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Design and properties of glutamic acid-based coumarin derivatives as organogelators

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ABSTRACT

Two kinds of glutamaic acid-based coumarin derivatives show a quite different trend against gelation in organic solvents in terms of inter- or intramolecular hydrogen bonds involved. It has been found out that addition of the valinate structure into the coumarine derivative could improve its gelation ability.

1. Introduction

Organogels based on low-molecular-weight gelators have received significant attentions as novel functional soft materials.[1] Their attractiveness lies in bottom-up strategy inspiring the development of the next generation of functional soft matter. From these points of view various kinds of small organic molecules capable of gelation such as amides,[2] peptides,[3] ureas[4] and so forth have been investigated. The process of gelation is considered to arise from the self-assembly of the gelators into networks that entangle and entrap organic solvents.[5] These procedures generally require specific intermolecular non-covalent interactions, including hydrogen bonding, π-π stacking, van der Waals forces and charge-transfer interactions among organic gelators.

On the other hand organogelators consisting of various aromatic units, including naphthalene,[6] anthracene,[7] pyrene,[8] perylene,[9] and other π-conjugated molecules have been studied due to their potential applications. Thus, we have been interested in the gelators having the cyclophane component[10] showing a dynamic structure and the europium complex[11] exhibiting a strong red emission. It is still difficult to predict gelation from the molecular structure of the gelator candidate. In many cases gelators have been discovered by chance. However, some fundamental requirements for the design of the molecular structure of the gelator candidate seem to be somewhat apparent and in fact the long alkyl chains, the aromatic and the multi hydrogen-bondings work efficiently and cooperatively to form three-dimensional network in most gelators. These requirements imply that properties of gelators particularly depend on what kind of hydrogen bonding units and aromatic components employed. This concept prompted us to design the glutamic-based molecular structures combined with the coumarin skeleton because the partial participation of multi hydrogen bonds could be achieved by using the coumarin skeleton, realizing the regulation of intermolecular and intramolecular hydrogen bonds in the similar motif. The intramolecular hydrogen bonds are usually not involved in formation of the gel. Although some organogelators based on the coumarin structure have been reported,[12] the attempt to regulate the hydrogen bonds using the coumarin unit has not been carried out.

Thus, we here report preparation of gelator candidates consisting of the coumarin basic skeleton and investigation of their gelation properties in terms of intermolecular and intramolecular hydrogen bondings.

2. Results and discussion

Two kinds of the coumarin skeleton carrying the carboxyl group at the different position (1, 2) were prepared from citric acid and meldrum's acid, respectively, according to the reported methods.[13,14]

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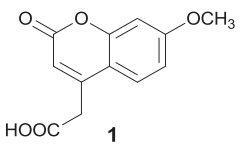
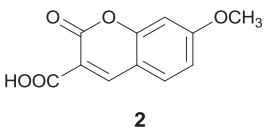




L-Glutamic acid derivatives having the alkyl chain were reacted with **1** or **2** using diethyl cyanophosphonate (DECP) in THF to give the desired coumarin derivatives (**3**, **4**)[14] as shown in Scheme 1. The gelation behaviors of the coumarine compounds (**3**, **4**) were studied in a variety of solvents by dissolution of the compound with heating in a given solvent, followed by cooling to room temperature and inversion of the vial.

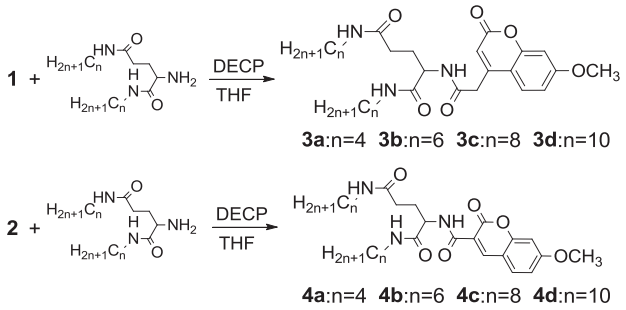
If the solution dose not flow out of the vial, the compound is designated to be a gelator for the corresponding solvent, denoted by the term "G". When the solvent is partially gelated, it is indicated by the term "PG" meaning a partial gel. If the compounds show no solubility in the solvent even when it is heated, the term "I" is assigned. When no change in the solution is observed after cooling the term is shown as "S". The term "P" is used for precipitates produced while cooling. Gelation properties of the compounds **3a-d** are summarized in Table 1.

