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Optically active polymer film tuned by a chirally self-assembled molecular organogel

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Abstract—Chirally-oriented lipid aggregates were doped into a solid polymer film, which was readily prepared by casting and removing a solvent from anionic L-glutamide-derived organogels and polystyrene. When a cationic achiral dye was mixed into this system, the resultant polymer film showed tunable circular dichroism (CD) due to chiral complex formation with the achiral dye on the highly-ordered structures based on the L-glutamide lipid.
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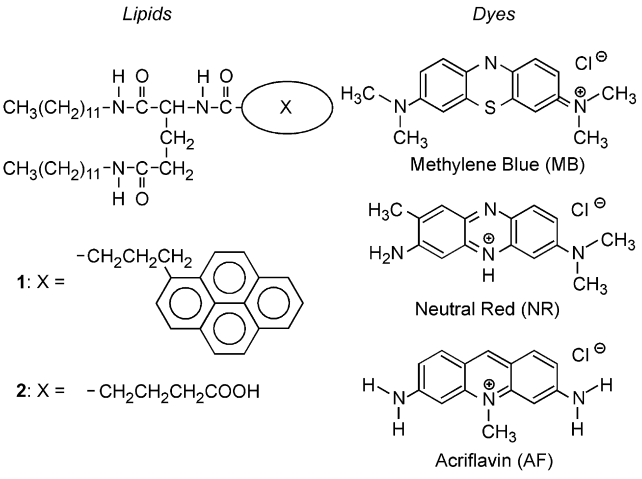
1. Introduction

Organogel systems with self-assembling low molecular compounds have been attractive as a construction tool for bottom-up nanotechnology because they are essentially generated through three-dimensional network formation from nano-sized one-dimensional fibrillar aggregates, constructed of highly-ordered assemblies like aqueous lipid bilayer membranes. It is also known that a number of chiral compounds form nano-sized one-dimensional unique aggregates with large curvatures such as nanotubes, nanohelices, and nanoribbons.[1] These aggregates are morphologically interesting and applicable as templates for the creation of nanomaterials. Gu et al.[2] and Hafkamp et al.[3] reported mesoporous polymer materials by using organogel systems. They were prepared by polymerization of a monomer, which was used as a solvent to produce an organogel and subsequent extraction of the nanofibrillar aggregates from the polymer. The other application has been the construction of inorganic nanomaterials by condensation of alkoxysilane or chlorosilane with self-assembled fibrous/helical aggregates as templates.[4] This template method has been also developed to create various inorganic,[5] metal,[6] and polymer[7] nanomaterials.

A specific circular dichroism (CD) signal is often observed in organogel systems[8–10] because of the chirality of organogelators. These CD patterns are rather unique compared with molecular chirality because they are usually induced by long-range chiral orientation among the chromophoric groups. Therefore, observed CD spectra are useful as an indicator to estimate their oriented structures. The enhanced chirality is one of the attractive features of self-assembling molecules and useful for sensing and switching because the chiral orientation of the molecules is strongly affected by environmental factors such as temperature, pH, and additives. We have reported that L-glutamide-derived lipids (Scheme 1), as chiral self-assembling compounds, can form gels in organic solvents. This is brought about through nanofibrous network formation and entrapment of solvent.



Scheme 1. Chemical structures of L-glutamide-derived lipids and cationic dyes.

Keywords: L-Glutamic acid; Induced circular dichroism; Self-organization; Nanofibrils; Polymer composite.
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Here, when a pyrenyl group was introduced onto the head part (**1**) as a chromophoric group, an enhanced CD signal was observed around the absorption band of the pyrenyl group.[11] This indicates that the process is driven by chiral stacking of the pyrenyl groups into highly-ordered structures. However, unfortunately the assembly is not stable because a temperature-induced gel-to-sol transition is commonly accompanied by disappearance of chiral stacking. To increase mechanical strength and heat stability of enhanced chirality, we have investigated the immobilization and stabilization of specific chiral microenvironments from an L-glutamide lipid by using a polymerizable solvent and following photo-induced (UV-light) polymerization.[10] By this method, both the CD pattern and strength could be maintained in the resultant polymer film and was stable even at temperature above the original gel-to-sol phase transition temperature.

