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Organogelators based on metacyclophane skeleton having urea units in the bridge

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ABSTRACT

Metacyclophanes having the urea units in their bridge have been prepared. It has been found out that some of them afford stable organogels in some solvents. It was also observed that addition of fluoride anion broke DMSO gel, and then this gel was formed again by addition of MeOH.

1. Introduction

Self-assembly is a key approach for the creation of the next generation of functional soft materials.[1] Supramolecular gels by self-assembly of the low-molecular-weight organogelators (LMOGs)[2] have received a great deal of attention because they are not only fundamental scientific interests, but also have a wide range of applications in various areas. Among a huge number of gelator candidates the gelators consisting of the cyclic component have also been investigated because of various functions relevant to the cyclic structure. As those cyclic gelators, macrocyclic compositions such as calixarene,[3] resorcinarene,[4] cucurbit[7]uril,[5] crown ether,[6] cyclodextrin,[7] cyclophane,[8] and dehydrobenzoannulene-based macrocycles[9] have often been employed. In contrast we have been interested in small-sized [n.n]metacyclophanes in terms of their specific π systems due to the strong transannular π-electronic interactions between aromatic components in close proximity.[10] As a gelator consisting of the small-sized cyclic component the [2.2]paracyclophane-bridged imidazole dimer with tetrapodal urea moieties forming organogel was reported.[11] We also have developed the [3.3]metacyclophanes having the urea units at outer position of the cyclophane skeleton that are capable of gelating some organic solvents.[12]

On the other hand bis-urea macrocycles assemble to form columnar nanotubes by their stacking based on the hydrogen bondings.[13] Thus, introducing the urea units into the bridge of the small-sized cyclophanes, it could be expected to create a new class of a cyclophane gelator.

Here we have designed metacyclophanes which carry the urea units in their bridges and investigated their gelating properties.

2. Results and discussion

We have synthesized two kinds of the cyclophane derivatives with the urea units introduced in their bridges as shown in Scheme 1. 5-Alkoxy-1,3-bis(aminomethyl)benzenes **1a–d** were obtained by reduction of the corresponding azides prepared in five steps from 5-hydroxyisophthalic acid with hydrogen gas in the presence of 10% Pd/C in the yields of 75–88%. 3,4,5-trialkoxybenzoic acid chlorides **2a–d** were prepared in three steps from ethyl gallate in the yields of 78–85%. The coupling of **2a–d** and dimethyl 5-aminoisophthalic acid, followed by reduction, chlorination, treatment of sodium azide and reduction gave the corresponding 1,3-bis(aminomethyl)benzenes carrying three long alkyl groups **3a–d** in the yield of 43–55% from the starting material. The reaction of **1a–d** and *m*-xylylene diiocyanate in chloroform under highly dilute conditions afforded the corresponding cyclophanes having the urea group in the bridge **4a–d** in the yields of 58–69%. Using the similar coupling reactions of **3a–d** with *m*-xylylene diiocyanate the cyclophanes carrying three long alkyl chains **5a–d** were obtained in the yields of 38–56%.

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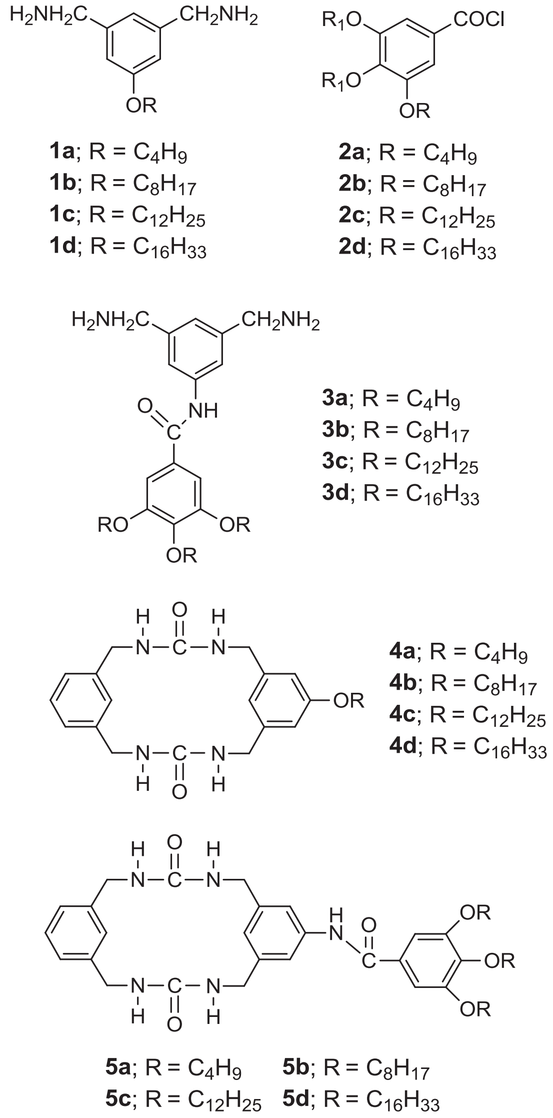

Scheme 1. Chemical structures of metacyclophanes having the area units in the bridges.

