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Ultrasound induced formation of organogel from a glutamic dendron

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Abstract—New L-glutamic acid based dendritic compounds: *N*-(2-naphthacarbonyl)-L-glutamic acid diethyl ester (NGE) and *N*-(2-naphthacarbonyl)-1,5-bis(L-glutamic acid diethyl ester)-L-glutamic diamide (NBGE) were designed. Although NGE could not form any gels in common solvents, NBGE could form stable gels in hexane, toluene, and water under ultrasound. Three dimensional network structures composed of fibers with various diameters were observed in the gel by SEM and TEM. FTIR spectral measurement revealed that ultrasound during cooling of the solution could destroy some of the hydrogen bond interactions and caused the gel formation. In solution, no CD signal was detected because the naphthyl chromophore is far from the chiral center. In the gel, however, CD signals assigned to the naphthyl group were observed, which indicated that the chirality of the chiral center could be transferred to the chromophore in the supramolecular organogel system.

1. Introduction

Gels are one class of important soft materials, in which liquids are immobilized by solutes. Although gels are widely found in polymer systems, there has recently been an increasing interest in low-molecular weight organogels.[1] In the organogels, small molecules are usually organized through the intra or intermolecular non-covalent interactions such as hydrogen bonds,[2] π–π stacking,[3] and ionic interactions[4] to form network structures in which the solvent is trapped. Such organogels have some advantages over polymer gels: the molecular structure of the gelator is defined and the gel process is usually reversible. Such properties make it possible to design various functional gel systems and produce more complicated, defined as well as controllable nanostructures. In order to form appropriate organogels, there are two important points. One is the design of the gelator molecules. The other is the adjustment of the external conditions. It is generally accepted that the external conditions such as the temperature, pH, light, and others have a great effect on the formation of the organogel.[5] In this paper, we report the ultrasound induced formation of organogels based on a newly designed L-glutamic acid based dendron.

Dendritic gelators,[6] the structure of which is between low-molecular weight gelators and polymer gelators, have received particular attention because dendritic molecules possess some of the advantages of both low-molecular weight and polymeric gelators. Some peptide based dendritic gelators including two component systems have been reported.[7] Glutamic acid is a good building block for supramolecular assemblies and several gelators containing glutamic acid have also been developed.[8] Previously, we have also designed a bolaform L-glutamic acid derivative and found that this compound showed remarkable gelation ability and formed helical structures with a mixed ethanol/water solvent.[9] Here, we designed and synthesized two new L-glutamic acid based dendritic compounds: *N*-(2-naphthacarbonyl)-L-glutamic acid diethyl ester (NGE) and *N*-(2-naphthacarbonyl)-1,5-bis(L-glutamic acid diethyl ester)-L-glutamic diamide (NBGE). In these compounds, the L-glutamic acid diethyl ester was directly attached to a naphthyl ring and unusually the compounds have no long alkyl chain. We have found that although NGE could not form any organogel in many solvents, NBGE could form gel in a lot of solvents. Furthermore, it was found that only under ultrasound organogels could be formed. Characterization of the organogel by SEM and TEM revealed three dimensional networks composed of nanofibers with various diameters. We have investigated the effect of the ultrasound on the formation of such organogels in detail and found that various kinds of hydrogen bond interactions among the molecules play an important role in the formation of the gel. Ultrasound can disrupt some kinds of hydrogen bond, which caused the

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precipitation of the molecule and induced the formation of the stable organogel.

2. Results and discussion

2.1. Synthesis

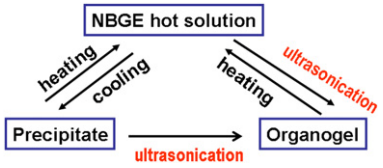
The target compounds are synthesized according to Scheme 1.

The synthesis started with 2-naphthoic acid purchased from Aldrich. Using a known modified method with $SOCl_2$, 2-naphthoic acid was transformed into its chloride, which was condensed with L-glutamic acid diethyl ester giving amide NGE.

