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L-Lysine based gemini organogelators: their organogelation properties and thermally stable organogels

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Novel gemini organogelators based on L-lysine, in which two L-lysine derivatives are linked by different alkylene chain lengths through the amide bond, have been simply and effectively synthesized, and their organogelation abilities and thermal stabilities have been investigated. In a series of L-lysine ethyl ester derivatives, the organogelation abilities decreased with increasing alkylene spacer length. In particular, bis(N^{ε}-lauroyl-L-lysine ethyl ester) oxalyl amide is a good organogelator that gels most organic solvents such as alcohols, cyclic ethers, aromatic solvents and acetonitrile. Various oxalyl amide derivatives with different alkyl ester groups such as hexyl, decyl, dodecyl, 2-ethyl-1-hexyl and 3,5,5-trimethylhexyl also showed good organogelation abilities. Furthermore, it was found that the cyclohexane gels formed by some oxalyl amide derivatives have a high thermal stability.

Introduction

A number of low-molecular-weight organic compounds have been found to be organogelators that can gel various organic solvents at relatively low concentrations.[1,2] Most organogels consist of long nanofibers that are self-assembled as a result of the usual array of noncovalent forces such as hydrogen bonding, van der Waals interaction, π-stacking, electrostatic and charge-transfer interactions. Noncovalent cross-links among the nanofibers and/or mechanical entanglements create a three-dimensional network. Solvent is entrapped within the interstices, thus leading to gelation.

Organogelators have received much attention not only for their organogelation properties but also for the formation of superstructures in organic solvents and organogels. One of the applications of organogelators is their use as organic templates for the fabrication of mesoporous polymer materials[3] and nano-scaled designed inorganic materials. Many organogelators have been used as organic templates.[4] Sol–gel polymerization of various metal alkoxides (Si, Ti, Ta, V, Ge, *etc*.) in the solvents containing self-assembled organogelators leads to hollow nanofibers of metal oxides upon calcination. Other applications are their use in sensors, molecular recognition, and so on.[5] Furthermore, these organogelators have been applied to industrial fields such as cosmetics, health care, textile, paper, foods and oil.[1] For wide applications, organogelators that can be cheaply, simply and effectively synthesized are desired. In addition, organogelators should be environmentally friendly materials (have features such as biodegradiation and no toxicity). In this paper, we describe the easy and effective synthesis of new gemini organogelators and their organogelation properties.

Results and discussion

Organogelation abilities

Two types of bis(N^{ε}-lauroyl-L-lysine) derivatives, acid type (**1**–**10**) and ethyl ester type (**11**–**20**), linked by different alkylene spacers (C_0–C_{10}) through the amide bonds were first synthesized (Fig. 1) and their organogelation abilities then examined. Though the acid types **2**–**10** had organogelation abilities for only aromatic solvents, **1** functioned as an excellent organogelator that could gel aromatic solvents, DMF, DMSO, $CHCl_3$, ketones and MeOH. On the other hand, though a series of N^{ε}-lauroyl-N^{α}-alkanoyl-L-lysine ethyl ester derivatives (alkanoyl = C_1–C_{18}) had no organogelation abilities,[6] the ethyl ester types **11**–**20** did (Table 1). With increasing length of the alkylene spacers, the gelation abilities tended to decrease due to their higher solvophilicity. Among the gemini compounds **11**–**20**, **11**, linked by an oxalyl amide, had the best organogelation ability; this could gel many organic solvents such as alcohols, ketones, cyclic ethers, aromatic liquids, DMF, CCl_4 and acetonitrile. Based on these results, we synthesized new bis(N^{ε}-lauroyl-L-lysine alkyl ester) derivatives **21**–**25**, linked by an oxalyl amide, with different ester groups and examined their organogelation abilities. The gelation properties of oxalyl amide derivatives in organic solvents are reported in Table 2. According to our expectations, these compounds could gel many organic solvents. The oxalyl amide derivative, **21**, possessing a hexyl ester group, had the best gelation ability. With increasing alkyl chain length of the ester groups, the organogelation ability decreased. This can be explained by the enhanced solvophilicity. Very interestingly, **24** and **25**, possessing branched alkyl esters, show almost the same organogelation abilities as **11** and **21**, while they have better organogelation abilities than **22** and **23** at 25 °C.

TEM

Fig. 2 shows TEM images of benzene gels formed by **11**, **22**, **24** and **25**. All the gelators self-assemble into fibrous aggregates with a diameter of 20–50 nm and create a three-dimensional network by entanglement of the nanofibers. Such nanofibers and three-dimensional network structures in the organogels are the same as those formed by common organogelators in their organogels.[1–4] Therefore, the organogelation occurs by entrapping the solvent molecules in the spaces of the three-dimensional networks.

^{1}H NMR and FTIR studies

It is well-known that hydrogen bonding is one of the driving forces for the self-assembly of organogelators in organic solvents.[1] The IR and ^{1}H NMR spectroscopies are powerful tools

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Table 1 Organogelation properties of **2**–**10** and **12**–**20** in organic solvents[a]

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**
c-C_6H_{12}	PG	I	I	I	I	I	I	VS	I	I	I	I	I	I	I	I	I	I	PG	I
MeOH	45	I	I	I	I	I	I	VS	I	I	28	S	S	S	S	S	S	S	S	PG
EtOH	PG	S	S	S	S	S	S	S	S	S	25	S	S	S	S	S	S	S	S	S
1-PrOH	PG	S	S	S	S	S	S	S	S	S	26	PG	20	10	18	S	PG	PG	S	S
1-BuOH	S	S	S	S	S	S	S	S	S	S	20	C	PG	13	18	I	I	PG	I	PG
AcOEt	15	S	S	S	S	S	PG	S	S	PG	25	S	S	S	S	S	S	S	S	PG
Acetone	18	P	P	P	I	S	PG	PG	PG	PG	50	S	S	S	S	S	S	S	S	PG
c-Hexanone	35	S	PG	S	25	PG	35	35	40	25	30	S	50	25	30	50	PG	PG	50	PG
THF	PG	S	30	S	PG	I	35	40	40	20	30	S	50	38	PG	28	30	45	PG	40
Dioxane	18	S	35	S	35	40	30	28	45	20	20	PG	15	20	15	30	PG	PG	PG	PG
PhH	35	PG	PG	PG	PG	40	PG	PG	PG	PG	20	45	35	35	30	20	15	15	25	30
$PhCH_3$	35	PG	50	PG	PG	40	30	10	25	8	12	25	26	15	32	15	38	PG	24	43
PhCl	12	40	35	32	20	40	12	25	35	PG	12	PG	32	40	12	28	38	PG	26	25
$PhNO_2$	38	40	45	PG	15	20	15	PG	20	8	PG	30	6	8	20	8	40	PG	48	28
DMF	30	S	S	S	S	S	S	S	S	S	28	S	S	PG	S	PG	S	S	S	PG
DMSO	15	S	S	S	S	S	S	S	S	S	S	S	PG	50	S	PG	PG	S	S	40
$CHCl_3$	8	PG	PG	PG	P	PG	PG	18	PG	10	S	S	S	S	S	S	S	S	S	S
CCl_4	25	PG	P	PG	S	I	PG	PG	PG	PG	15	5	50	PG	50	PG	PG	PG	PG	PG
CH_3CN	I	I	P	PG	I	I	I	I	I	I	30	PG	10	10	8	5	PG	PG	45	20

[a] Values refer to minimum gel concentration (MGC) necessary for gelation. I: almost insoluble; PG: partial gel; VS: viscous solution at 5 wt%. S: solution at 5 wt%; P: precipitate.