The present work is aimed to develop this method for the preparation of optically active polymer composites because there are still some disadvantages: for instance, the chromophoric group of an organogelator is decomposed by photo (UV-light) irradiation. Also a mechanical property of the resultant polymer film is hardly controllable because of difficulty in controlling the polymerization degree. In this article, we introduce a facile method to create an optically active polymer composite using an L-glutamide lipid-derived organogel and also demonstrate that the resultant optical activity is quite tunable by induced chirality based on a doped achiral dye.

2. Results and discussion

2.1. Pyrenyl group-induced chirality

The lipid **1** (0.5 mM) and poly(methylmethacrylate) (PMMA, 500 unit-mM) were dissolved in benzene at 70 °C and then cooled to 10 °C to form a gel. Fibrous network formation was observed both in the cast film and xerogel[12] by TEM and SEM, respectively. No similar aggregates were found in the absence of **1**. The TEM image (Fig. 1a) indicates that the minimum diameter of the fibrous aggregates is approximately 30 nm, which corresponds to almost 10 lipid molecules. Therefore, it is estimated that the aggregates entangle each other, which leads to three-dimensional network structures.

The critical aggregation concentration (cac) and critical gelation concentration (cgc) of **1** in a benzene solution exist at 0.2–0.5 mM and 2.0–3.0 mM at room temperature, respectively.[11] No significant change in these values was found in the mixed system with PMMA. Figure 2 (left) shows UV and CD spectra of the mixed system. It is found that a strong CD signal was detected at 10 °C but not at 70 °C. This is due to the fact that the mixed system underwent a gel-to-sol phase transition at temperature around 60 °C. To support this, DSC measurement showed distinct endothermic peaks at 59 °C and 67 °C. These phenomena are very close to those in the absence of PMMA. This indicates that PMMA does not disturb the aggregation of **1** and that the gelation due to **1** is brought about through the formation of chirally-ordered aggregates at temperatures below their phase transition temperature.

The solid film was prepared by casting the mixture on a glass plate and removal of solvent. The resultant film was almost transparent and colorless. Figure 2 includes UV and CD spectra of the film. The CD pattern was similar to that in the gel at 10 °C but no change was observed, even at 70 °C. These results indicate that the specific chirality from the aggregates of **1** remains, even after casting, and is stable at elevated temperature. Here, we have established a facile method to immobilize specific chirality based on a **1**-organogel into a polymer solid film.

2.2. Chirality tune with induced chirality

It would be supposed that the CD pattern would be tunable by changing the head group of the L-glutamide-derived lipid.

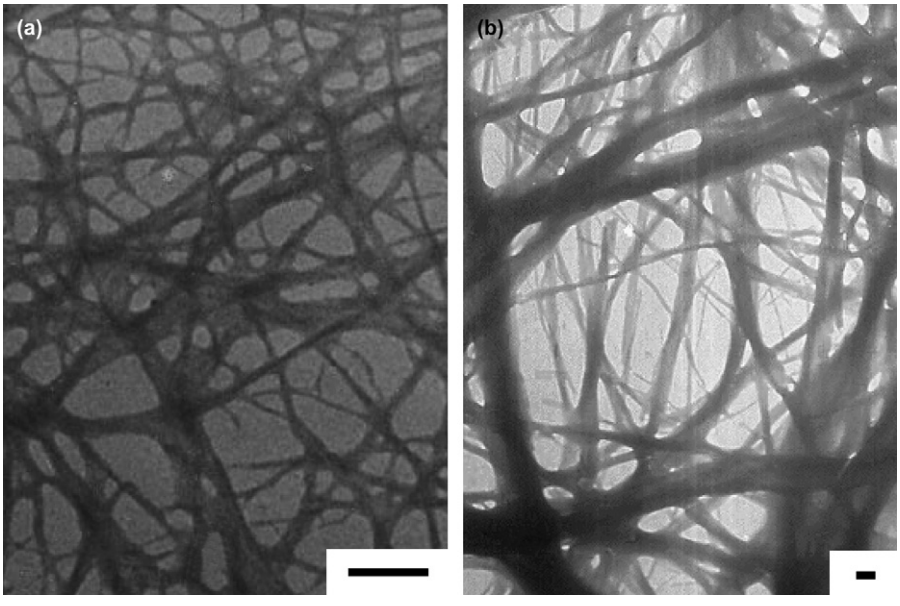


Figure 1. TEM images of **1** (a) and **2** (b) aggregates prepared from benzene solutions. Scale bars indicate 200 nm.