Ester protecting groups were removed by NaOH in methanol to yield the deprotected acid NGA. Then the acid NGA was condensed with L-glutamic acid diethyl ester again in the presence of *N*,*N*′-dicyclohexylcarbodiimide (DCC) as a dehydrant and 4-dimethylaminopyridine (DMAP) as a catalyst and the target product NBGE was obtained after column chromatographic purification.

2.2. Gel formation

The gelation properties of compounds *N*-(2-naphthacarbonyl)-L-glutamic acid diethyl ester (NGE) and NBGE were tested in a range of solvents by means of the inverted test-tube method. In a typical experiment, the compound was dissolved in a solvent with the aid of few drops of good solvent (dichloromethane or THF for low polarity systems; DMSO, THF, or methanol for aqueous systems) and heated. The solution was then allowed to cool down to room temperature under ambient condition or under ultrasound. In the case of NGE, no gel could be formed in any condition. This may be due to the weak intermolecular interactions between NGE and good solubility in the solvent. In the case of NBGE, however, stable gels either in low polarity solvents such as hexane and toluene, or in high polarity water, were obtained under ultrasound. This is similar to the gelation properties of dendritic gelators based on lysine derivatives reported by Smith et al.[7a,e] Very interestingly, we have found that ultrasound is necessary for gel formation. Without ultrasound, only NBGE precipitated. This implied that ultrasound can influence the aggregation properties of NBGE molecules in the solvents. In addition, through the ultrasound of the precipitate in the solvent, an organogel could also be obtained. For the sake of clarity, such a process is illustrated in Scheme 2. The process between NBGE hot solution and precipitate or organogel was reversible upon heating and cooling. The organogel is very stable at ambient temperature. From the precipitate, we can also obtain the organogel through ultrasonication.



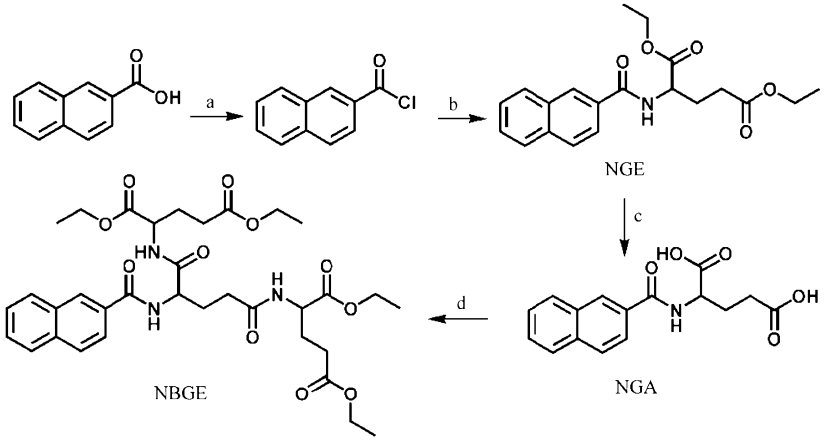
Scheme 2. Schematic illustration of the process to obtain the organogel.

2.3. Morphology

To get a deeper insight into the aggregation mode of the gels, the morphologies of xerogels were observed by SEM and TEM. Figure 1 gives the SEM and TEM pictures of the xerogel from hexane and from water. In Figure 1A, a network composed of many fibrous structures is observed. The width of each single fiber is about 50 nm, and its length can be extended to tens of micrometers. These fibers tangled and aggregated to form some fibrous structures with lager width (~200 nm). The TEM pictures confirmed the above results, and even clearer network structures could be seen from the TEM image. Although the drying process may influence the original structures of the gel, both SEM and TEM observations confirmed that the NBGE molecules self-assembled to form slim fibers when the solution was cooled, and then these fibers aggregated or tangled to form more thick fibers. Similar fiber structures were obtained from water system (Fig. 1C and D).

2.4. FTIR spectra

It is well-known that hydrogen bonding plays an important role in the formation of organogels. In order to further clarify



Scheme 1. Synthetic procedure for the two dendrons: (a) $SOCl_2$, benzene, reflux; (b) TEA, CH_2Cl_2, 80%; (c) methanol/H_2O, NaOH, 90%; (d) TEA, DCC, DMAP, 65%.