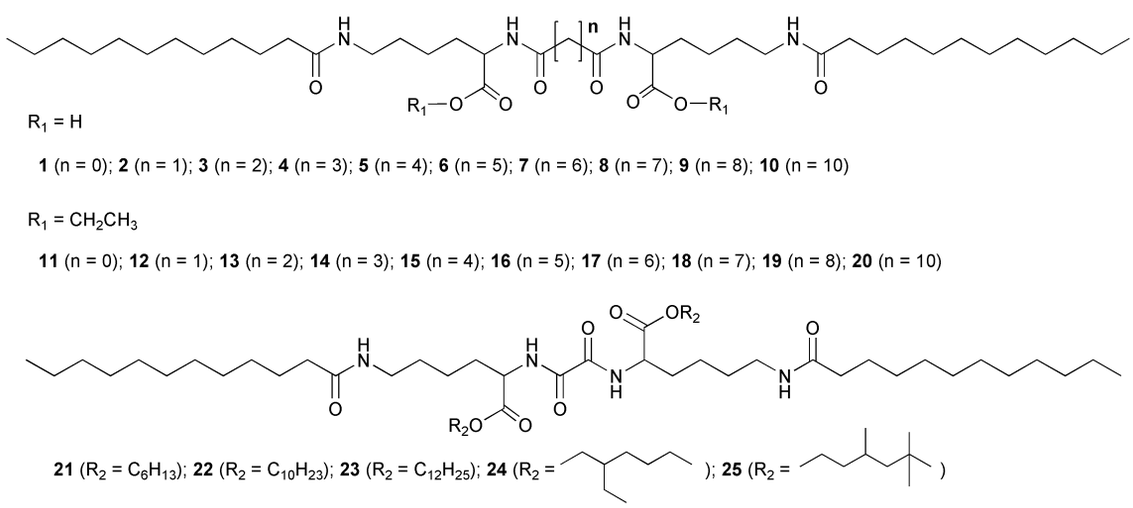


Fig. 1 Chemical structures of a series of gemini organogelators.

Table 2 Gelation properties of oxalyl amide derivatives in organic solvents[a]

	1	**11**	**21**	**22**	**23**	**24**	**25**
c-C_6H_{12}	PG	I	4	25	6	10	4
MeOH	45	28	20	P	S	25	20
EtOH	PG	25	20	PG	S	25	40
1-PrOH	PG	26	30	PG	S	25	40
1-BuOH	S	20	20	PG	S	30	S
AcOEt	15	25	25	35	PG	50	35
Acetone	18	50	40	PG	I	35	30
c-Hexanone	35	30	40	40	PG	PG	40
THF	PG	30	PG	PG	PG	PG	PG
Dioxane	18	20	20	45	40	30	30
PhH	35	20	8	35	45	25	12
$PhCH_3$	35	12	8	25	30	20	18
PhCl	12	12	8	30	45	20	20
$PhNO_2$	38	PG	15	26	35	40	10
DMF	30	28	30	PG	S	30	35
DMSO	15	S	15	PG	S	20	10
$CHCl_3$	8	S	S	S	S	S	S
CCl_4	25	15	6	15	PG	25	40
CH_3CN	I	30	25	P	I	25	22

[a] Values refer to minimum gel concentration (MGC) necessary for gelation. I: almost insoluble; PG: partial gel; S: solution at 5 wt%; P: precipitate

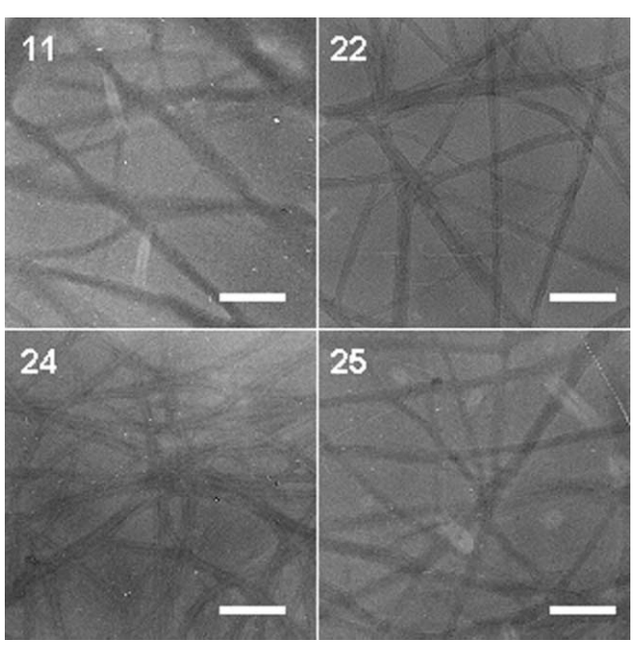


Fig. 2 TEM images of benzene gels formed by **11**, **22**, **24** and **25** (20 mg mol^{-1}). The bar is 100 nm.

to study hydrogen bonding interactions. Fig. 3 shows the ^{1}H NMR spectra of **11** in $CDCl_3$ and $CDCl_3$–CCl_4 (1 : 1) solutions.[7] In $CDCl_3$, in which **11** forms no nanofibers, the chemical shifts of the amide protons at N^{ε} (N–H_a) and N^{α} (N–H_b) positions are observed at 5.61 and 7.81 ppm, respectively. With the addition of CCl_4, the chemical shift of N–H_a shifts downfield (5.84 ppm), indicating that the N–H_a undergoes hydrogen bonding. In contrast, the chemical shift of the N–H_b only slightly changes (7.81 ⟶ 7.84 ppm). As a control experiment, we measured the ^{1}H NMR spectrum in $CDCl_3$ of N^{α}, N^{ε}-bis-(lauroyl)-L-lysine ethyl ester as an analogue (Fig. 3(D)). This analogue never self-assembles and shows no interaction with $CDCl_3$. The ^{1}H NMR spectrum showed the non-interacted N^{α}–H (corresponding to N–H_b) around 6.8 ppm. Compared with this value, the chemical shift of N–H_b in **11** appears at lower field ($\Delta\delta \approx 1$ ppm) in $CDCl_3$. In addition, the chemical shift is independent of the gelator concentration (Fig. 3(A)); therefore, the N–H_b should undergo intramolecular hydrogen bonding with the C=O of the oxalyl amide.

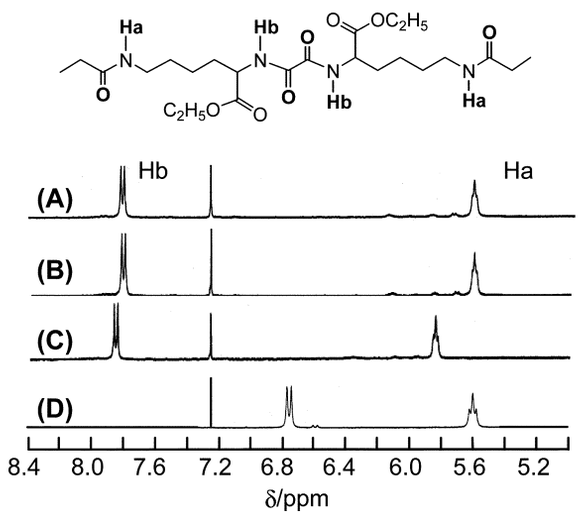


Fig. 3 ^{1}H NMR spectra of **11** and N^{α}, N^{ε}-bis(lauroyl)-L-lysine ethyl ester. (A) 5 mg ml^{-1} of **11** in $CDCl_3$; (B) 20 mg ml^{-1} of **11** in $CDCl_3$; (C) 20 mg ml^{-1} of **11** in $CDCl_3$–CCl_4 (1 : 1); (D) 20 mg ml^{-1} of N^{α}, N^{ε}-bis(lauroyl)-L-lysine ethyl ester in $CDCl_3$.

