Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Fabrication of TiO_2 using L-lysine-based organogelators as organic templates: a control of their nanostructures

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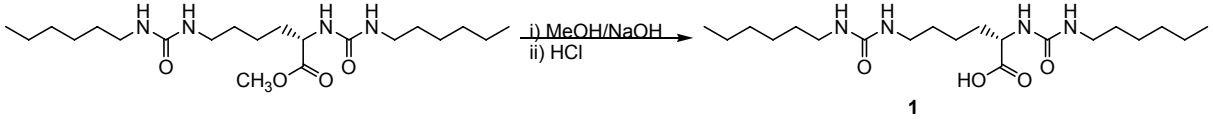
Experimental

Materials

Methyl 2,6–diisocyanatohexanoate (LDI) prepared by L–lysine was obtained from the Kyowa Hakko Kogyo Co., Ltd. N^{ε}-Lauroyl–L–lysine was obtained from the Ajinomoto Co., Inc. N^{α}, N^{ε}–Bis(hexylaminocarbonyl)–L–lysine methyl ester was prepared according to the literature.[1] N^{ε}–Lauroyl–L–lysine ethyl ester was synthesized by the method reported previously.[2] The other chemicals were of the highest commercially available grade and were used without further purification. All solvents used in the syntheses were purified, dried, or freshly distilled as required.

Synthesis

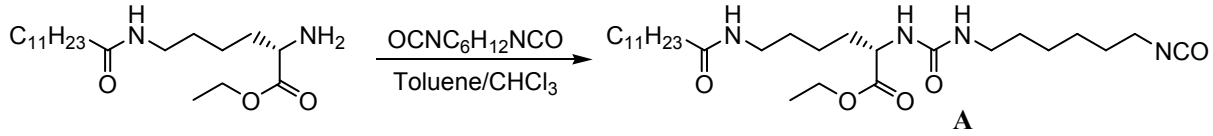
N^{ε},N^{α}–Bis(hexylaminocarbonyl)–L–lysine (**1**)



1

N^{ε}–Bis(hexylaminocarbonyl)–L–lysine methyl ester (10 mmol) was dissolved in MeOH–H_2O (400 ml–20 ml) and 4M NaOH (5 ml) was added. The reaction mixture was heated at 70°C for 24 h. The resulting solution was evaporated to ca. 100 ml, and water (600 ml) was added. The aqueous solution was adjusted to ca. pH = 1 by addition of 6M HCl with vigorous stirring. The white precipitate was filtered, washed with water, and then dried. The product was obtained by reacrystallization from MeOH-ethyl acetate (92%). IR (KBr): 3334 cm^{-1} (νN–H), 1782 cm^{-1}, 1701 cm^{-1} (νC=O, CO_2H), 1621 cm^{-1} (νC=O, urea), 1582 cm^{-1} (δN–H); ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ = 0.87 (t, J = 6.6Hz, 6H; C*H3*), 1.27 (br, 14H; alkyl), 1.38–1.51 (m, 6H; $CH_2CH_2NHCON^{\varepsilon}HCH_2CH_2$, $N^{\alpha}HCONHCH_2CH_2$), 1.71–1.81 (CH_2CH), 3.11 (br, 6H; $CH_2NHCON^{\varepsilon}HCH_2$, $N^{\alpha}HCONHCH_2$), 4.26 (br, 1H; C*H*), 5.41 (br, 1H; $N^{\alpha}HCONH$), 5.64 (br, 1H; $NHCON^{\varepsilon}H$), 5.89 (br, 1H; $N^{\alpha}H$), 6.19 (br, 1H; $N^{\varepsilon}H$). Elemental analysis calcd (%) for $C_{20}H_{40}N_4O_4$ (400.56): C, 59.97; H, 10.07; N, 13.99. Found: C, 60.14; H, 10.22; N, 14.03.

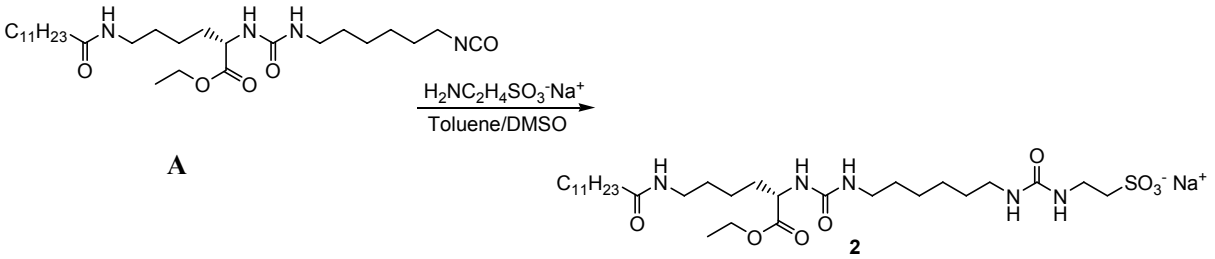
N^{α}-(6-Isocyanatehexylaminocarbonyl)-N^{ε}-lauroyl-L-lysine ethyl ester