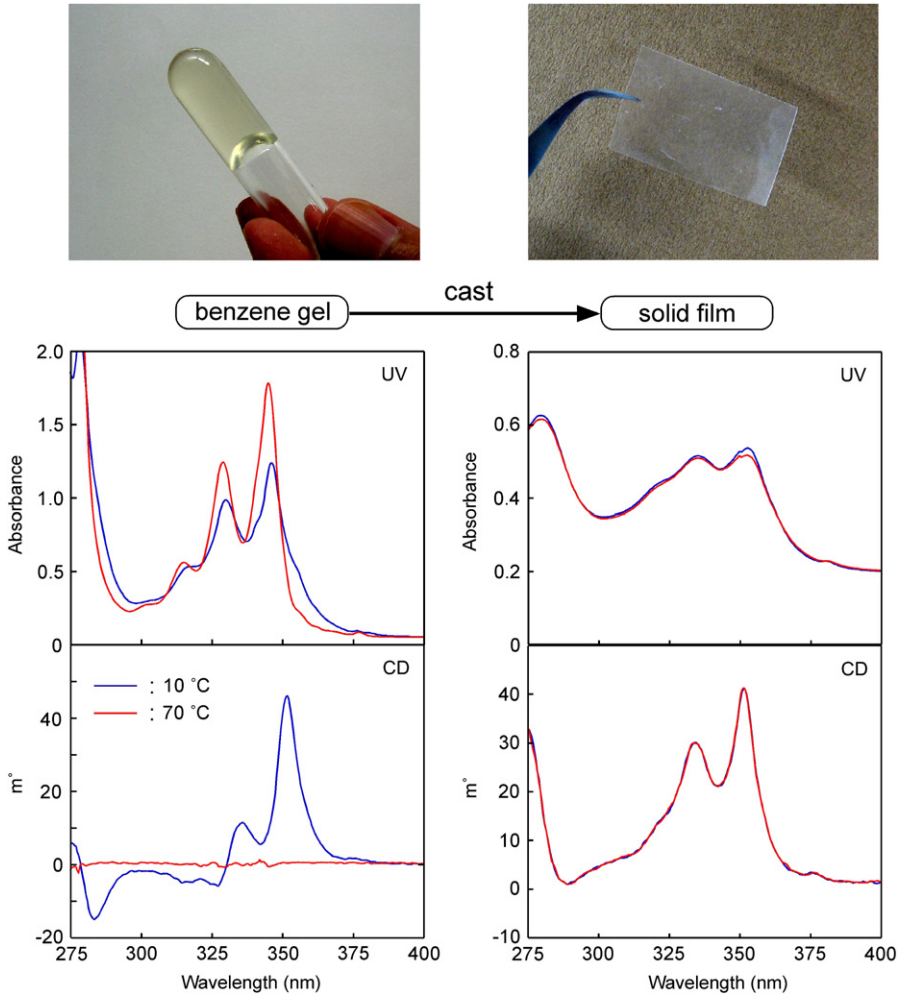


Figure 2. UV and CD spectra of **1** aggregates–PMMA mixed system in a benzene solution (left) and in a solid film (right) at 10 °C and 70 °C. Benzene solution: [**1**]=0.5 mM, [PMMA]=500 unit-mM.

For instance, azobenzene[8] and spiropyran[13] derivatives formed highly-ordered structures with specific chirality in organic solvents. However, a bulky chromophoric group often prevents adequate molecular packing for highly-ordered aggregation. On the other hand, it is well known that a chiral stacking phenomenon can be induced in achiral molecules bound to chirally-oriented aggregates.[9,14,15] Therefore, a dye-on-lipid aggregate complex as a host–guest system would be attractive and useful to tune the optical activity of a polymer composite film because the combination of self-assembled aggregates and a chromophoric guest molecule can be easily varied.