Further information was obtained from the FTIR spectroscopy. Fig. 4 shows the FTIR spectra of **11** in the $CHCl_3$ solution and CCl_4 gel. The FTIR spectrum in $CHCl_3$, in which no self-assembly occurs, showed absorption bands at 3450 and 1681 cm^{-1}, characteristic of the non-hydrogen bonding N–H (amide A) and C=O (amide I) stretching vibration, respectively. In addition, an absorption band was observed at 3387 cm^{-1} arising from the amide A undergoing intramolecular hydrogen bonding (N–H_b).[8] On the other hand, the FTIR spectrum in the

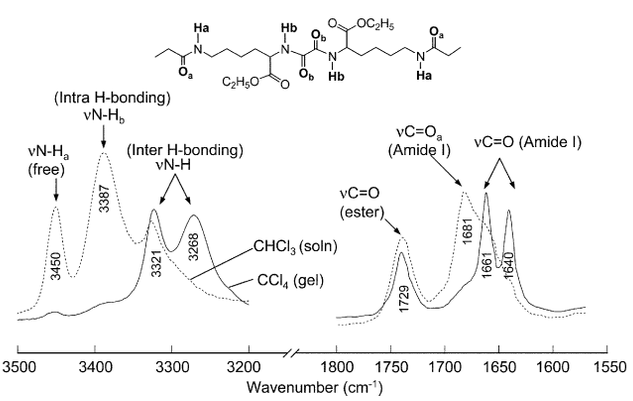


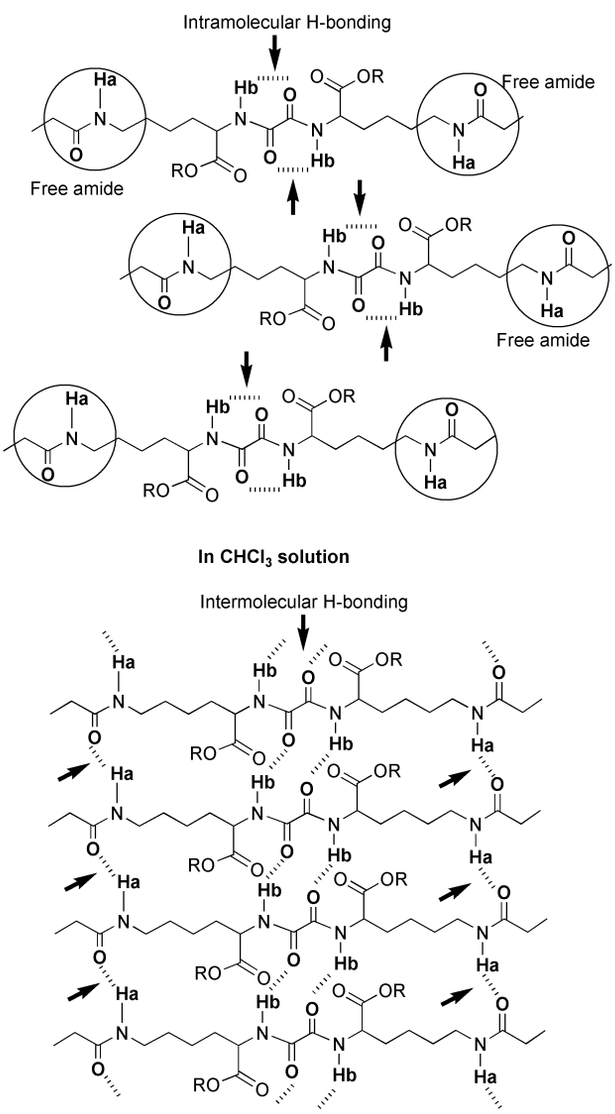
Fig. 4 FTIR spectra of **11** in $CHCl_3$ solution (solid line) and CCl_4 gel (dashed line) at 20 mg ml^{-1}.

CCl_4 gel showed absorption bands at 3321 and 3268 cm^{-1} (amide A) as well as at 1661 and 1640 cm^{-1} (amide I), arising from the intermolecular hydrogen bonded amide groups. The absorption bands of the intramolecular hydrogen bonded N–H and free N–H did not appear in the CCl_4 gel, indicating that all amide groups participated in the intermolecular hydrogen bonding.

The FTIR measurements also provide information on the alkyl groups. The absorption bands of the antisymmetric (ν_{as}) and symmetric (ν_s) CH_2 stretching vibrations of **11** appeared at 2928 cm^{-1} (ν_{as}, C–H) and 2855 cm^{-1} (ν_s, C–H) in $CHCl_3$, while, in the CCl_4 gel, they shifted to 2923 and 2850 cm^{-1}. Such a lower frequency shift is induced by restriction of the alkyl chains in **11**,[9] thus indicating that van der Waals interaction between the alkyl chains also plays an important role in the self-assembly into the nanofibers.

Organogelation mechanism

These spectroscopic results allow us to propose the organogelation mechanism as illustrated in Scheme 1. In $CHCl_3$, the oxalyl amide gelators do not self-assemble and have free (N–N_a and C=O_a) as well as intramolecular hydrogen bonded amide groups (N–H_b and C=O_b). In the CCl_4 gels, the gelators self-assemble into nanofibers through intermolecular hydrogen bonding between most amide groups; the free amide groups (N–H_a, C=O_a) undergo hydrogen bonding and



Scheme 1

N–H_b and C=O_b groups switch the hydrogen bonding mode from intramolecular to intermolecular. They then create the three-dimensional networks by entanglement of the self-assembled nanofibers. Consequently, the organogelation occurs by entrapping solvent molecules in the spaces of the three-dimensional networks.

Thermal behavior of cyclohexane gels

Fig. 5 shows the temperature dependence of the minimum gel concentration (MGC, mg mol^{-1}) necessary for organogelation in cyclohexane. For **21** and **23**, possessing linear alkyl ester groups, the MGC values of **21** and **23** are almost constant up to 50 °C, and they can gel cyclohexane below 1 wt%. A further temperature increase increases the MGC values. However, **22** forms a thermally stable cyclohexane gel and the MGC value does not change in the temperature range of 25–70 °C. At 70 °C, the MGC values decrease with increasing alkyl chain length of the ester groups (**21** > **22** > **23**); namely, the organogelation abilities increase. This is attributed to the fact that the van der Waals interaction between the alkyl ester groups is strong. On the other hand, **24** and **25**, possessing branched alkyl ester groups, show a superior thermal stability; the MGC values are almost independent of temperature up to 70 °C. Compounds **24** and **25** can gel cyclohexane at 1.2 and 0.7 wt%, even at 70 °C, respectively.

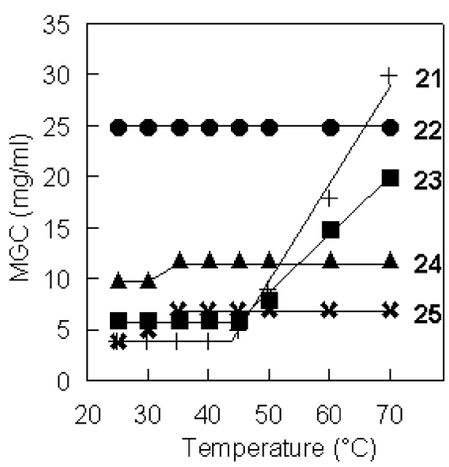


Fig. 5 Temperature dependence of minimum gel concentration (MGC) for cyclohexane gels formed by **21** (+), **22** (●), **23** (■), **24** (▲) and **25** (**X**).

