidating the detailed structure of supramolecular gels. A widely accepted mechanism of gelation is the spontaneous self-assembly of individual molecules into fibers and subsequent entanglement of these fibres into fibrous networks, including solvents in the interstices. The driving force for the self-assembly of molecules into fibres are non-covalent forces[1] such as hydrogen bonding, π-π stacking, van der Waals interactions, solvophobic interaction etc.

In a preliminary communication, we described a new family of (S)-aminoacid type gelators obtained *via* an easy and inexpensive way.[6] These novel gelling agents are very easily prepared from cheap starting materials and allowed many structural variations of the side chain. In order to go deeply into the organogelation phenomenon, we point out in this paper the self-assembling behaviour of gelator **1** (see chart 1) which bears a fluorescent

Chart 1. Gelator **1**.



chromophore (a naphthalimide moiety) through IR, NMR, fluorescence spectroscopy *and molecular simulation*. Highly oriented network structures were observed at gel state and disappeared in isotropic solution.
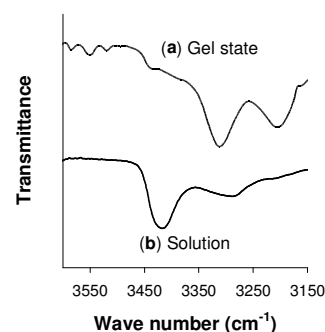
## Results and Discussion

*1. Highlight major self-assembling interactions of organogelators*

In order to evaluate the driving force for gelation, we recorded the FT-IR spectra. Figure 1 shows the FT-IR spectra of **1** in chloroform solution and in toluene gel. In CHCl$_3$ solution (no organogelation), the typical IR bands, arising from non-hydrogen bonded NH groups, appeared at 3420 and 3285 cm$^{-1}$ characteristic of the N-H stretching vibration. The IR spectra of toluene gel showed the bands at 3310 and 3210 cm$^{-1}$, characteristics of hydrogen bonded NH groups. Such IR shifts indicate

Fig.1. IR spectra of gelators **1** in (a) toluene (10 mg/mL, gel state) and CHCl$_3$ (10 mg/mL, solution) at 25 °C.

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the presence of the intermolecular hydrogen bonding interaction.[7]

Further information was obtained from the NMR spectra. In most of the cases reported in the literature, the gelator NMR signals com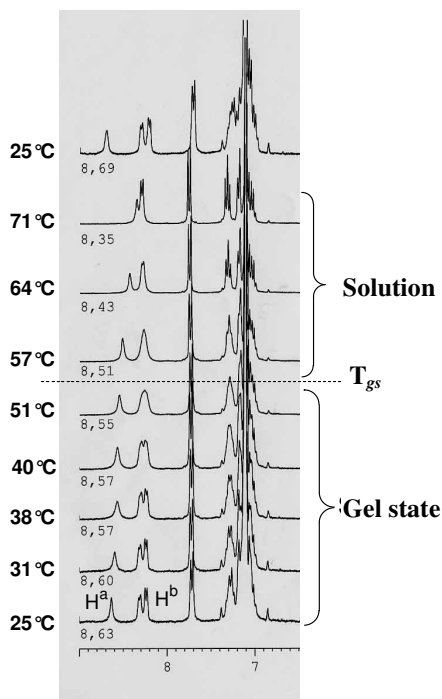pletely disappear in the gel state while they are present in the liquid state.[8] This can be explained by the fact that the gel fiber can be considered as a crystal of the gelator in which the molecular motion is very limited and the solvent molecules are excluded from the fiber. Therefore, disappearance of the $^1$H NMR peaks has been described to be one criterion for *"dry gels"*. For instance, some of the organogels studied by Weiss *et al.* are composed of crystalline fibers for which the molecular packing is the same as in the crystalline state.[9] As an example, Figure 2 shows the $^1$H NMR spectra of **1** in $CCl_4$ / $C_6D_6$ (4/1: v/v, 5 mg/mL) at different temperatures between the gel state 25 °C and solution 70 °C (*gel-to-solution* transition temperature $T_{gs}$ = 55 °C). It is remarkable that NMR peaks do not disappear and remain very sharp in the gel state. This result suggests that the gelator molecules still keep a good thermal motion in the fibers; this feature is consistent, according to Sakurai *et al.*, with a *"wet gel"* for which the solvent molecules are incorporated into the gel fibers.[10] Furthermore, no new peaks are detected. We observe that the chemical shift of N-H$^a$ is quite invariant up to the gel-to-solution transition temperature ($T_{gs}$) suggesting their implication in strong intermolecular hydrogen bonds in the network structures. These protons are shifted upfield at higher temperature, above the $T_{gs}$. Then, the hydrogen bonding involved this NH$^a$ is broken up in solution. This observation, concerning the presence of hydrogen bonding in gel state, is in good agreement with IR result.



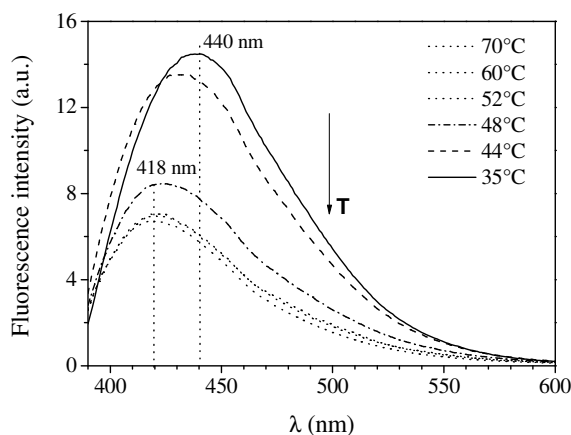Fig.2. A part of NMR spectra of **1** in $CCl_4$/ $C_6H_6$ (4/1, v/v), recorded between 25 °C and 71 °C.