On the basis of this idea, we applied an induced CD (ICD) effect for preparing optically active polymer composites. For this purpose, we selected lipid **2** as an organogelator because we have already found that **2** can form fibrous aggregates in organic solvents such as benzene, toluene, and cyclohexane, and when a cationic achiral cyanine dye was added to the **2**-benzene gel, distinct ICD appeared around the absorption band of a cyanine dye.[9] In the present work, we used several cationic dyes, such as methylene blue (MB), acriflavin (AF), and neutral red (NR) instead of a cyanine dye because a cyanine dye is relatively fragile in light and also very sensitive when subjected to environmental factors.

An ethanol solution of MB as an achiral guest molecule was added to a benzene solution of a mixture of **2** and polystyrene as a supporting polymer. The final concentrations of **2**, MB, and polystyrene were adjusted to 5 mM, 0.25 mM, and 400 unit-mM, respectively. The solvent ratio of benzene and ethanol was 100:1. The mixed solution was heated to 70 °C and cooled rapidly to 10 °C and then aged for 15 min. The solution formed a transparent blue organogel. The organogel was shaken well in a vial to become a liquid and cast on a glass plate to obtain a blue solid film (Fig. 3c). Figure 4 shows UV and CD spectra of a **2**–MB mixture in a benzene solution and a solid film. The absorption band appeared at 655 nm as λ_{max} in a sol state (at 70 °C), which was assigned to a monomeric dispersion state of MB. In a gel state (at 10 °C), the λ_{max} shifted to 607 nm accompanied with induction of CD with a positive signal at 667 nm and a negative signal at 594 nm. These results indicate that MB undergoes a monomer-to-aggregate transition[16] according to a sol-to-gel transition of the solution of **2** and the observed CD signals are induced for both monomeric and *H*-like aggregated MBs. It should be also noted that CD spectra showed almost no change in the absence and presence of polystyrene, and thus the chiral environment experienced by MB due to **2**-aggregates is therefore insensitive to polystyrene.

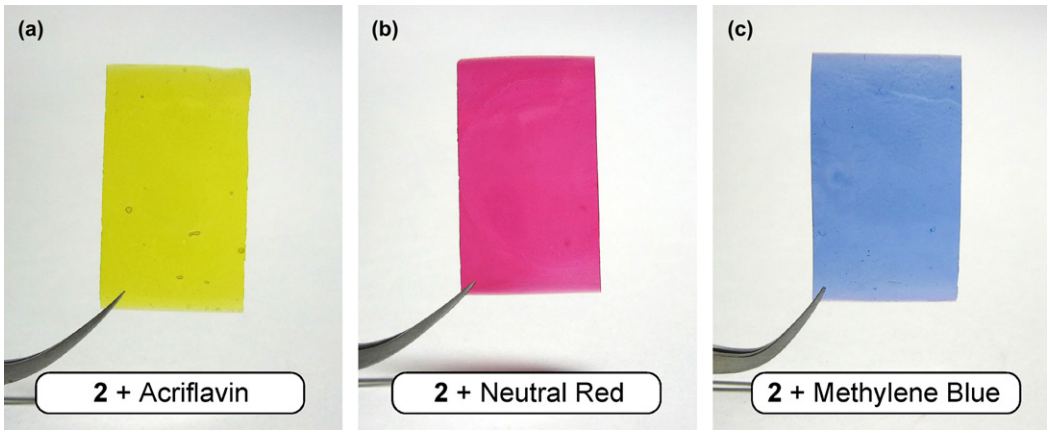


Figure 3. Photos of polymer composite films prepared from the **2**–cationic dye mixture in benzene.

UV and CD spectra of the MB-containing solid film are shown in Figure 4. There are several similarities with the case of the pyrenyl lipid **1** system: (1) aggregation of MB was promoted while the monomer-to-aggregate composition was slightly different, (2) ICD was detected, and (3) there was no significant change in the CD pattern and its intensity was independent of temperature.

A similar procedure was applied for the other cationic dyes, AF and NR, and transparent yellow (Fig. 3a) and red (Fig. 3b) solid films were obtained, respectively. Typical CD spectra are shown in Figure 5. The CD patterns, which appeared at each absorption band of the dyes in benzene solution, were retained in the solid films. Therefore, the optical activity of the polymer films is readily tunable by proper selection of dyes.