Conclusion

We revealed a series of new gemini organogelators (**1**–**25**) that can be easily and effectively synthesized and the organogelation properties as well as the thermal stabilities of their cyclohexane gels were investigated. These gemini compounds have two L-lysine derivatives linked by different alkylene spacers (C_0–C_{10}) through the amide bonds. Among these gemini compounds, the oxalyl amide derivatives (**1**, **11**, **21**–**25**) showed superior organogelation abilities and can gel many organic solvents. The FTIR and ^{1}H NMR spectrum measurements demonstrated that the amide groups interact with each other through intermolecular hydrogen bonding, which leads to the creation of the three-dimensional networks followed by the formation of self-assembled nanofibers. Furthermore, these oxalyl amide organogelators can form highly thermally stable cyclohexane gels; particularly, **24** and **25** possessing branched alkyl ester groups, gel cyclohexane, even at 70 °C, at 1.2 and 0.7 wt%, respectively. Considering the organogelation abilities, cheap availabilities, simple and effective syntheses and thermal stabilities, the oxalyl amide derivatives possessing the branched alkyl esters are the best organogelators.

Experimental section

Materials

N^{ε}-Lauroyl-L-lysine was obtained from the Ajinomoto Co., Inc. N^{ε}-lauroyl-L-lysine ethyl ester was synthesized according to the literature.[2a] The other chemicals were of the highest commercially grade available and used without further purification. All solvents used in the syntheses were purified, dried, or freshly distilled as required.

Apparatus for measurements

The elemental analyses were performed using a Perkin-Elmer series II CHNS/O analyzer 2400. The FTIR spectra were recorded on a JASCO FS-420 spectrometer. The UV-Vis absorption spectra were acquired on a JASCO V-570 UV/VIS/NIR spectrometer. The TEM images were obtained using a JEOL JEM-2010 electron microscope at 200 kV. 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 with TMS as the standard.

Gelation test

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

Transmittance electron micrograph (TEM)

Samples were prepared as follows: benzene solutions of the gelators were added dropwise on a collodion- and carbon-coated 400 mesh copper grid and immediately dried in a vacuum for 24 h. After adding dropwise a 2 wt% phosphotungstic acid solution, the grids were dried under reduced pressure for 24 h.

FTIR study

FTIR spectroscopy was performed in $CHCl_3$ (15 mg ml^{-1} of gelator) and in CCl_4 (10 mg ml^{-1} of gelator) operating at 2 cm^{-1} resolution with 32 scans. A spectroscopic cell with a CaF_2 window and 50 μm spacers was used for the measurements.

^{1}H NMR study

Solutions of **11** were prepared in $CDCl_3$ at 5 and 20 mg mol^{-1} and in $CDCl_3$–CCl_4 (1 : 1) at 20 mg mol^{-1}. In addition, a $CDCl_3$ solution of N^{ε},N^{α}-Bis(lauroyl)-L-lysine ethyl ester was 20 mg mol^{-1}.

Syntheses

***N*$^{\varepsilon}$-Lauroyl-L-lysine hexyl ester.** A hexanol (500 ml) suspension of N^{ε}-lauroyl-L-lysine (0.33 mol) was saturated with dry hydrogen chloride in an ice bath. After standing overnight at room temperature, the excess HCl was removed by evaporation. Ethyl ether (500 ml) was added and the solution was allowed to stand for 6 h in a refrigerator. The resulting white precipitate was filtered off, washed with ether and then dried. The HCl salt of N^{ε}-lauroyl-L-lysine hexyl ester was dissolved in methanol (500 ml) and a large excess of morpholine (1 mol) was added. The resulting solution was poured onto vigorously stirring water (2 L). The white precipitate was collected by filtration, washed with water, and then dried. The product was purified by recrystallization from methanol–diethyl ether (powder, 93%). IR (KBr): 3376 (νN–H, amine), 3285 (νN–H, amide A), 1714 (νC=O, ester), 1633 (νC=O, amide I), 1560 cm^{-1} (δN–H, amide II); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 30 °C): δ 0.86–0.91

(m, 6H; CH_3), 2.14 (t, J = 7.6 Hz, 2H; CH_2CONH), 3.25 (q, J = 6.1 Hz, 2H; $NHCH_2$), 3.40–3.43 (m, 1H; CH), 4.10 (t, J = 6.8 Hz, 2H; OCH_2), 5.52 (br, 1H; $N^{\varepsilon}H$); elemental analysis: calc. (%) for $C_{24}H_{48}N_2O_3$ (412.65): C, 69.86; H, 11.72; N, 6.79; found: C 69.99; H, 11.94; N, 6.80.

***N*$^{\varepsilon}$-Lauroyl-L-lysine decyl ester.** A benzene solution (400 ml) of *N*$^{\varepsilon}$-lauroyl-L-lysine (0.13 mol), 1-decanol (0.2 mol) and *p*-toluenesulfonic acid monohydrate (0.26 mol) was refluxed on an oil-bath at 130 °C for 48 h while removing water. The excess benzene was evaporated and the residue was dissolved in methanol (250 ml). A large excess of morpholine (0.80 mol) was added with stirring. The white precipitate was filtered off and washed with methanol. The filtrate and washings were mixed and concentrated to *ca.* 100 ml. The solution was added to vigorously stirring water (3 L). The white precipitate was filtered off, washed with water, and then dried. The product was purified by recrystallization from methanol–ether (powder, 91%). IR (KBr): 3390 (νN–H, amine), 3333 (νN–H, amide A), 1724 (νC=O, ester), 1643 (νC=O, amide I), 1543 cm^{-1} (δN–H, amide II); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 30 °C): δ 0.86–0.89 (m, 6H; CH_3), 2.14 (t, J = 7.3 Hz, 2H; CH_2CONH), 3.25 (q, J = 6.0 Hz, 2H; $NHCH_2$), 3.39–3.42 (m, 1H; CH), 4.10 (t, J = 6.8 Hz, 2H; OCH_2), 5.50 (br, 1H; $N^{\varepsilon}H$); elemental analysis: calc. (%) for $C_{28}H_{56}N_2O_3$ (486.76): C, 71.74; H, 12.04; N, 5.98; found: C, 71.93; H, 12.55; N, 6.07.

***N*$^{\varepsilon}$-Lauroyl-L-lysine dodecyl ester.** The same procedure as for decyl ester using a dodecyl alcohol (powder, 89%). IR (KBr): 3328 (νN–H, amide A), 1735 (νC=O, ester), 1642 (νC=O, amide I), 1531 cm^{-1} (δN–H, amide II); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 30 °C): δ 0.88 (t, J = 7.2 Hz, 6H; CH_3), 2.14 (t, J = 7.6 Hz, 2H; CH_2CONH), 3.25 (q, J = 6.1 Hz, 2H; $NHCH_2$), 3.40–3.43 (m, 1H; CH), 4.10 (t, J = 6.8 Hz, 2H; OCH_2), 5.52 (br, 1H; $N^{\varepsilon}H$); elemental analysis: calc. (%) for $C_{30}H_{60}N_2O_3$ (496.81): C, 72.53; H, 12.17; N, 5.64; found: C, 72.55; H, 12.75; N, 5.67.

