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Low molecular mass organogel from mesomorphic *N*-(4-hexyloxybenzoyl)-*N′*-(4′-nitrobenzoyl)hydrazine

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The mesomorphic compound *N*-(4-hexyloxybenzoyl)-*N′*-(4′-nitrobenzoyl)hydrazine (C6-NO_2), containing a dihydrazide unit in the rigid core, exhibited a highly stable SmA_1 phase (between 172.2 and 259.5°C) and strong gelation ability in chloroform and other non-protonic organic solvents. Both SEM observations and X-ray diffraction data indicated that the molecules self-assembled into fibrous aggregates with a diameter of about 50 nm, and retained a head-to-tail configuration within layers. FTIR and ^{1}H NMR studies confirmed that intermolecular hydrogen bonding played a key role in the formation of the supra-structures, and this was considered to be the driving force. Additionally, aggregation-induced enhanced emission was observed in the organogels, and this was attributed to aggregation induced planarization and *J*-aggregate formation.

1. Introduction

Self-assembling processes are common throughout nature and technology [1]. Self-assembled materials, such as liquid crystals and organogels formed by non-covalent bonding have attracted much attention because they are promising candidates for the next generation of materials, from which a dynamic response, environmental compatibility, and low energy processing are required [2].

The liquid crystalline state represents fascinating states of soft matter combining order and mobility on a molecular and supra-molecular level [3]. Organogels are a new class of nanostructured materials composed of a self-assembled supra-structure of a low molecular mass organogelator through specific intermolecular interactions, and a large volume of organic liquid immobilized therein [4]. In both cases, it is important to control the intermolecular interactions to achieve a balance between the tendencies of the molecules to form an isotropic, anisotropic liquid, a fluid or to crystallize in the temperature interval studied; or to dissolve, gelate, or precipitate in the solution. In general, it is more difficult to find low molecular mass compounds capable of both gelling solvents and exhibiting thermotropic mesomorphic behaviour [5].

Among non-covalent interactions, hydrogen bonding has been most commonly used to direct the self-assembling process. Many low molecular mass organogelators, containing, for example, amide [6] and urea groups [7], have been reported to show strong gelation ability in organic solvents, and in these cases intermolecular hydrogen bonding was considered to be the driving force. Unlike these studies on organogels, and although much attention has been paid to hydrogen-bonded supra-molecular liquid crystals in recent years [8], little attention has been given to lateral intermolecular hydrogen bonding in rod-like liquid crystals [9]. This is because it is generally considered that suppressing the rotations of the rod around the long axis by lateral hydrogen bonding will destabilize the liquid crystal phase, and stabilize the crystalline state [9]. Recently, we have designed and prepared a series of linear non-symmetric dihydrazide derivatives, the *N*-(4-alkoxybenzoyl)-*N′*-(4′-nitrobenzoyl)hydrazines (C*n*-NO_2), as shown in scheme 1, in which the dihydrazide unit is part of the rigid core, with an aim intermolecular hydrogen bonding between the rigid cores [10]. Interestingly, all the compounds C*n*-NO_2 (n=3, 6, 12, 16) showed stable liquid crystalline properties and strong gelation ability, but here we focus on the mesophase properties and gelation ability of C6-NO_2.

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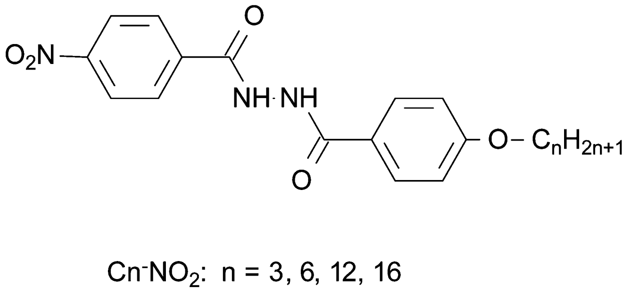

Scheme 1. The molecular structure of C*n*-NO$_2$.

2. Experimental

2.1. *Materials and gelation experiments*

The dihydrazide derivatives (C*n*-NO$_2$) were synthesized in our laboratory, and their structures confirmed by FTIR, ^{1}H NMR spectra and elemental analysis. The synthetic details were reported elsewhere [10]. The powdered compound and weighed amounts of solvent were sealed in a glass tube, and gently heated to completely dissolve the gelator. The resulting solution was cooled in air or in an ice–water bath (in the low concentration case) for several minutes, and then gelation was checked visually. If upon inversion of the test tube no fluid ran down the walls of the tube, we judged 'gelation' to have occurred. The xerogels were obtained by slowly evaporating the solvents from the organogels, which were kept under air pressure at about 4°C.