No gel was formed in any solvents tried here for the compound **3a** having the short alkyl chain. Although the compounds **3a-d** are soluble in DMF and DMSO regardless of the length of the alkyl chain, distinct gelation of these solvents has not been observed. The compounds **3b** and **3c** gave a gel in chloroform, especially the compound **3c** can gelate chloroform at very low concentration.

On the other hand no gel was formed in chloroform by the compound **3d**. **3a** was not dissolved in chloroform. The aromatic solvents such as benzene and toluene can be gelated by **3d**. Partial gels of benzene and toluene were obtained by **3c**. Interestingly **3b** and **3c** afforded the partial gel in ethanol. As the example the optical image and SEM analysis of the gel from **3d** in toluene are shown in Fig. 1. A developed network of elongated fibers was observed.

The gelation test similar to **3a-d** was carried out for the compounds **4a-d**. Although the compounds 4b and 4c dissolved in chloroform, no gel was formed even at relatively high concentrations despite many trials. There was observed no particular change in the solutions of the compound **4d** in benzene or toluene on cooling. On the contrary the compounds **4b** and **4c** gave the precipitate in benzene or toluene solution when the temperature decreased. It should be noted that no gel has been formed from **4a-d** in any solvents examined even at high concentrations.

The molecular structures of **3a-d** are very similar to those of **4a-d** except the connection between the coumarin skeleton and the amide group. These two kinds of compounds also show similar solubility, however, their tendency as the gelators is quite different



Scheme 1. Preparation of coumarin derivatives **3** and **4**.

Table 1
Gelation properties of coumarin derivatives (**3a-d**) in various solvents.[a]

	Coumarin derivative			
	3a	**3b**	**3c**	**3d**
Hexane	I	I	I	I
Cyclohexane	I	I	I	I
DMF	S	S	S	S
DMSO	S	S	S	S
Ethanol	I	PG	PG	S
Chloroform	I	G(9.0)	G(0.5)	S
Bebzene	I	I	PG	G(8.5)
Toluene	I	I	PG	G(8.0)

The values given in parentheses are the minimum concentration (wt%) to achieve gelation.
[a] I: insoluble, S: soluble, PG: partial gel, G: gel.

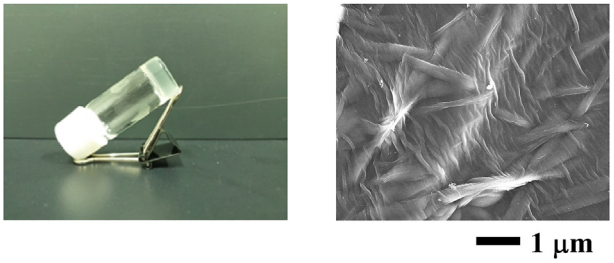
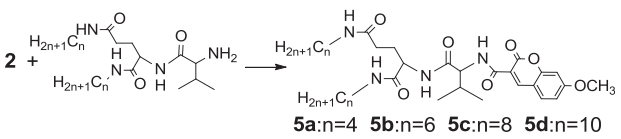


Fig. 1. Optical and SEM images of gel from **3d** in cyclohexane.

each other as shown above. It has been well known that intermolecular hydrogen-bondings play a key role in formation of three-dimensional network resulting in the gel. In both structures there exist three amide groups which could contribute formation of the intermolecular hydrogen-bondings. However, the oxygen atom of the carbonyl group on the coumarin skeleton possibly forms the hydrogen-bonding with the neighboring amide group resulting in an intramolecular hydrogen-bonding in **4a-d**. This might be supported by formation of the stable 6-membered ring. In order to confirm involvement of the carbonyl group on the coumarin skeleton in the intramolecular hydrogen-bonding IR spectroscopy has been employed. The stretching of the carbonyl group on the coumarin skeleton in **1** was observed at 1718 cm^{-1}. The corresponding carbonyl group in **3** exhibited its stretching at the same wavenumber as that in **1**. Although the stretching at 1743 cm^{-1} was confirmed for the carbonyl group on the coumarin skeleton in **2**, the corresponding stretching shifted to 1696 cm^{-1} in **4**. This result strongly suggests that the carbonyl group on the coumarin skeleton in **4** participates in the intramolecular hydrogen-bonding. Such an intramolecular hydrogen-bonding could not be involved in intermolecular aggregate formation.

It is noted that one amide unit adjacent to the aromatic ring could be crucial for gel formation. In order to assure this point we have introduced one more amide unit using valine moiety into the basic skeleton of the compound **4**. Thus, we have prepared the coumarin derivatives consisting of two kinds of amino acid moieties (**5a-d**)[14] as shown in Scheme 2.

Gelation properties of **5a-d** were examined. The results are



Scheme 2. Preparation of coumarin derivatives **5**.