***N*$^{\varepsilon}$-Lauroyl-L-lysine 3,5,5-trimethylhexyl ester.** The same procedure as for *N*$^{\varepsilon}$-lauroyl-L-lysine 2-ethyl-1-hexyl ester using a 3,5,5-trimethylhexanol (oil, 90%). IR (Nujol): 3294 (νN–H, amide A), 1736 (νC=O, ester), 1645 (νC=O, amide I), 1556 cm^{-1} (δN–H, amide II); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 30 °C): δ 0.86–0.91 (m, 15H; CH_3), 0.94–0.96 (m, 3H; CH_3), 2.15 (t, J = 7.3 Hz, 2H; $CH_2CON^{\varepsilon}H$), 3.23 (q, J = 6.3 Hz, 2H; $N^{\varepsilon}HCH_2$), 4.12–4.17 (m, 2H; OCH_2), 5.56 (br, 1H; $N^{\varepsilon}H$).

***N*$^{\varepsilon}$,*N*$^{\alpha}$-Bis(lauroyl)-L-lysine ethyl ester (A).** To a dry THF solution (400 ml) of *N*$^{\varepsilon}$-lauroyl-L-lysine ethyl ester (20 mmol) and triethylamine (10 ml), lauroyl chloride (10 mmol) was added with stirring. After stirring for 24 h at room temperature, the white precipitate was filtered hot, and the filtrate was evaporated to dryness. The product was obtained by two recrystallizations from ethyl acetate–ether (powder, 96%). IR (KBr): 3309 (νN–H, amide A), 17390 (νC=O, ester), 1642 (νC=O, amide I), 1546 cm^{-1} (δN–H, amide II); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 30 °C): δ 0.88 (t, J = 6.6 Hz, 6H; CH_3), 2.15 (t, J = 7.3 Hz, 2H; $N^{\alpha}HCOCH_2$), 2.23 (t, J = 7.7 Hz, 2H; $CH_2CON^{\varepsilon}H$), 3.24 (q, J = 6.6 Hz, 2H; $N^{\varepsilon}HCH_2$), 4.19 (q, J = 7.1 Hz, 2H; OCH_2), 4.53–4.58 (m, 1H; CH), 5.68 (t, J = 5.5 Hz, 1H; $N^{\varepsilon}H$), 7.15 (d, J = 7.8 Hz, 1H; $N^{\alpha}H$); elemental analysis: calc. (%) for $C_{32}H_{62}N_2O_4$ (538.85): C, 71.33; H, 11.60; N, 5.20; found: C, 71.36; H, 12.00; N, 5.21.

***N*$^{\alpha}$,*N*$^{\alpha\prime}$-Oxalyl-bis(*N*$^{\varepsilon}$-lauroyl-L-lysine) (1).** *N*$^{\varepsilon}$-Lauroyl-L-lysine (60 mmol) was dissolved in water (600 ml) containing NaOH (600 mmol) and ethyl ether was then added. Freshly distilled oxalyl chloride (25 mmol) was slowly added to the ether layer. The biphasic solution was vigorously stirred at 0 °C for 1 h and then at room temperature for 23 h. The resulting solution was carefully acidified by conc. HCl (up to pH ≈ 1). The white precipitate was filtered, washed with water, and then dried. The product was obtained by two recrystallizations from MeOH–ether (powder, 65%). IR (KBr): 3317 (νN–H, amide A), 1733 (νC=O, CO_2H), 1661 cm^{-1}, 1640 (νC=O, amide I), 1541 cm^{-1} (δN–H, amide II); ^{1}H NMR (400 MHz, $CDCl_3$–DMSO-d_6 (1 : 1), TMS, 30 °C): δ 0.87 (t, J = 6.6 Hz, 6H; CH_3), 1.78–1.88 (m, 4H; $CHCH_2$), 2.05 (t, J = 7.3 Hz, 4H; CH_2CONH, $NHCOCH_2$), 3.03–3.08 (m, 4H; $NHCH_2$, CH_2NH), 4.24–4.30 (m, 2H; CH), 7.61 (t, J = 5.6 Hz, 2H; $N^{\varepsilon}H$), 8.51 (d, J = 8.1 Hz, 2H; $N^{\alpha}H$); elemental analysis: calc. (%) for $C_{38}H_{70}N_4O_8$ (710.98): C, 64.19; H, 9.92; N, 7.88; found: C, 64.22; H, 10.31; N, 7.89.

***N*$^{\alpha}$,*N*$^{\alpha\prime}$-Malonyl-bis(*N*$^{\varepsilon}$-lauroyl-L-lysine) (2).** The same procedure as for **1** using malonyl chloride (powder, 70%). IR (KBr): 3310 (νN–H, amide A), 1739 (νC=O, CO_2H), 1639 (νC=O, amide I), 1546 cm^{-1} (δN–H, amide II); ^{1}H NMR (400 MHz, $CDCl_3$–DMSO-d_6 (1 : 1), TMS, 25 °C): δ 0.88 (t, J = 6.8 Hz, 6H; CH_3), 2.17 (t, J = 7.3 Hz, 4H; CH_2CONH, $NHCOCH_2$), 3.19–3.24 (m, 4H; $NHCH_2$), 3.32 (s, 2H; $NHCOCH_2CONH$), 4.19 (q, J = 7.1 Hz, 4H; OCH_2), 4.49–4.54 (m, 2H; CH), 6.03 (t, J = 5.8 Hz, 2H; $N^{\varepsilon}H$), 7.57 (d, J = 7.8 Hz, 2H; $N^{\alpha}H$); elemental analysis: calc. (%) for $C_{39}H_{72}N_4O_8$ (725.01): C, 64.61; H, 10.01; N, 7.73; found: C, 64.77; H, 10.37; N, 7.74.

***N*$^{\alpha}$,*N*$^{\alpha\prime}$-Succinyl-bis(*N*$^{\varepsilon}$-lauroyl-L-lysine) (3).** The same procedure as for **1** using succinyl chloride (powder, 68%). IR (KBr): 3310 (νN–H, amide A), 1728 (νC=O, CO_2H), 1640 (νC=O, amide I), 1547 cm^{-1} (δN–H, amide II); ^{1}H NMR (400 MHz, $CDCl_3$–DMSO-d_6 (1 : 1), TMS, 30 °C): δ 0.87 (m, 6H; CH_3), 2.06 (br, 4H; $CH_2CON^{\varepsilon}H$, $N^{\varepsilon}HCOCH_2$), 2.42 (br, 4H; $N^{\alpha}HCOCH_2CH_2CON^{\alpha}H$), 3.04 (br, 4H; $NHCH_2$), 4.19 (br, 2H; CH), 7.70 (br, 2H; $N^{\alpha}H$), 8.02 (br, 2H; $N^{\varepsilon}H$); elemental analysis: calc. (%) for $C_{40}H_{74}N_4O_8$ (739.04): C, 65.01; H, 10.09; N, 7.58; found: C, 65.11; H, 10.62; N, 7.58.