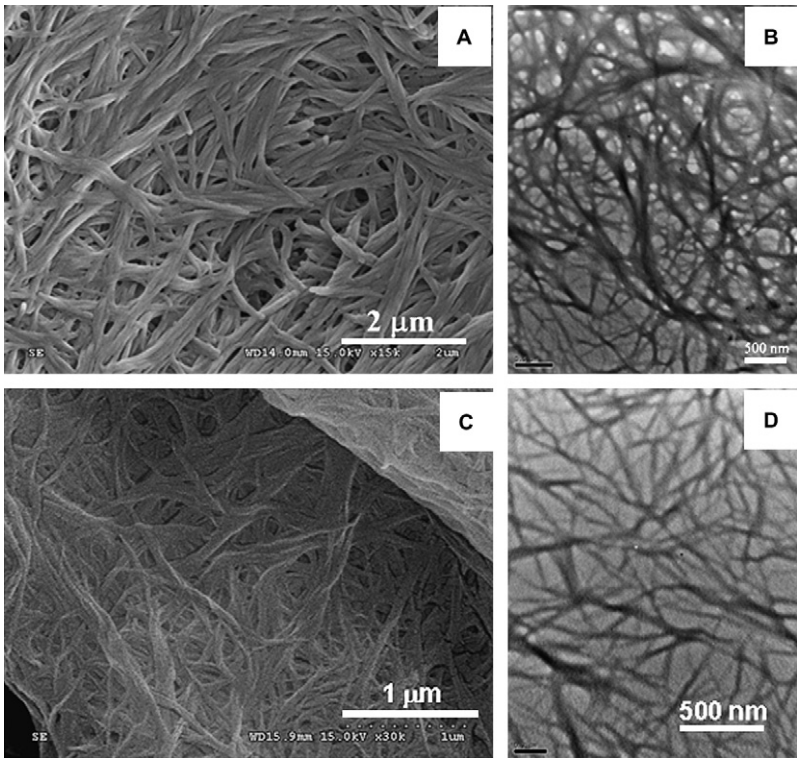


Figure 1. SEM (A, C) and TEM (B, D) images of xerogel of NBGE from hexane (A, B) and from water (C, D); the scale bar is 2 μm, 500 nm, 1 μm, and 500 nm, respectively.

this, we have measured the FTIR spectra of NBGE both in solution and xerogel forms. Figure 2 shows the FTIR spectra of NBGE in different conditions. In Figure 2d, which is the spectrum of the NBGE chloroform solution, three main peaks are observed at 3356, 1736, and 1682 cm^{-1}. These bands can be assigned to the N–H stretching, C═O stretching of ester, and the amide I band, respectively. As far as the xerogel was concerned (Fig. 2a and b), these bands shifted to 3308, 1731, and 1637 cm^{-1}, respectively. The red-shift of these bands indicates H-bond formation in the gel state. Because both the C═O stretching signal of the ester and the amide groups were red-shifted, we can conclude that there exists at least two types of H-bonds in the gel. One is formed between two amide groups, and the other is formed between amide and ester groups. Compared with the spectra of xerogels from different solvents, we found that the spectrum of xerogel from hexane is almost the same as that from water. This implies that there are similar H-bond interactions in these xerogels, even though they are from very different solvent systems. The amide II band in the range from 1500 to 1600 cm^{-1} turned from three peaks in solution to one broad band in the xerogel. This further supported the H-bond formation in the organogel.

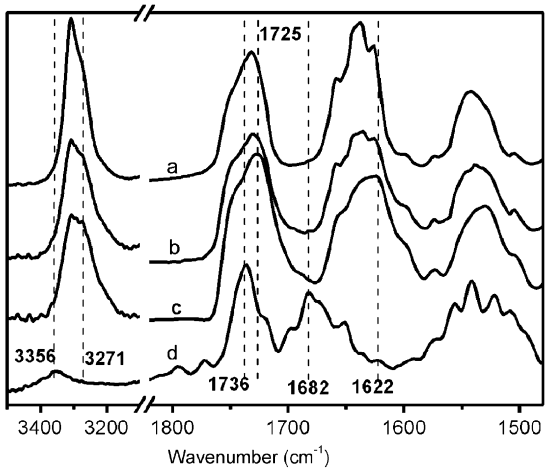


Figure 2. FTIR spectra of NBGE xerogel from hexane (a), from water (b), NBGE precipitate from hexane (c), and NBGE chloroform solution (d).