A

To a dry toluene-$CHCl_3$ solution (500ml; toluene 100ml and $CHCl_3$ 400 ml) of 1,6-hexamethylenediisocyanate (600 mmol), a dry THF solution (200 ml) of N^{ε}-lauroyl-L-lysine ethyl ester (60 mmol) was slowly added with vigorous stirring. The resulting solution was evaporated to *ca*. 150 ml, and then the ethyl ether (700 ml) was added with stirring. The white precipitate was filtered, washed with ether, and then dried (92%). IR (KBr): 3354 cm^{-1} (νN–H, urea), 3296 cm^{-1} (νN–H, amide A), 2261 cm^{-1} (–NCO), 1730 cm^{-1} (νC=O, ester), 1641 cm^{-1} (νC=O, amide I), 1625 cm^{-1} (νC=O, urea), 1562 cm^{-1} (δN–H, urea), 1549 cm^{-1} (δN–H, amide II). ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ = 0.88 (t, J = 6.6 Hz, 3H, C*H*$_3$), 1.25–1.44 (m, 25H, alkyl), 1.45-1.55 (m, 4H, C*H*$_2$CH$_2$CON$^{\varepsilon}$H, C*H*$_2$CH$_2$NCO), 1.58–1.65 (m, 4H, NHCONHCH$_2$C*H*$_2$, N$^{\varepsilon}$HCH$_2$C*H*$_2$), 1.67–1.88 (m, 2H, C*H*$_2$CHN$^{\alpha}$H), 2.16 (t, J = 6.8 Hz, 2H, C*H*$_2$CON$^{\varepsilon}$H), 3.14-3.26 (m, 4H, NHC*H*$_2$, N$^{\varepsilon}$HC*H*$_2$), 3.29 (t, J = 6.6 Hz, 2H, C*H*$_2$NCO), 4.18 (q, J = 7.1 Hz, 2H, OC*H*$_2$), 4.38–4.43 (m, 1H, C*H*), 4.91 (t, J = 5.6 Hz, 1H, N*H*), 5.34 (d, J = 7.6 Hz, 1H, N$^{\varepsilon}$*H*), 5.82 (t, J = 5.6 Hz, 1H, N$^{\alpha}$*H*). Elemental analysis calcd (%) for $C_{28}H_{52}N_4O_5$ (524.74): C, 64.09; H, 9.99; N, 10.68. Found: C, 64.17; H, 10.21; N, 10.69.

*Sodium N^{α}-[6-(2-ureidoethylsulfonate) hexylaminocarbonyl]-N^{ε}-lauroyl-L-lysine ethyl ester(**2**)*



A **2**

To a dry $CHCl_3$ solution (200ml) of **A** (20 mmol), a dry DMSO solution (20 ml) of taurine sodium salt (21 mmol) was added, and then the reaction mixture was heated at 100°C for 10 min. The resulting solution was evaporated to dryness. The product was obtained by reacrystallization from MeOH–ether (93%). IR (KBr): 3355 cm^{-1} (νN–H, urea), 3294 cm^{-1} (νN–H, amide A), 1731 cm^{-1} (νC=O, ester), 1640 cm^{-1} (νC=O, amide I), 1621 cm^{-1} (νC=O, urea), 1565 cm^{-1} (δN–H, urea), 1551 cm^{-1} (δN–H, amide II). ^{1}H-NMR (400 MHz, DMSO–d_6, TMS): δ = 0.85 (t, J = 6.6 Hz, 3H, C*H*$_3$), 1.17 (t, J = 7.1 Hz, 3H; C*H*$_3$ in ester), 1.23 (br, 22H, alkyl), 1.30–.39 (m, 6H; N$^{\varepsilon}$HCH$_2$C*H*$_2$, N$^{\alpha}$HCONHCH$_2$C*H*$_2$, C*H*$_2$CH$_2$NH), 1.42–1.61 (m, 4H, C*H*$_2$CH$_2$CON$^{\varepsilon}$H, C*H*$_2$CH), 2.02 (t, J = 7.3 Hz, 2H, C*H*$_2$CON$^{\varepsilon}$H), 2.49–2.51 (m, 2H; C*H*$_2$SO$_3$Na), 2.82–3.01 (m, 6H, NHC*H*$_2$, N$^{\alpha}$HCONHC*H*$_2$, N$^{\varepsilon}$HC*H*$_2$), 3.24 (q, J = 6.0 Hz, 2H, NHC*H*$_2$CH$_2$SO$_3$K), 4.04–4.10 (m, 3H, C*H*, OC*H*$_2$), 5.85 (t, J = 5.6 Hz, 1H, N*H*), 5.96 (t, J = 5.8 Hz, 1H; N$^{\alpha}$HCON*H*), 6.11–6.14 (m, 2H, N*H*CH$_2$CH$_2$SO$_3$Na, N$^{\alpha}$*H*), 5.82 (t, J = 5.6 Hz, 1H, N$^{\varepsilon}$*H*). Elemental analysis calcd (%) for $C_{30}H_{58}N_5NaO_8S$ (671.86): C, 53.63; H, 8.70; N, 10.42. Found: C, 53.99; H, 8.94; N, 10.43.

