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Low molecular weight organogelators derived from threefold symmetric tricarbamates

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ABSTRACT

A group of new low molecular weight organogelators based on threefold symmetric tricarbamate were synthesized and characterized. The tricarbamates with long alkyl chains were able to gelate a wide range of polar and nonpolar organic solvents such as acetonitrile and cyclohexane, generally at concentrations lower than 20 g/L. The best organogel formation was obtained using a threefold symmetric tricarbamate in *n*-dodecane, in which a sufficiently transparent gel was formed at the critical gelation concentration 1 g/L. Intermolecular hydrogen bonding by the tricarbamate in a nonpolar solvent benzene-*d*₆ was indicated by ¹H NMR spectra. Its maximum UV absorption was 11 nm higher in chloroform than in *n*-dodecane, and this red shift indicated increased conjugation between the benzene core and the carbamate substituents, which confirmed a change in its conformation from nonpolar to polar solvent. The self-assembling behavior of the tricarbamate in dilute solutions was investigated by TEM. Fiber-like networks were observed in a large range of solution concentrations.

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Introduction

Low Molecular Weight Organogelators (LMOGs) have been attracting attention not only for their potential applications ranging from oil spill remediation¹ to art conservation,² but also for their capacity to form a variety of interesting self-assemblies as fibers, sheets, tapes or strands that researchers do not fully understand.³ The gelation process of LMOGs is thermo-reversible: small molecules self-assemble into three-dimensional supramolecular networks that entrap solvents by surface tension. Models for supramolecular structures of the aggregates have been proposed, but the true nature of the aggregation phenomenon is still under investigation.^{4,5} Meanwhile, despite the fact that many efforts have been made to fully understand the mechanism and establish guidelines for the rational design of organogelators, many novel organogelators have been discovered by serendipity rather than design.^{3c,6}

In this communication, we report a new group of LMOGs based on threefold symmetric tricarbamates that were found during our study of a series of supramolecular atropisomers^{5a,7} and symmetric monomers with multiple reactive centers.⁸ In contrast to the numerous reports on LMOGs based on other N- and O-containing

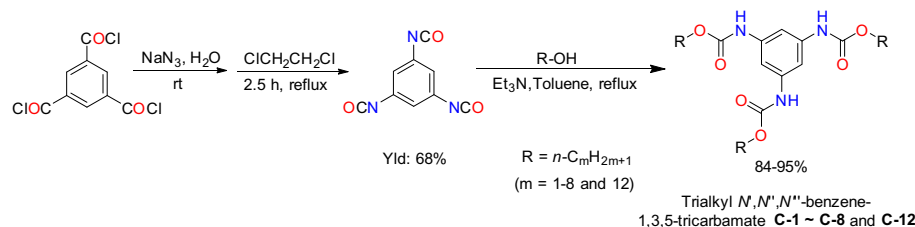
compound counterparts such as amide, amino, and urea, only a limited number of reports have studied LMOGs based mainly on intermolecular H-bonding of carbamate.⁹ There are a number of advantages of this new tricarbamate system: Their syntheses were accomplished using readily available and inexpensive benzene-1,3,5-tricarbonyl trichloride, sodium azide, and alcohols in good yields. Threefold symmetry allows installation of a corresponding side-chain group to each carbonyl group at the same time,¹⁰ with long alkyl group-containing chains generally improve solubility of the resulting compound. The tricarbamates showed good thermal stability due to the presence of a large conjugated system. Moreover, considering the multitude of alcohols that are commercially available or easy to synthesize, there is an opportunity to further tweak the properties of the LMOGs of threefold symmetric tricarbamates according to the future academic study or per industrial production requirements.

Result and discussion

Nine threefold symmetric tricarbamates were readily synthesized in excellent yield as shown in Scheme 1 by reacting the corresponding primary alcohol with 1,3,5-triisocyanatobenzene,¹¹ derived from 1,3,5-benzenetricarbonyl chloride in a two-step, one-pot reaction. After purification by column chromatography, tricarbamates were characterized by ¹H NMR, ¹³C NMR, FT-IR,

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Scheme 1. Synthesis of the tricarbamates.

and mass spectroscopy. The nine symmetric tricarbamates are labeled as **C-*n*** (**C-1** ~ **C-8** and **C-12**), where the *n* is the carbon number of its alkyl chain. Details of the synthetic procedure and characterization are included in the [supporting information](#). The tricarbamates were very stable under ambient conditions and did not decompose after one-year storage.