In order to clarify the effect of ultrasound on gel formation, we further measured the IR spectrum of NBGE precipitate from hexane, as shown in Figure 2c. This precipitate was obtained by cooling NBGE solution without ultrasound. In the spectrum of the precipitate, three strong bands appeared at 3271, 1725, and 1622 cm^{-1}, which is more red-shifted in comparison with those of the xerogels. This indicates that there were stronger H-bond interactions in the precipitate than in the xerogel sample. These data clearly indicated that there are many sites to potentially form hydrogen bonds. When the clear solution at elevated temperature was cooled down without perturbation, strong H-bonds between the molecules would occur and finally cause the precipitation of the compounds in solvent. However, if the solution was subjected to the ultrasound, some of the hydrogen bond would be destroyed and an organogel was formed. In order to further confirm this, we put the precipitate in hexane solvent to the ultrasound and found that organogel was also formed after several minutes. FTIR measurement showed the same spectrum as that of the gel formed by cooling under ultrasound. Recently, some literature has reported the ultrasound induced gel systems of low-molecular weight

gelators,[10] but they did not show why ultrasound is necessary. Here, we have clearly shown that in a multi-hydrogen bonding system, too much hydrogen bonding between the molecules could only produce precipitate, while ultrasound could partially destroy the hydrogen bond network and benefits the formation of the organogel.

2.5. UV–vis and CD spectra

We have further investigated the role of the naphthyl group in the gel by measuring the UV–vis spectra of both the gel and solution, as shown in Figure 3. It is observed that π–π transition of naphthalene group blue-shifted from 233 nm in the solution to 224 nm in the gel, indicating that the chromophore stacked in a face-to-face manner or H-aggregate in the gel state. Obviously, the π–π stacking of naphthalene group is another driving force for the formation of the gel in this system. Since the compound has a chiral center based on the glutamic acid, we have also measured the CD spectra of both solution and gel. No CD signal was detected for the naphthyl group in the ethanol solution. This may be due to the fact that the chromophore is far from the chiral center. However, when we measured the CD spectrum of the gel, we observed a positive Cotton effect in the range from 250 to 300 nm and a negative Cotton effect at 224 nm in gel state. The position of the Cotton effect is consistent with the absorption maximum of the compound, indicating that a supramolecular chirality is obtained for the gel system. Such chirality could be regarded as the chiral transfer from the chiral center localized in the L-glutamic acid to the chromophore through the non-covalent interactions in the gel system.

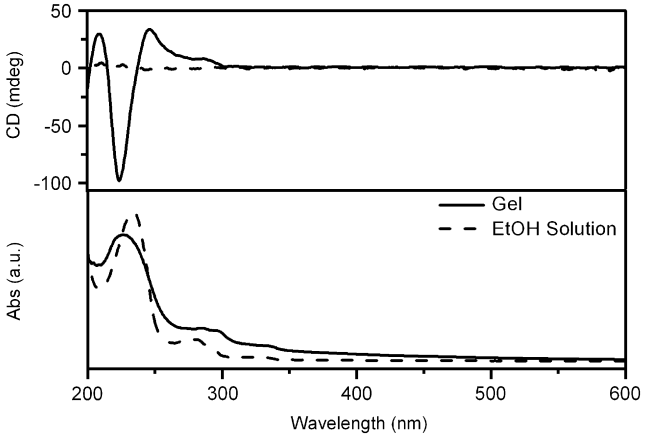


Figure 3. UV–vis (bottom) and CD spectra (up) of the NBGE solution (10 mg/mL) and its gel from hexane (10 mg/mL).