2.2. *Characterization*

^{1}H NMR spectra were recorded using a Bruker Avance 500 MHz spectrometer, using tetramethylsilane (TMS) as an internal chemical shift reference. FTIR spectra were recorded with a Perkin-Elmer spectrometer (Spectrum One B), the sample was in the form of a pressed tablet with KBr, or a cast film on KBr discs. Phase transition properties were investigated using a Mettler Star DSC 821^e, at a heating and cooling rate of 10°C min^{-1}. X-ray diffraction (XRD) was performed using a Rigaku D/max 2500 PC X-ray diffractometer (Cu K$_\alpha$, λ=1.5406 Å). T_ms were determined by the 'falling drop' method [11]. An inverted gel was immersed in a water bath initially at or below room temperature. The water was heated slowly up to T_m, the temperature at which the gel fell due to the force of gravity.

3. Results and discussion

As reported previously [10], C6-NO$_2$ showed a very stable enantiotropic SmA phase between the melting point at 172.2°C (ΔH=19.17 kJ mol^{-1}) and the transition to the isotropic state at 259.5°C (ΔH=9.07 kJ mol^{-1}). The layer spacing in the SmA phase was measured to be 25.4 Å, which is 2.9 Å longer than the calculated molecular length (l=22.5 Å). The d/l ratio (1.13) is somewhat smaller than 1.4, which suggested that C6-NO$_2$ was not arranged in interdigitated or semi-bilayers as commonly observed in polar systems, but instead adopted a head-to–tail configuration in monolayers, termed SmA$_1$, in which the nitro groups overlap around the layer boundaries cancelling out the strong molecular dipole moments. In addition, it was confirmed that intermolecular hydrogen bonding occurred in the SmA phase, and contributed to stabilize the mesophase. This was also thought to be the origin of the high transition temperature and the large associated enthalpy change [10].

Interestingly, we found that C6-NO$_2$ showed strong gelation ability in chloroform. Turbid gels were formed in chloroform at very low concentrations (<1.0 wt%). The gelation property of C6-NO$_2$ was also tested for several different solvents. As shown in table 1, C6-NO$_2$ exhibits good gelation ability for non-protonic organic solvents, such as chloroform, and benzene, but with the exception of tetrachloromethane, in which C6-NO$_2$ is insoluble. C6-NO$_2$ can be dissolved in methanol by heating, but precipitates on cooling. A possible reason for this is that protonic methanol prevents the potential supra-molecular aggregation based on the intermolecular hydrogen bonding. These results indicate that intermolecular hydrogen bonding between the hydrazide groups may be the driving force for the gelation. Figure 1 shows the melting temperature (T_m) of the chloroform gels based on C6-NO$_2$ as a function of concentration. The T_m increases from 13 to 68°C as the concentration of C6-NO$_2$ increases from 0.53 to 4.98 wt%.

In order to investigate the aggregation morphology of these organogels, the xerogels were prepared and subjected to observation by SEM and XRD. As shown in figure 2, the SEM image suggests that the organogel of these compounds consists of bundles of fibrous

Table 1. Organic solvents tested for gelation by C6-NO$_2$.

Solvents	C6-NO$_2$^{a}
Methanol	P
Chloroform	G
Benzene	G
Toluene	G
1,2-Dichloroethane	G
Tetrachloromethane	I

^{a}P=precipitate; G=gel; I=insoluble.

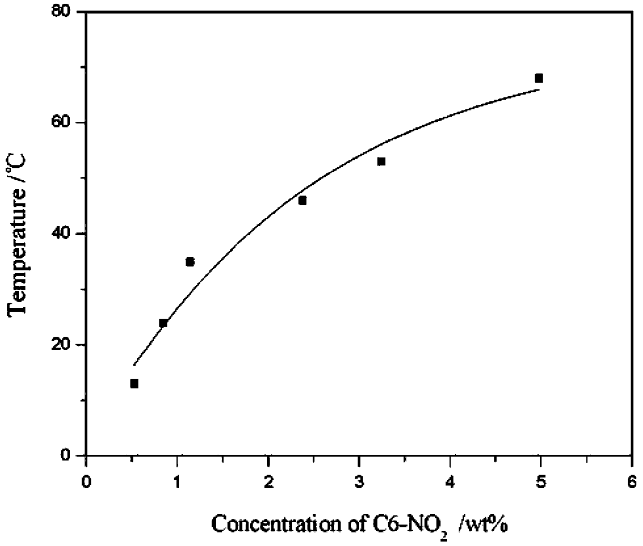

Figure 1. Concentration-dependent melting temperature of chloroform gel based on C6-NO$_2$.