In contrast to the poor solubility of linear long-chain carbamates in most solvents,^{9d} threefold symmetric tricarbamates are generally soluble in common organic solvents. The increased solubility is perhaps because it is difficult for the three-armed carbamates to quickly form repeatable close packing in the solid state, especially for those with long alkyl chains.⁵ Their high solubility makes it easy to test the gelation properties. The gelation capability of this group of tricarbamates was tested with different solvents and shown in [Table 1](#). In a typical concentration of 20 g/L (2.6×10^{-2} M) in *n*-dodecane, the tricarbamates such as **C-1** and **C-2** with short alkyl side chains had relatively low solubility and formed crystalline precipitate, and crystals grew on the sidewall of the vial upon slow evaporation of the solvent. With the increase of the alkyl side chain length, the tricarbamates solubility in *n*-dodecane increased accordingly and did not precipitate rapidly. The partial organogels of **C-5** and **C-6** showed high viscosity, but could not pass the vial inversion test. However, as the alkyl chain length was further increased, the solid gels formed quickly and held their position during vial inversion. As shown in [Fig. 1](#), while **C-7** organogel lost about 5% of *n*-dodecane solvent during the vial inversion test, **C-8** and **C-12** organogel were able to completely immobilize the solvent.

Tricarbamate **C-12** was chosen to further study its gelation capability. It was found that **C-12** was able to form organogels with a wide range of solvents from polar solvents, like acetonitrile, to nonpolar solvents, such as toluene, generally at a critical gel concentration (CGC) around 20 g/L in these solvents. The results are summarized in [Table 2](#). Decalin and methylcyclohexane could be gelled at concentration of 10 g/L. The best gelation result of tricarbamate **C-12** was observed in a nonpolar solvent, *n*-dodecane, in which the critical gelation concentration of 1 g/L (1.3×10^{-3} M) was remarkably low. To the best of our knowledge, the above value of 1 g/L is among the best gelation capabilities of all reported organogelators. A further interesting feature is that the 1 g/L of tricarbamate **C-12** gel in *n*-dodecane is nearly transparent ([Fig. 2](#)), which expands its potential applications.

The formation of intermolecular hydrogen bonding was indicated by ¹H NMR spectra of tricarbamate **C-12** in benzene-*d*₆. As shown in [Fig. 3](#), as the concentration of the solution decreases from 100 mM to 1.5 mM, the chemical shift of the active proton of the carbamate group is gradually moved upfield.¹² The substantial upfield-shifting of the carbamate proton signal upon dilution is

consistent with the presence of intermolecular hydrogen bonding interaction in solution. Because the formation of strong intramolecular hydrogen bonding is impossible for compound **C-12** due to the location and distance between the three carbamate groups around the aromatic core, the concentration dependence of the N-H chemical shift can be explained by intermolecular hydrogen bonding. With the change of the concentration, the geometry and composition of the hydrogen bonded aggregates change accordingly, so the chemical environment change of hydrogen bonded N-H within the aggregates causes the upfield-shifting of its ¹H NMR signal. If the **C-12** molecules had presented as individual molecules in benzene-*d*₆, the N-H would have been able to freely find its most comfortable conformation despite its concentration and there would have not been significant change upon dilution.

As presented in [Fig. 4](#), the absorption maximum was at 234 nm in *n*-dodecane. In a more polar solvent, chloroform, it was shifted to 245 nm, which was 11 nm higher than in *n*-dodecane. Similar shifts of absorbance peak have been observed in benzene-1,3,5-tricarboxamides systems.¹³ The potential of forming six or more hydrogen bonds makes it unfavorable for the tricarbamate **C-12** or similar compounds to present as individual molecules in chloroform. Thus, the red shift might indicate an increase in conjugation between the benzene unit and the carbamate substituent due to conformational change in the hydrogen bonded aggregates from nonpolar *n*-dodecane to polar chloroform solvent.

To explore the supramolecular structure of the **C-12** organogel, powder X-ray Powder Diffraction (XRD) analysis was performed. There was only one small peak around 7 degrees and a broad peak around 20 degrees in the powder XRD pattern ([Fig. S8 in the ESI](#)), so the tricarbamate **C-12** did not form a well-defined crystalline aggregate as its tricarbamate and triamide analogues.^{5a,7} To explore the microscopic structure of the transparent organogel, electron microscopic analysis was performed. [Fig. 5a](#) shows a Transmission Electron Microscopy (TEM) image of the *n*-dodecane gel of tricarbamate **C-12** at a concentration of 1 g/L (1.3×10^{-3} M). From the TEM images, entangled fiber-like structures were observed with diameters ranging from about twenty to several hundred nanometers. The elongated self-assemblies reach dozens of micrometers in length, which is corresponding to thousands of tricarbamate molecules assembled together. During the testing of the critical gelation concentration of tricarbamate **C-12** in *n*-dodecane, it was found *n*-dodecane could still be partially congealed when the concentration was diluted to 5×10^{-4} M. Three concentrations of solution ranging from 10^{-4} to 10^{-5} M were cooled down from near the boiling point of *n*-dodecane, dried in the air, and photographed using TEM. As shown in the [Fig. 5 \(b–d\)](#), fiber-like structures were also

Table 1
Gelation capability of **C-1** ~ **C-8** and **C-12** in *n*-dodecane (20 g/L).

C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-12
Crystalline precipitate	Sparingly soluble	Suspension	Suspension	Partial gel	Partial gel	Solid gel	Solid gel	Solid gel

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