***N*$^{\alpha}$,*N*$^{\alpha\prime}$-Glutaryl-bis(*N*$^{\varepsilon}$-lauroyl-L-lysine) (4).** The same procedure as for **1** using glutaryl chloride (powder, 79%). IR (KBr): 3308 (νN–H, amide A), 1732 (νC=O, CO_2H), 1640 (νC=O, amide I), 1555 cm^{-1} (δN–H, amide II); ^{1}H NMR (400 MHz, $CDCl_3$–DMSO-d_6 (4 : 1), TMS, 30 °C): δ 0.88 (t, J = 6.6 Hz, 6H; CH_3), 2.16 (t, J = 7.3 Hz, 4H; $CH_2CON^{\varepsilon}H$, $N^{\varepsilon}HCOCH_2$), 2.25 (t, J = 7.3 Hz, 4H; $CH_2CON^{\alpha}H$, $N^{\alpha}HCOCH_2$), 3.15–3.27 (m, 4H; $NHCH_2$), 4.49–4.54 (m, 2H; CH), 6.61 (t, J = 5.3 Hz, 2H; $N^{\varepsilon}H$), 6.95 (d, J = 7.8 Hz, 2H; $N^{\alpha}H$); elemental analysis: calc. (%) for $C_{41}H_{76}N_4O_8$ (753.06): C, 65.39; H, 10.17; N, 7.44; found: C, 65.41; H, 10.45; N, 7.48.

***N*$^{\alpha}$,*N*$^{\alpha\prime}$-Adipoyl-bis(*N*$^{\varepsilon}$-lauroyl-L-lysine) (5).** The same procedure as for **1** using adipoyl chloride (powder, 80%). IR (KBr): 3310 (νN–H, amide A), 1724 (νC=O, CO_2H), 1641 (νC=O, amide I), 1544 cm^{-1} (δN–H, amide II); ^{1}H NMR (400 MHz, $CDCl_3$–DMSO-d_6 (3 : 2), TMS, 25 °C): δ 0.88 (t, J = 6.8 Hz, 6H; CH_3), 2.14 (t, J = 7.3 Hz, 4H; $CH_2CON^{\varepsilon}H$, $N^{\varepsilon}HCOCH_2$), 2.27 (t, J = 6.6 Hz, 4H; $CH_2CON^{\alpha}H$, $N^{\alpha}HCOCH_2$), 3.18 (q, J = 6.1 Hz, 4H; $NHCH_2$), 4.42–4.47 (m, 2H; CH), 6.88 (t, J = 5.6 Hz, 2H; $N^{\varepsilon}H$), 7.17 (d, J = 7.8 Hz, 2H; $N^{\alpha}H$); elemental analysis: calc. (%) for $C_{42}H_{78}N_4O_8$ (767.09): C, 65.76; H, 10.25; N, 7.30; found: C, 65.79; H, 10.64; N, 7.29.

***N*$^{\alpha}$,*N*$^{\alpha\prime}$-Pimeloyl-bis(*N*$^{\varepsilon}$-lauroyl-L-lysine) (6).** The same procedure as for **1** using pimeloyl chloride (powder, 82%). IR (KBr): 3309 (νN–H, amide A), 1731 (νC=O, CO_2H), 1641 (νC=O, amide I), 1550 cm^{-1} (δN–H, amide II); ^{1}H NMR (400 MHz, $CDCl_3$–DMSO-d_6 (3 : 2), TMS, 25 °C): δ 0.88 (t, J = 6.6 Hz, 6H; CH_3), 2.11 (t, J = 7.6 Hz, 4H; $CH_2CON^{\varepsilon}H$, $N^{\varepsilon}HCOCH_2$), 2.21 (t, J = 7.6 Hz, 4H; $N^{\alpha}HCOCH_2$, $CH_2CON^{\alpha}H$), 3.12 (q, J = 6.1 Hz, 4H; $NHCH_2$), 4.32–4.36 (m, 2H; CH), 7.34 (t, J = 5.6 Hz, 2H; $N^{\varepsilon}H$), 7.55 (d, J = 7.8 Hz, 2H;

$N^{\alpha}H$); elemental analysis: calc. (%) for $C_{43}H_{80}N_4O_8$ (781.12): C, 66.12; H, 10.32; N, 7.17; found: C, 66.24; H, 10.68; N, 7.20.

***N*$^{\alpha}$,*N*$^{\alpha\prime}$-Suberoyl-bis(*N*$^{\varepsilon}$-lauroyl-L-lysine) (7).** The same procedure as for **1** using suberoyl chloride (powder, 82%). IR (KBr): 3312 (*ν*N–H, amide A), 1723 (*ν*C=O, CO_2H), 1642 (*ν*C=O, amide I), 1543 cm^{-1} (*δ*N–H, amide II); ^1H NMR (400 MHz, $CDCl_3$–DMSO-d_6 (1 : 1), TMS, 25 °C): *δ* 0.87 (t, *J* = 6.6 Hz, 6H; CH_3), 2.05 (t, *J* = 7.3 Hz, 4H; $CH_2CON^{\alpha}H$, $N^{\alpha}HCOCH_2$), 2.14 (t, *J* = 7.3 Hz, 4H; $CH_2CON^{\varepsilon}H$, $N^{\varepsilon}HCOCH_2$), 3.05 (q, *J* = 6.6 Hz, 4H; $NHCH_2$), 4.17–4.23 (m, 2H; CH), 7.61 (t, *J* = 5.6 Hz, 2H; $N^{\varepsilon}H$), 7.84 (d, *J* = 7.8 Hz, 2H; $N^{\alpha}H$); elemental analysis: calc. (%) for $C_{44}H_{82}N_4O_8$ (795.14): C, 66.46; H, 10.39; N, 7.05; found: C, 66.51; H, 10.54; N, 7.08.

***N*$^{\alpha}$,*N*$^{\alpha\prime}$-Azelaoyl-bis(*N*$^{\varepsilon}$-lauroyl-L-lysine) (8).** The same procedure as for **1** using azelaoyl chloride (powder, 82%). IR (KBr): 3309 (*ν*N–H, amide A), 1731 (*ν*C=O, CO_2H), 1639 (*ν*C=O, amide I), 1548 cm^{-1} (*δ*N–H, amide II); ^1H NMR (400 MHz, $CDCl_3$–DMSO-d_6 (4 : 1), TMS, 25 °C): *δ* 0.88 (t, *J* = 6.6 Hz, 6H; CH_3), 2.14 (t, *J* = 7.3 Hz, 4H; $CH_2CON^{\varepsilon}H$, $N^{\varepsilon}HCOCH_2$), 2.22 (t, *J* = 7.3 Hz, 4H; $CH_2CON^{\alpha}H$, $N^{\alpha}HCOCH_2$), 3.18 (q, *J* = 6.3 Hz, 4H; $NHCH_2$), 4.43–4.49 (m, 2H; CH), 6.73 (t, *J* = 5.6 Hz, 2H; $N^{\varepsilon}H$), 6.96 (d, *J* = 7.8 Hz, 2H; $N^{\alpha}H$); elemental analysis: calc. (%) for $C_{45}H_{84}N_4O_8$ (809.17): C, 66.79; H, 10.46; N, 6.92; found: C, 66.88; H, 10.84; N, 6.94.

***N*$^{\alpha}$,*N*$^{\alpha\prime}$-Sebacoyl-bis(*N*$^{\varepsilon}$-lauroyl-L-lysine) (9).** The same procedure as for **1** using sebacoyl chloride (powder, 83%). IR (KBr): 3313 (*ν*N–H, amide A), 1727 (*ν*C=O, CO_2H), 1641 (*ν*C=O, amide I), 1545 cm^{-1} (*δ*N–H, amide II); ^1H NMR (400 MHz, $CDCl_3$–DMSO-d_6 (1 : 1), TMS, 25 °C): *δ* 0.87 (t, *J* = 6.6 Hz, 6H; CH_3), 2.06 (t, *J* = 7.3 Hz, 4H; $CH_2CON^{\alpha}H$, $N^{\alpha}HCOCH_2$), 2.14 (t, *J* = 7.3 Hz 4H; $CH_2CON^{\varepsilon}H$, $N^{\varepsilon}HCOCH_2$), 3.06 (q, *J* = 6.6 Hz, 4H; $NHCH_2$), 4.19–4.25 (m, 2H; CH), 7.58 (t, *J* = 5.6 Hz, 2H; $N^{\varepsilon}H$), 7.81 (d, *J* = 7.8 Hz, 2H; $N^{\alpha}H$); elemental analysis: calc. (%) for $C_{46}H_{86}N_4O_8$ (823.20): C, 67.12; H, 10.53; N, 6.81; found: C, 67.24; H, 10.79; N, 6.84.