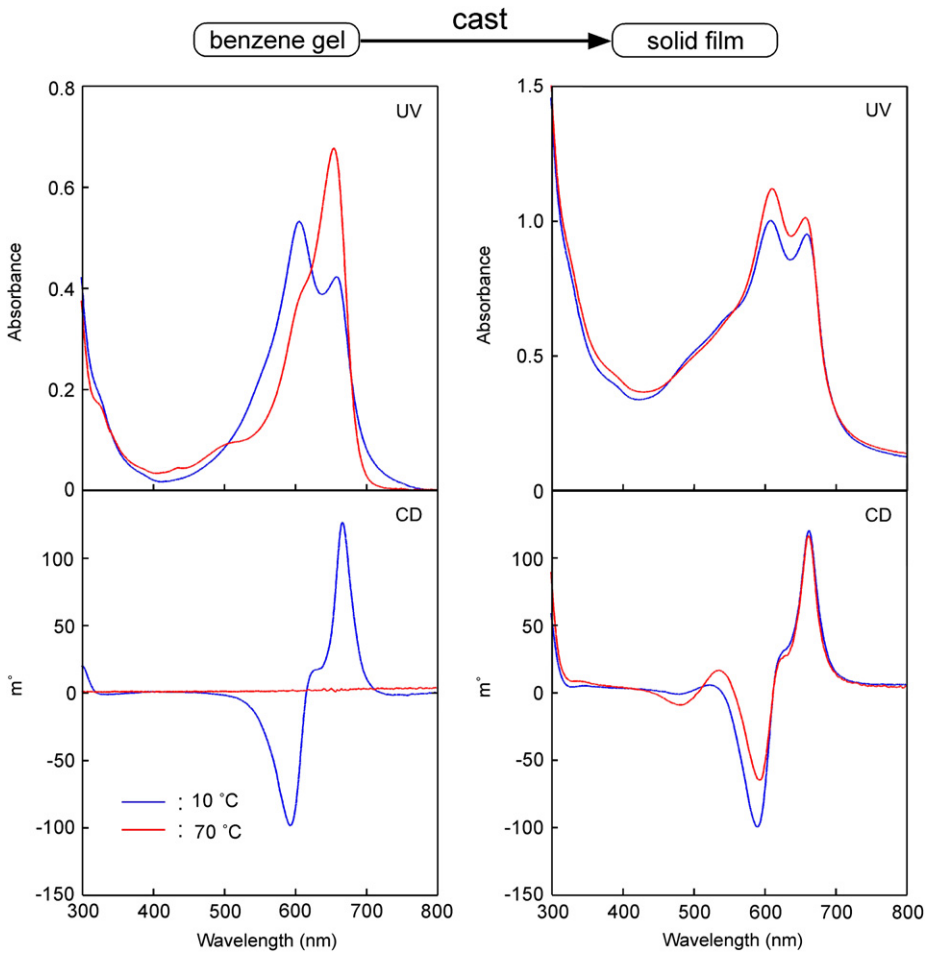


Figure 4. UV and CD spectra of methylene blue (MB) with **2** and polystyrene in a benzene solution (left) at 10 °C and 70 °C, and in a solid film (right) at 10 °C before and after heat treatment at 70 °C for 10 min. Benzene solution: [MB]=0.25 mM, [**2**]=5 mM, [polystyrene]=400 unit-mM.

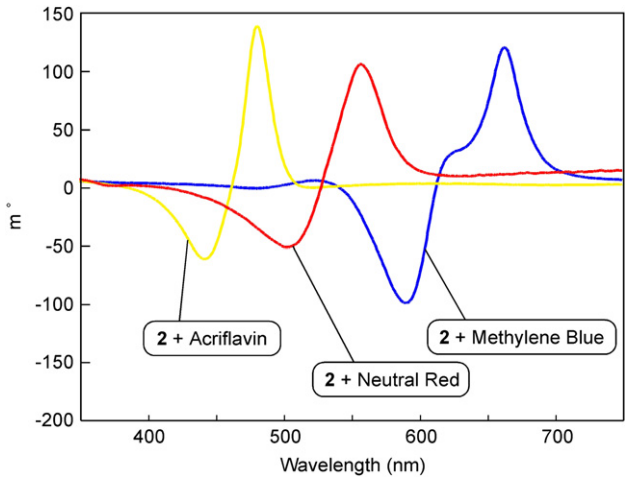


Figure 5. CD spectra of cationic dyes with **2**-aggregates in polystyrene films. Solid films were prepared from benzene solutions ([AF]=[MB]=0.25 mM, [NR]=0.50 mM, [**2**]=5 mM, [polystyrene]=400 unit-mM).