Apparatus for measurements

The elemental analyses were performed using a Perkin-Elmer series II CHNS/O analyzer 2400. The FT-IR spectra were recorded on a JASCO FS-420 spectrometer. The FE-SEM

observation was carried out using a Hitachi S-5000 field emission scanning electron microscope. The ^{1}H-NMR spectra were measured using a Bruker AVANCE 400 spectrometer.

Gelation test

A mixture of a weighed gelator in solvent (1ml) in a sealed test tube was heated until a clear solution appeared. After allowing the solutions to stand at 25°C for 6h, the state of the solution was evaluated by the "stable to inversion of a test tube" method.[2]

Field emission scanning electron micrograph (FE-SEM)

The samples were dried overnight in a vacuum before the observation. The dried gels were sputtered using a gold target.

FT-IR study

The FT-IR spectroscopy was performed using the spectroscopic cell with a CaF_2 window and 50 μm spacers operating at a 2 cm^{-1} resolution with 32 scans.

Organogelation test

Table S1 Organogelation properties of **1** and **2** at 25 °C

Solvent	**1**	**2**
Methanol	**Loose gel**	**Gel (50)**
Ethanol	**Gel (30)**	Insoluble
1-Propanol	**Gel (50)**	**Gel (10)**
1-Butanol	Viscous solution	**Gel (15)**
Ethyl acetate	**Loose gel**	Insoluble
Acetone	**Loose gel**	Insoluble
Cyclohexanone	**Loose gel**	**Gel (5)**
THF	Partial gel	Insoluble
1,4-Dioxane	**Loose gel**	Insoluble
Benzene	**Gel (50)**	Insoluble
Toluene	Viscous solution	Insoluble
Chlorobenzene	Partial gel	**Gel (12)**
Nitrobenzene	**Loose gel**	**Gel (5)**
DMF	Solution	Solution
DMSO	Solution	Insoluble
Chloroform	Solution	Insoluble
Acetonitrile	**Loose gel**	Insoluble

Values denote minimum gel concentration (MGC, g/L). Partial gel consists of gel phase and solution phase.

FT-IR spectra

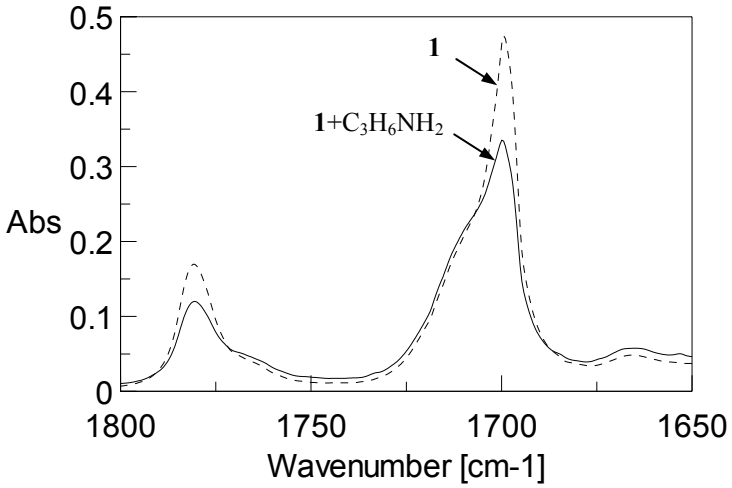


Fig. S1 FT–IR spectra of ethanol gels of **1** (dashed line) and **1**+$C_3H_6NH_2$ (solid line)

References

1 M. Suzuki, Y. Nakajima, M. Yumoto, M. Kimura, H. Shirai and K. Hanabusa, *Langmuir*, 2003, **19**, 8622.
2 M. Suzuki, M. Yumoto, M. Kimura, H. Shirai and K. Hanabusa, *Chem. Commun*., 2002, 884.
3 M. Suzuki, S. Owa, H. Shirai and K. Hanabusa, *Macromol. Rapid Commun*., 2005, **26**, 803.