We have examined 15 kinds of solvents for the gelation behaviors of the cyclophanes **4a**–**d**, however, they show very poor solubility regardless of the length of the alkyl chains. Although all cyclophanes were well dissolved in DMSO by heating, the precipitate was produced on cooling. DMF can also dissolve the cyclophanes except **4a** by heating.

In contrast of DMSO formation of gel was confirmed for **4b**–**d** during cooling down to the room temperature in DMF. The minimum concentrations of **4b**, **4c** and **4d** to gelate DMF are 12%, 9% and 8%, respectively. Fig. 1 shows the optical image and the SEM analysis of the gel from **4d** in DMF. Relatively thick fibers were observed.

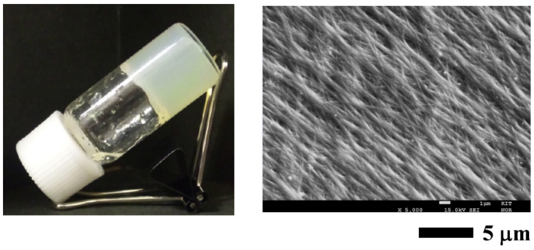

Fig. 1. Optical and SEM images of gel from **4d** in DMF.

Introducing three alkyl long chains, better solubility has been achieved. Thurs, the gelation properties of the cyclophanes **5a**–**d** were examined in various solvents as summarized in Table 1.

Table 1
Gelation properties of cyclophanes (**5a**–**d**) in various solvents

Cyclophane	5a	5b	5c	5d
H_2O	I	I	I	I
DMSO	S	G (2.0)	G (1.0)	PG
DMF	G (8.0)	G (4.0)	G (4.0)	PG
$CHCl_3$	I	PG	PG	PG
CH_2C1_2	I	I	P	P
CH_3CN	P	I	I	I
Acetone	PG	I	I	I
Ethyl acetate	I	I	I	I
Ethanol	G (0.2)	G (0.2)	I	I
Methanol	P	I	I	I
2-Propanol	G (0.2)	G (0.2)	G (0.2)	I
Toluene	I	PG	PG	G (5.0)
Benzene	I	PG	PG	G (5.0)
Hexane	I	I	P	PC

I:insoluble, S:soluble, G:gel, PG:partial gel.
The values given in parentheses are the minimum concentration (mg/mL) to achieve gelation.

A wide variety of solvents can be gelated by the cyclophanes **5a**–**d**. **5b** and **5c** gave a stable gel in DMSO and DMF, however, a partial gel was only formed by the cyclophane **5d** having the long alkyl chain (C16) because of its excellent solubility for these solvents. The partial gel means that the gel once formed on cooling tends to collapse after a while. In contrast **5d** is the only cyclophane that can gelate toluene and benzene while **5b** and **5c** give a partial gel. Alcohols such as ethanol and 2-propanol can be effectively gelated by **5a**–**c** at a low concentration. As an example the optical image and the SEM analysis of the gel formed from **5d** in benzene are shown in Fig. 2. Developed fibers can be observed.

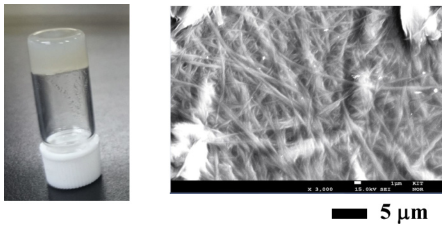

Fig. 2. Optical and SEM images of gel from **5d** in benzene.

Driving force for formation of gel is considered as the extension of hydrogen-bonding networks. Thus, the behavior of the amide and urea protons reflecting formation of the hydrogen-bondings of **5b** in DMSO-d_6 was examined by using the temperature-dependent NMR as shown in Fig. 3.

As the temperature was lowered both signals of amide and urea protons showed downfield shifts. A slight broadening of the urea protons was also observed. These results indicate that building of hydrogen-bonding networks is induced on cooling resulting in formation of gel.

It has been known that a urea-based molecules show a strong binding affinity for fluoride anion.[14] Addition of fluoride anion might have some effect on the gel state because the urea units play a key role in formation of gel. Thus, to DMSO gel formed by **5b** was added DMSO solution of tetrabutylammonium fluoride. After the