3. Conclusion

Two new L-glutamic acid based dendrons: *N*-(2-naphthacarbonyl)-L-glutamic acid diethyl ester (NGE) and *N*-(2-naphthacarbonyl)-1,5-bis(L-glutamic acid diethyl ester)-L-glutamic diamide (NBGE) were designed and their gelation ability in various solvents was discussed. The lower generation dendron could not form a gel due to weak intermolecular interaction and good solubility in the solvent. The higher generation dendron formed organogel under ultrasound. The ultrasound is necessary in the present system. It was revealed that ultrasound destroyed some of the hydrogen bonds in the system. The results suggested that an appropriate intermolecular interaction, neither too strong nor too weak, is necessary for the formation of the organogel. In addition, it was confirmed that the chirality of the chiral center could be transferred to the chromophore in the supramolecular organogel system.

4. Experimental

4.1. General

All the starting compounds were used as received. Solvents were purified and dried according to literature methods. TLC was performed on silica gel HF254 and column chromatography on silica gel of 230–400 mesh size. NMR spectra were recorded with a Bruker ARX400 (400 MHz) spectrometer in chloroform ($CDCl_3$) or DMSO-d_6 using Me_4Si as an internal standard. FESEM was performed using a Hitachi S-4300 system and TEM images were obtained on a JEM-100CXII electron microscope operating at accelerating voltages of 15 and 100 kV, respectively.

4.2. Synthesis of *N*-(2-naphthacarbonyl)-L-glutamic acid diethyl ester (NGE)

Step a: 2-naphthoic acid (1.72 g, 0.01 mol) was suspended in dry benzene (50 mL) and then $SOCl_2$ (2 mL) was added. The mixture was refluxed under strong stirring for 4 h. The solvent and the surplus $SOCl_2$ were then removed by rotary evaporation and yellowy solid, 2-naphthacarbonyl chloride was obtained and using without further purification.

Step b: L-glutamic acid diethyl ester hydrochloride (2.40 g, 0.01 mol) was dissolved in dry CH_2Cl_2 (40 mL) and triethylamine (TEA) (3 mL) was added to the solution. The mixture was stirred for 30 min at room temperature. Then 2-naphthacarbonyl chloride dissolved in dry CH_2Cl_2 (40 mL) was added dropwise to the above solution within 30 min. The mixture was stirred for another 2 h. After the reaction, the solution was washed with 0.01 M HCl (3×30 mL) and pure water (3×30 mL), and dried over $MgSO_4$. The solvent was removed by rotary evaporation and crude product was obtained. After recrystallization from ethanol/diethyl ether, fine crystals were obtained, mp: 99 °C (2.88 g, 80%). FTIR (KBr): 3345, 1728, 1624, 1522, 1013 cm^{-1}. ^1H NMR ($CDCl_3$), δ (ppm): 1.22 (t, 3H, J=8.0 Hz, CH_3), 1.32 (t, 3H, J=8.0 Hz, CH_3), 2.20–2.54 (m, 4H, CH_2), 4.12 (q, 2H, J=4.0 Hz, –OCH_2), 4.28 (q, 2H, J=4.0 Hz, –OCH_2), 4.86 (q, 1H, J=4.0 Hz, CH), 7.16 (d, 1H, J=8.0 Hz, ArH), 7.54–7.59 (m, 2H, ArH), 7.86–7.95 (m, 4H, ArH), 8.35 (s, 1H, NH). ESI-MS, calculated for $C_{20}H_{23}NO_5$: 357.2; found: 358.2 ($M+H^+$, 100%), 380.2 ($M+Na^+$). Elemental analysis, calculated for $C_{20}H_{23}NO_5$ (%): C 67.21, H 6.49, N 3.92; found: C 67.31, H 6.55, N 4.06.

4.3. Synthesis of 2-(2-naphthacarbonyl)-L-glutamic acid (NGA)

NGE (3.57 g, 0.01 mol) was dissolved in methanol (50 mL). NaOH (4 g, 0.1 mol) was dissolved in water (50 mL). Under