Moreover, interesting observation can be made concerning naphthalimide aromatic protons (H$^b$ at ~ 8.6 ppm). In the gel state (25 °C), the signal for H$^b$ is composed of two doublets (the two H$^b$ protons = non equivalent). Upon warming the sample to 70 °C (solution), it becomes a single doublet (the two H$^b$ protons = equivalent). This latter is strong evidence of a free rotation of the naphthalimide moiety in solution. On the contrary, in the gel state, the aromatic part of the naphthalimide group is no longer symmetrical in the NMR time scale because of a hindered rotation, this anchimeric phenomenon being the result of a hydrogen bond network involving N-H and π-stacking interactions between the naphthalimide moieties.

*2. Fluorescence spectroscopy for studying the molecular arrangement inside the fibers*

Fluorescence spectroscopy is a powerful tool which can be used as an optical method well suited to give information on the supra-molecular organization. Naphthalimide incorporated in the molecular assemblies would act as a instrinsic probe to characterize its self-assembling behaviour and therefore insight molecular assembling manner. Prior to the fluorescence measurements, UV-vis spectra were recorded (data not shown). The fluorescence spectra of **1** in toluene (0.93 wt. %) at different temperature are given in Fig. 3 ($\lambda_{exc}$ = 378 nm). One can notice that the fluorescence emission maximum is shifted to shorter wavelength when the gel is melt into isotropic solution (above $T_{gs}$ ~ 50 °C).

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It has already been reported that fluorescence emission depends on the aggregation morphology such as H-type or J-type aggregation.[11] H-aggregates correspond to molecules which are aligned parrallel to each other with strong intermolecular interaction and induce non radiative deactivation processes (blueshift of UV absorption band), whereas J-aggregates contain molecules that are



Fig.3. Fluorescence emission spectra of **1** in toluene at different temperatures.
↓: increasing of the temperature ($\lambda_{exc}$ = 378 nm)

arranged in head-to-tail direction and induce a relatively high fluorescence efficiency (redshift of UV absorption). In other word, suppose that α is the angle between the coplanar transition dipoles and the axis interconnecting the units of the dimer or aggregate, α would range from 0° to 54° for J-type aggregates and from 54° to 90° for H-type ones. Our results suggest that the molecules **1** are aligned and form J-aggregates in toluene.

*3. Schematic model for explaining the supramolecular arrangement*
Summarizing, experimental results suggest that molecules **1** might form J-type aggregates, through hydrogen binding and possible π-stacking interaction between naphthalimide moieties. Beside, preliminary computer calculations, *in vacuum*, proposed that a "tail-to-tail" superstructure seems to be energetically more stable than "head-to-tail" one (head: naphthalimide moiety). Our model is described as followed (Fig. 4):
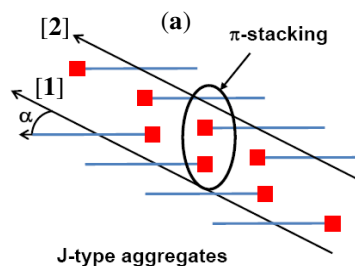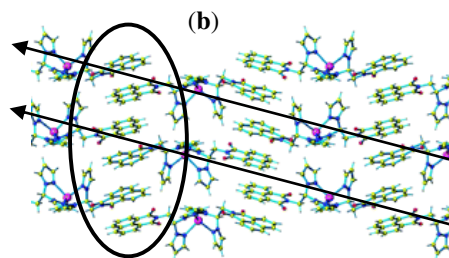


Fig.4. (a) Two molecular sets represented the supramolecular self-organization of **1**. (square: naphthalimide moiety). (b) Perpendicular view of the sheet architecture in studied compound, generated by similar π-π stacking interactions of naphthalimide synthons, from ref 12.

As we can observed in Fig. 4a, molecules **1** self-assembled, *via* hydrogen bonding, into molecular set [**1**], with a shift one to each other, resulting in a J-type aggregate (in which angle α is comprised between 0° and 54°). It is clearly that naphthalimide moieties of set [**1**] could not interact themselves. Nevertheless, when another molecular set, [**2**], approaches, π-tacking interactions may appear between naphthalimide moieties of two sets. This hypothesis is in good agreement with observations of Reger *et al.*, as showed in Fig. 4b.[12]

**Conclusions**
The spectroscopic results obtained suggested that the molecules **1** can self-assemble into a fibrous structure. Regarding the nature of these molecules, the self-aggregation phenomena can be occurred *via* hydrogen bonds. Moreover, it is showed that **1** formed J-type aggregates. Our

schematic model allows us to understand possible π-stacking interaction between naphthalimide moieties. In fact, naphthalimide moieties of two different molecular sets could interact themselves in order to reinforce the fibrous network.

**Experimental section**

*Preparation of the gels*. The gels were prepared by heating the solvent and the organogelator in a flask fitted with a reflux condenser until the complete dissolution of the solid. The solution was transferred into a closed vial and cooled to 4°C. Most of the time, the formation of the gel occurred within few minutes.

*Instrumentation*. IR spectra were obtained by using a Tensor 27 Brucker instrument, with KBr cell. Absorption spectra were recorded on a Perkin-Elmer (Lambda 2, Courtaboeuf, France) UV-visible spectrophotometer. Fluorescence spectra were recorded on a SPEX Fluorolog-3 spectrofluorimeter (Jobin Yvon, Longjumeau, France) equipped with a thermostated cell compartment, using a 450 W Xenon lamp. The gel samples were directly prepared in quartz cells having a 2 mm optical pathlength.

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