3. Conclusions

Generation and enhancement of supramolecular functions are often observed in self-assembling systems. Induction of chirality is one of the typical features of self-assembling systems. In this study, we have established a facile method to embed a supramolecular complex composed of chirally-ordered lipid aggregates and achiral dyes into a solid polymer film. As a result, optical activity of the polymer film is readily tunable using ICD around the absorption bands of the dyes as schematically illustrated in Figure 6. This method would be useful for the design of new soft materials with interesting optical properties.

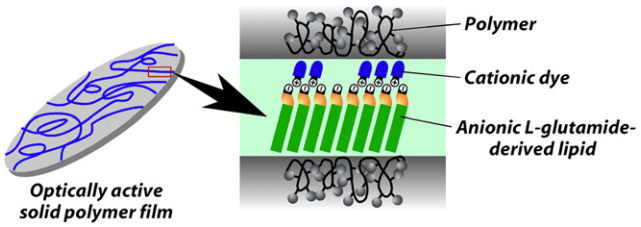


Figure 6. Schematic illustration of optically active solid polymer film.

4. Experimental

4.1. General information

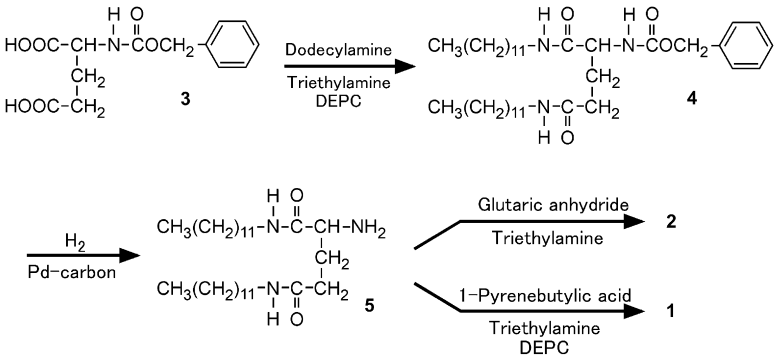
All chemicals were reagent grade and purchased from chemical suppliers. The polymerization degrees of PMMA and polystyrene were 13,500–14,000 and 2700, respectively. The L-glutamide-derived lipids with pyrene or carboxylic acid head group were synthesized as shown in Scheme 2. The chemical structures of these compounds were identified by melting point, FTIR, ^{1}H NMR, and elemental analysis. Melting points were determined on a micro melting point apparatus. FTIR spectra were performed on a JASCO FT/IR-4000 spectrometer. ^{1}H NMR spectra were recorded by a JEOL JNM-EX400 spectrometer using tetramethylsilane as an internal standard. The following abbreviations are used: s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, and b=broad.

4.1.1. Preparation of N^1,N^5-didodecyl-N^2-benzyloxycarbonyl-L-glutamide (4). *N*-Benzyloxycarbonyl-L-glutamic acid (**3**, 7.0 g, 25 mmol), dodecylamine (12 ml, 53 mmol), and triethylamine (8.9 ml, 63 mmol) were dissolved in THF (350 ml). The solution was cooled to 0 °C and diethylphosphorocyanidate (DEPC) (10 ml, 64 mmol) was added to the solution. The mixture was stirred for 1 h at this temperature. After being stirred for 12 h at room temperature, the solution was concentrated in vacuo, and the residue was dissolved in chloroform. The solution was washed with 0.2 M NaOH (aq), 0.2 M HCl (aq), and water. The solution was dried over Na_2SO_4, concentrated in vacuo, and the residue was recrystallized from methanol to yield white solid powder: yield 10.7 g (68%); mp 141–143 °C; IR spectrum (KBr) 3287 (N–H), 2917 (C–H), 2850 (C–H), 1686 (C=O, urethane), 1637 (C=O, amide), 1536 (N–H); ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) δ 0.88 (t, J=6.84 Hz, 6H, CH_3), 1.20–1.37 (m, 36H, CH$_3$ (CH_2)$_9$), 1.43–1.54 (m, 4H, CH_2CH$_2$NHC(=O)), 1.91–2.15 (m, 2H, CH_2C*), 2.23–2.43 (m, 2H, NHC(=O)CH_2), 3.10–3.35 (m, 4H, CH_2NHC(=O)), 4.09–4.20 (m, 1H, *CH), 5.10 (s, 2H, CH_2-Phe), 7.29–7.45 (m, 5H, aromatics). Elemental analysis. Found: H, 10.9; C, 71.8; N, 6.75. Calcd for $C_{37}H_{65}N_3O_4$: H, 10.6; C, 72.1; N, 6.82%.