stirring, the NaOH solution was added into NGE solution dropwise. After the mixture was stirred for 12 h at room temperature, the solution was neutralized by 0.1 M HCl. Then methanol was removed by rotary evaporation and acidified by 0.1 M HCl. Obtained white solid was filtered and dried under vacuum, mp: 179 °C (2.70 g, 90%). FTIR (KBr): 3290, 1708, 1638, 1538 cm^{-1}. ^1H NMR (DMSO-d_6), δ (ppm): 1.95–2.15 (m, 2H, CH_2), 2.38–2.42 (q, J=4.0 Hz, 2H, CH_2), 4.44–4.50 (q, 1H, J=4.0 Hz, CH), 7.59–7.65 (m, 2H, ArH), 7.95–8.05 (m, 4H, ArH), 8.50 (s, 1H, NH), 8.77–8.79 (d, 1H, J=8.0 Hz, ArH), 12.45 (br, 1H, –OH). ESI-MS, calculated for $C_{16}H_{15}NO_5$: 301.1; found: 324.1 ($M+Na^+$, 100%), 340.1 ($M+K^+$), 302.1 ($M+H^+$). Elemental analysis, calculated for $C_{16}H_{15}NO_5$ (%): C 63.78, H 5.02, N 4.65; found: C 64.14, H 5.10, N 4.75.

4.4. Synthesis of *N*-(2-naphthacarbonyl)-1,5-bis(L-glutamic acid diethyl ester)-L-glutamic diamide (NBGE)

L-Glutamic acid diethyl ester hydrochloride (3.6 g, 0.015 mol) was dissolved in dry CH_2Cl_2 (60 mL) and triethylamine (TEA) (6 mL) was added in the solution. After the mixture was stirred for 30 min, NGA (1.5 g, 0.005 mol), DCC (3 g, 0.015 mol), and DMAP (0.03 g, 0.00024 mol) were added in the mixture. The mixture was stirred for 24 h at room temperature. The produced white solid was removed by filtration and the obtained solution was washed with 0.01 M HCl (3×30 mL) and pure water (3×30 mL), and dried over $MgSO_4$. The solvent was removed by rotary evaporation and crude product was obtained. After purified by silica column chromatography (THF/*n*-hexane=1/2, R_f=0.34), the target product was obtained as fine white solid, mp: 117 °C (2.23 g, 65%). FTIR (KBr): 3307, 1733, 1640, 1536, 1025 cm^{-1}. ^1H NMR ($CDCl_3$), δ (ppm): 1.19–1.32 (m, 12H, CH_3), 2.40–2.51 (m, 12H, CH_2), 4.08–4.23 (m, 8H, –OCH_2), 4.60–4.62 (m, 3H, CH), 7.53–7.66 (m, 2H, ArH), 7.85–7.96 (m, 4H, ArH), 8.14 (t, 1H, J=8.0 Hz, ArH), 8.33 (s, 1H, NH). ESI-MS, calculated for $C_{34}H_{45}N_3O_{11}$: 671.3; found: 694.3 ($M+Na^+$, 100%), 672.3 ($M+H^+$), 710.3 ($M+K^+$). Elemental analysis, calculated for $C_{34}H_{45}N_3O_{11}$ (%): C 60.79, H 6.75, N 6.26; found: C 60.14, H 6.32, N 6.05.

4.5. Gel test

A gelator (10.0 mg) and appropriate solvent (1.0 ml) were mixed in a closed-capped test tube and the mixture was heated until the solid was dissolved. The solution was subsequently cooled in air or under ultrasound to room temperature. Gelation was determined by the absence of flow of the solvent when the tube was inverted.

4.6. CD and UV–vis spectra

CD and UV–vis spectra were obtained using JASCO J-810 CD and JASCO UV-550 spectrophotometers, respectively. The gel sample was cast on a quartz slide and then the solvent was evaporated in vacuum. The obtained quartz slide was used for spectral measurement. In the process of CD spectrum measurement, the slides were placed perpendicular to the light path and rotated within the film plane to avoid polarization-dependent reflections and eliminate the possible angle dependence of the CD signals.

4.7. FTIR spectra

FTIR spectra were obtained by a JASCO FT/IR-660 plus spectrophotometer. The gel sample was cast on a silica slide and dried in vacuum. Then the FTIR spectra were measured using blank silica as background. The FTIR spectrum of the solution was obtained from 0.1 mM solution in dry chloroform using pure chloroform as background. The measurement was done using a 1 mm KBr cell and scanning from 1000 to 4000 cm^{-1}.

Acknowledgements

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