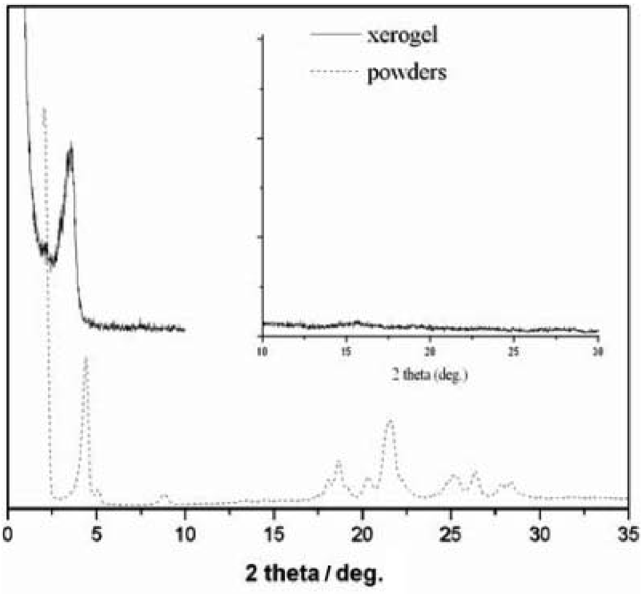

Figure 3. X-ray diffraction pattern of C6-NO$_2$ in crystal powders (lower, dashed line) and xerogels (upper, solid line).

aggregates with an average diameter of 50 nm. The XRD of the xerogels is quite different from that of the crystalline powders, as shown in figure 3, and only one reflection, corresponding to a *d*-spacing of 25.4 Å, was observed in the small angle region, which is equal to the layer spacing of the SmA$_1$ phase. Thus it may be speculated that the C6-NO$_2$ molecules in the xerogels retain the same arrangement as in the SmA$_1$ phase.

The formation of elongated fibre-like aggregates indicates that the self-assembly of C6-NO$_2$ is driven by strong directional intermolecular interactions. To ascertain whether hydrogen bonding plays a role in the gelation process, the infrared spectrum of the C6-NO$_2$ organogel in chloroform was examined. The presence of N–H stretching vibrations at 3195 cm^{-1} and C=O stretching vibrations at 1640 cm^{-1} for C6-NO$_2$ in the gel state unambiguously implies hydrogen bonding through N–H···O=C interactions. The hydrogen bonding was confirmed to be intermolecular in nature through ^{1}H NMR studies. As can be found in [10], decreasing the concentration of C6-NO$_2$ in CDCl$_3$ from15.6mM to 0.2mM causes both N–H1 (near to nitro phenyl, $\Delta\delta$=0.57 ppm) and N–H2 (near to alkoxy phenyl, $\Delta\delta$=0.19 ppm) to shift upfield remarkably. Furthermore, both N–H1 and N–H2 of C6-NO$_2$ showed large shifts with temperature (5.85×10^{-3} and 7.74×10^{-3} ppm K^{-1}, respectively) in 20% DMSO-d_6/CDCl$_3$. These results strongly suggest that N–H groups were exclusively involved in intermolecular hydrogen bonding [10, 12, 13]. Based on SEM observations, XRD patterns, and IR and NMR spectra, it may be concluded that intermolecular hydrogen bonding is the driving force for the gel formation.

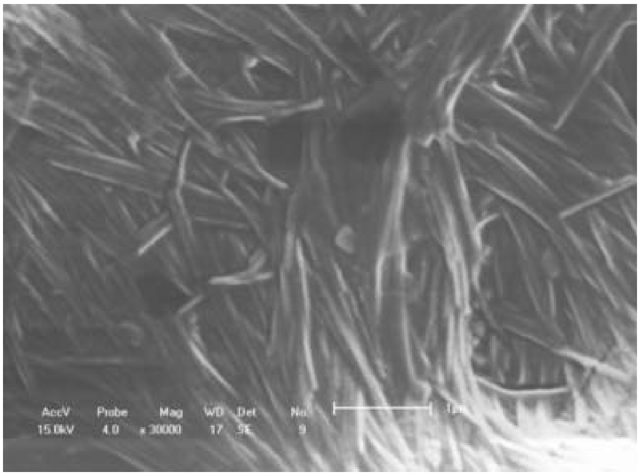

Figure 2. SEM image of xerogel from C6-NO$_2$ in chloroform (0.45 wt%).