4.1.2. Preparation of N^1,N^5-didodecyl-L-glutamide (5). Compound **4** (10.0 g, 16 mmol) was dissolved in 300 ml of ethanol with heating and Pd–carbon (1 g) was added to the solution. H_2 gas was bubbled slowly into the solution for 8 h at 70 °C. Pd–carbon was removed by filtration. The solution was concentrated in vacuo and the residue was recrystallized from methanol to yield a white solid powder: yield 6.77 g (88%); mp 117–118.5 °C; IR spectrum (KBr) 3324 (N–H), 2917 (C–H), 2810 (C–H), 1632 (C=O, amide), 1528 (N–H); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.88 (t, J=6.82 Hz, 6H, CH_3), 1.15–1.38 (m, 36H, CH$_3$(CH_2)$_9$), 1.41–1.70 (m, 4H, CH_2CH$_2$NHC(=O)), 1.83–2.03 (m, 2H, CH_2C*), 2.22–2.41 (m, 2H, NHC(=O)CH_2), 3.14–3.30 (m, 4H, CH_2NHC(=O)), 3.35–3.47 (m, 1H, *CH), Elemental analysis. Found: H, 12.2; C, 72.1; N, 8.74. Calcd for $C_{29}H_{59}N_3O_2$: H, 12.3; C, 72.3; N, 8.72%.

4.1.3. Preparation of N^1,N^5-didodecyl-N^2-[4-carboxybutanoyl]-L-glutamide (1). Compound **1** was synthesized according to the previous report;[11] mp 190–195 °C; Elemental analysis. Found: H, 9.6; C, 77.5; N, 5.4. Calcd for $C_{49}H_{73}N_3O_3$: H, 9.8; C, 78.2; N, 5.6%.

4.1.4. Preparation of N^1,N^5-didodecyl-N^2-[4-carboxybutanoyl]-L-glutamide (2). Compound **5** (2.0 g, 4.2 mmol) and triethylamine (1.75 ml, 12.6 mmol) were dissolved in 50 ml of THF and glutaric anhydride (0.96 g, 8.4 mmol) was added to the solution. After being stirred for 1 day at room temperature the solution was concentrated in vacuo. The residue was recrystallized from methanol and dried in vacuo, which gives a white solid powder: yield 0.76 g (32%); mp 145–147 °C; IR spectrum (KBr) 3294 (N–H), 2920 (C–H), 2851 (C–H), 1701 (C=O, carboxylic acid), 1635 (C=O, amide), 1546 (N–H); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.87 (t, J=6.84 Hz, 6H, CH_3), 1.15–1.38



Scheme 2. Synthetic procedure of L-glutamide-derived lipids.

(m, 36H, $(CH_2)_9$), 1.90–2.17 (m, 4H, CH_2C^*, $CH_2CH_2C(=O)OH$) 2.20–2.54 (m, 6H, $NHC(=O)CH_2$, $NHC(=O)CH_2CH_2CH_2C(=O)OH$), 3.11–3.34 (m, 4H, $CH_2NHC(=O)$), 4.40–4.45 (m, 1H, *CH). Elemental analysis. Found: H, 11.0; C, 67.1; N, 6.94. Calcd for $C_{34}H_{65}N_3O_5$: H, 11.0; C, 68.5; N, 7.05%.

4.2. Measurements

Transmission electron micrographs were recorded by using a JEOL JEM-2000FX. The samples were spotted on polyvinylformal-coated copper grids (200 Å). After excess of the samples was removed by a tissue paper and air-dried, they were stained with 2 wt % aqueous ammonium molybdate. UV–vis and CD spectra were recorded on a JASCO V-560 and JASCO J-725 spectrometers, respectively, and temperature was controlled by Peltier thermostatted cell holder.

Acknowledgements

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