***N*$^{\alpha}$,*N*$^{\alpha\prime}$-Dodecanedioyl-bis(*N*$^{\varepsilon}$-lauroyl-L-lysine) (10).** The same procedure as for **1** using dodecandioyl chloride (powder, 80%). IR (KBr): 3315 (*ν*N–H, amide A), 1725 (*ν*C=O, CO_2H), 1643 (*ν*C=O, amide I), 1544 cm^{-1} (*δ*N–H, amide II); ^1H NMR (400 MHz, $CDCl_3$–DMSO-d_6 (3 : 2), TMS, 25 °C): *δ* 0.87 (t, *J* = 6.6 Hz, 6H; CH_3), 2.12 (t, *J* = 7.6 Hz, 4H; $CH_2CON^{\varepsilon}H$, $N^{\varepsilon}HCOCH_2$), 2.20 (t, *J* = 7.6 Hz, 4H; $CH_2CON^{\alpha}H$, $N^{\alpha}HCOCH_2$), 3.14 (q, *J* = 6.3 Hz, 4H; $NHCH_2$), 4.34–4.39 (m, 2H; CH), 7.18 (t, *J* = 5.6 Hz, 2H; $N^{\alpha}H$), 7.36 (d, *J* = 7.8 Hz, 2H; $N^{\varepsilon}H$); elemental analysis: calc. (%) for $C_{48}H_{90}N_4O_8$ (851.25): C, 67.73; H, 10.66; N, 6.58; found: C, 67.81; H, 10.92; N, 6.61.

***N*$^{\alpha}$,*N*$^{\alpha\prime}$-Oxalyl-bis(*N*$^{\varepsilon}$-lauroyl-L-lysine ethyl ester) (11).** To a dry THF solution (400 ml) of *N*$^{\varepsilon}$-lauroyl-L-lysine ethyl ester (20 mmol) and triethylamine (10 ml), the diacid dichloride (10 mmol) was added with stirring. After stirring for 24 h at room temperature, the white precipitate was filtered hot, and the filtrate was evaporated to dryness. The product was obtained by two recrystallizations from ethyl acetate–ether (powder, 90%). IR (KBr): 3316 cm^{-1}, 3282 (*ν*N–H, amide A), 1740 (*ν*C=O, ester), 1663 cm^{-1}, 1642 (*ν*C=O, amide I), 1539 cm^{-1} (*δ*N–H, amide II); ^1H NMR (400 MHz, $CDCl_3$, TMS, 30 °C): *δ* 0.88 (t, *J* = 6.3 Hz, 6H; CH_3), 1.76–1.94 (m, 4H; $CHCH_2$), 2.14 (t, *J* = 7.6 Hz, 4H; CH_2CONH, $NHCOCH_2$), 3.24 (q, *J* = 6.6 Hz, 4H; $NHCH_2$, CH_2NH), 4.22 (q, *J* = 7.1 Hz, 4H; OCH_2), 4.51–4.57 (m, 2H; CH), 5.62 (t, *J* = 5.5 Hz, 1H; $N^{\varepsilon}H$), 7.82 (d, *J* = 8.6 Hz, 1H; $N^{\alpha}H$); elemental analysis: calc. (%) for $C_{42}H_{78}N_4O_8$ (767.09): C, 65.76; H, 10.25; N, 7.30; found: C, 65.81; H, 10.66; N, 7.28.

***N*$^{\alpha}$,*N*$^{\alpha\prime}$-Malonyl-bis(*N*$^{\varepsilon}$-lauroyl-L-lysine ethyl ester) (12).** The same procedure as for **11** using malonyl chloride (powder, 90%). IR (KBr): 3309 (*ν*N–H, amide A), 1738 (*ν*C=O, ester), 1663 cm^{-1}, 1644 (*ν*C=O, amide I), 1547 cm^{-1} (*δ*N–H, amide II); ^1H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): *δ* 0.88 (t, *J* = 6.8 Hz, 6H; CH_3), 2.17 (t, *J* = 7.3 Hz, 4H; CH_2CONH, $NHCOCH_2$), 3.19–3.24 (m, 4H; $NHCH_2$), 3.32 (s, 2H; $NHCOCH_2CONH$), 4.19 (q, *J* = 7.1 Hz, 4H; OCH_2), 4.49–4.54 (m, 2H; CH), 6.03 (t, *J* = 5.8 Hz, 2H; $N^{\varepsilon}H$), 7.57 (d, *J* = 7.8 Hz, 2H; $N^{\alpha}H$); elemental analysis: calc. (%) for $C_{43}H_{80}N_4O_8$ (781.12): C, 66.12; H, 10.32; N, 7.17; found: C, 66.17; H, 10.67; N, 7.20.

***N*$^{\alpha}$,*N*$^{\alpha\prime}$-Succinyl-bis(*N*$^{\varepsilon}$-lauroyl-L-lysine ethyl ester) (13).** The same procedure as for **11** using succinyl chloride (powder, 95%). IR (KBr): 3310 (*ν*N–H, amide A), 1737 (*ν*C=O, ester), 1644 (*ν*C=O, amide I), 1547 cm^{-1} (*δ*N–H, amide II); ^1H NMR (400 MHz, $CDCl_3$, TMS, 30 °C): *δ* 0.88 (t, *J* = 5.8 Hz, 6H; CH_3), 2.16 (t, *J* = 7.6 Hz, 4H; $CH_2CON^{\varepsilon}H$, $N^{\varepsilon}HCOCH_2$), 2.49–2.67 (m, 4H; $N^{\alpha}HCOCH_2CH_2CON^{\alpha}H$), 3.12–3.31 (m, 4H; $NHCH_2$), 4.18 (q, *J* = 7.1 Hz, 4H; OCH_2), 4.49–4.54 (m, 2H; CH), 6.06 (t, *J* = 5.3 Hz, 2H; $N^{\varepsilon}H$), 6.57 (d, *J* = 7.8 Hz, 2H; $N^{\alpha}H$); elemental analysis: calc. (%) for $C_{44}H_{82}N_4O_8$ (795.14): C, 66.46; H, 10.39; N, 7.05; found: C, 66.52; H, 10.64; N, 7.04.

***N*$^{\alpha}$,*N*$^{\alpha\prime}$-Glutaryl-bis(*N*$^{\varepsilon}$-lauroyl-L-lysine ethyl ester) (14).** The same procedure as for **11** using glutaryl chloride (powder, 95%). IR (KBr): 3307 (*ν*N–H, amide A), 1736 (*ν*C=O, ester), 1644 (*ν*C=O, amide I), 1547 cm^{-1} (*δ*N–H, amide II); ^1H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): *δ* 0.88 (t, *J* = 6.6 Hz, 6H; CH_3), 2.03–2.31 (m, 8H; CH_2CONH, $NHCOCH_2$), 3.18–3.27 (m, 4H; $NHCH_2$), 4.20 (q, *J* = 6.8 Hz, 4H; OCH_2), 4.55–4.61 (m, 2H; CH), 5.68 (t, *J* = 5.3 Hz, 2H; $N^{\varepsilon}H$), 7.76 (d, *J* = 8.3 Hz, 2H; $N^{\alpha}H$); elemental analysis: calc. (%) for $C_{45}H_{84}N_4O_8$ (809.17): C, 66.79; H, 10.46; N, 6.92; found: C, 66.81; H, 10.55; N, 6.94.