Interestingly, although the dilute chloroform solution of C6-NO$_2$ was almost non-fluorescent, a strongly enhanced fluorescence emission was induced by the gelation process, as shown in figure 4. Isolated C6-NO$_2$ molecules in the dilute chloroform solution are considered to be significantly twisted, because the two aromatic rings were joined by the flexible linking group (–CO–NH–), which generally suppresses the radiative decay channel [14]. Through density functional theory

(DFT) geometry optimization [15], we found that the bond length of C–N in the hydrazide group is 1.36 Å (near to nitro phenyl) and 1.37 Å (near to alkoxy phenyl); which is much shorter than the theoretical value of the C–N single bond (1.47 Å), while almost the same as that of C=N (1.34 Å). This indicates that the C–N bonds in the hydrazide group possess partial double bond properties and, can be effectively conjugated with the aromatic rings, which must be the origin of the light emission. Moreover, a more planar and conjugated conformation of C6-NO_2 may be induced in the solid or other condensed states due to strong intermolecular forces, which tend to optimize the close packing between molecules [14, 16]. This aggregation-induced planarization extends the effective π-conjugation length in the C6-NO_2 molecules. Considering the head-to-tail arrangement in the xerogel, *J*-aggregation of C6-NO_2 molecules in the organogel may be another contribution to the enhanced emission. Consequently, the aggregation-induced enhanced emission (AIEE) phenomenon in the gelation process was attributed to the synergistic effect of aggregation-induced planarization and *J*-aggregate formation. This is evidenced by a remarkable red shift in photoluminescent spectroscopic studies. As shown in figure 4, the emission maximum peak of C6-NO_2 is red-shifted by about 60 nm with an impressive increase in PL intensity on going from the dilute solution to the organogel. Figure 4 also shows the absorption spectrum of C6-NO_2 in chloroform, which exhibited a maximum at about 260 nm. Because of the presence of a semi-rigid linking group as well as the fluorescence quenching nitro group, the PL intensity is somewhat weaker than that of luminescent materials, such as phenylene-vinylene derivatives. However, understanding the mechanism was thought to be important to mitigate aggregation quenching [16*a*].

4. Conclusion

We have demonstrated the unique self-assembling ability of the compound C6-NO_2, which showed a stable thermotropic SmA_1 phase and strong gelation ability in chloroform. A head-to-tail molecular arrangement within the layers was found both in the liquid crystalline state and in the xerogels. Intermolecular hydrogen bonding between the dihydrazide groups was demonstrated to be the major driving force for both self-assembling processes. Interestingly, aggregation-induced enhanced emission was observed in the organogels, and was attributed to aggregation induced planarization and *J*-aggregate formation.

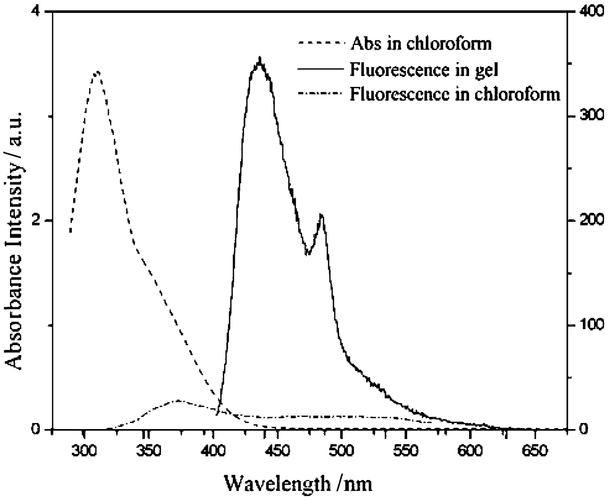

Figure 4. Absorption spectra of C6-NO_2 in chloroform (dashed line, 0.2mM); PL spectrum of C6-NO_2 gel in chloroform (solid line, 0.86 wt%), and in chloroform (dash dot line, 2.66×10^{-5} M).

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