***N*$^{\alpha}$,*N*$^{\alpha\prime}$-Adipoyl-bis(*N*$^{\varepsilon}$-lauroyl-L-lysine ethyl ester) (15).** The same procedure as for **11** using adipoyl chloride (powder, 94%). IR (KBr): 3309 (*ν*N–H, amide A), 1738 (*ν*C=O, ester), 1644 (*ν*C=O, amide I), 1544 cm^{-1} (*δ*N–H, amide II); ^1H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): *δ* 0.88 (t, *J* = 5.8 Hz, 6H; CH_3), 2.15 (t, *J* = 7.8 Hz, 4H; $CH_2CON^{\varepsilon}H$, $N^{\varepsilon}HCOCH_2$), 2.29 (br, 4H; $CH_2CON^{\alpha}H$, $N^{\alpha}HCOCH_2$), 3.21–3.24 (m, 4H; $NHCH_2$), 4.19 (q, *J* = 7.1 Hz, 4H; OCH_2), 4.49–4.55 (m, 2H; CH), 5.94 (br, 2H; $N^{\varepsilon}H$), 6.52 (d, *J* = 7.6 Hz, 2H; $N^{\alpha}H$); elemental analysis: calc. (%) for $C_{46}H_{86}N_4O_8$ (823.20): C, 67.12; H, 10.53; N, 6.81; found: C, 67.21; H, 10.54; N, 6.82.

***N*$^{\alpha}$,*N*$^{\alpha\prime}$-Pimeloyl-bis(*N*$^{\varepsilon}$-lauroyl-L-lysine ethyl ester) (16).** The same procedure as for **11** using pimeloyl chloride (powder, 96%). IR (KBr): 3311 (*ν*N–H, amide A), 1736 (*ν*C=O, ester), 1645 (*ν*C=O, amide I), 1544 cm^{-1} (*δ*N–H, amide II); ^1H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): *δ* 0.88 (t, *J* = 5.8 Hz, 6H; CH_3), 2.15 (t, *J* = 7.6 Hz, 4H; $CH_2CON^{\varepsilon}H$, $N^{\varepsilon}HCOCH_2$), 2.23–2.27 (m, 4H; $N^{\alpha}HCOCH_2$, $CH_2CON^{\alpha}H$), 3.20–3.26 (m, 4H; $NHCH_2$), 4.18 (q, *J* = 7.3 Hz, 4H; OCH_2), 4.52–4.57 (m, 2H; CH), 5.87 (t, *J* = 5.0 Hz, 2H; $N^{\varepsilon}H$), 6.37 (d, *J* = 7.6 Hz, 2H; $N^{\alpha}H$); elemental analysis: calc. (%) for $C_{47}H_{88}N_4O_8$ (837.22): C, 67.42; H, 10.59; N, 6.69; found: C, 67.44; H, 10.67; N, 6.70.

***N*$^{\alpha}$,*N*$^{\alpha\prime}$-Suberoyl-bis(*N*$^{\varepsilon}$-lauroyl-L-lysine ethyl ester) (17).** The same procedure as for **11** using suberoyl chloride (powder, 96%). IR (KBr): 3312 (*ν*N–H, amide A), 1733 (*ν*C=O, ester), 1651 cm^{-1}, 1644 (*ν*C=O, amide I), 1539 cm^{-1} (*δ*N–H, amide II); ^1H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): *δ* 0.88 (t, *J* = 7.0 Hz, 6H; CH_3), 2.15 (t, *J* = 7.3 Hz, 4H; $CH_2CON^{\varepsilon}H$, $N^{\varepsilon}HCOCH_2$), 2.22–2.26 (m, 4H; $CH_2CON^{\alpha}H$, $N^{\alpha}HCOCH_2$), 3.22 (q, *J* = 6.1 Hz, 4H; $NHCH_2$), 4.19 (q, *J* = 7.1 Hz, 4H; OCH_2), 4.53–4.58 (m, 2H; CH), 5.92 (t, *J* = 5.6 Hz, 2H; $N^{\varepsilon}H$), 6.45 (d, *J* = 7.8 Hz, 2H; $N^{\alpha}H$); elemental analysis: calc. (%) for $C_{48}H_{90}N_4O_8$

(851.25): C, 67.73; H, 10.66; N, 6.58; found: C, 67.77; H, 11.18; N, 6.59.

N^{α},$N^{\alpha'}$-Azelaoyl-bis(N^{ε}-lauroyl-L-lysine ethyl ester) (18). The same procedure as for **11** using azelaoyl chloride (powder, 96%). IR (KBr): 3316 (νN–H, amide A), 1734 (νC=O, ester), 1646 (νC=O, amide I), 1544 cm^{-1} (δN–H, amide II); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): δ 0.86–0.89 (m, 6H; CH_3), 2.13–2.24 (m, 8H; CH_2CONH, NHCOCH_2), 3.22–3.25 (m, 4H; NHCH_2), 4.16–4.22 (m, 4H; OCH_2), 4.55 (br, 2H; CH), 5.85 (br, 2H; N^{ε}H), 6.29 (br, 2H; N^{α}H); elemental analysis: calc. (%) for $C_{49}H_{92}N_4O_8$ (865.28): C, 68.02; H, 10.72; N, 6.48; found: C, 68.11; H, 11.04; N, 6.49.

N^{α},$N^{\alpha'}$-Sebacoyl-bis(N^{ε}-lauroyl-L-lysine ethyl ester) (19). The same procedure as for **11** using sebacoyl chloride (powder, 97%). IR (KBr): 3312 (νN–H, amide A), 1731 (νC=O, ester), 1645 (νC=O, amide I), 1543 cm^{-1} (δN–H, amide II); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): δ 0.88 (t, J = 5.8 Hz, 6H; CH_3), 2.15 (t, J = 7.8 Hz, 4H; CH_2CON$^{\varepsilon}$H, N$^{\varepsilon}$HCOCH_2), 2.20–2.24 (m, 4H; CH_2CON$^{\alpha}$H, N$^{\alpha}$HCOCH_2), 3.23 (q, J = 6.6 Hz, 4H; NHCH_2), 4.19 (q, J = 7.0 Hz, 4H; OCH_2), 4.53–4.58 (m, 2H; CH), 5.76 (t, J = 4.6 Hz, 2H; N^{ε}H), 6.22 (d, J = 7.6 Hz, 2H; N^{α}H); elemental analysis: calc. (%) for $C_{50}H_{94}N_4O_8$ (879.30): C, 68.30; H, 10.78; N, 6.37; found: C, 68.33; H, 10.99; N, 6.39.

N^{α},$N^{\alpha'}$-Dodecanedioyl-bis(N^{ε}-lauroyl-L-lysine ethyl ester) (20). The same procedure as for **11** using dodecanedioyl chloride (powder, 96%). IR (KBr): 3303 (νN–H, amide A), 1746 (νC=O, ester), 1645 (νC=O, amide I), 1545 cm^{-1} (δN–H, amide II); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): δ 0.88 (t, J = 6.1 Hz, 6H; CH_3), 2.15 (t, J = 7.8 Hz, 4H; CH_2CON$^{\varepsilon}$H, N$^{\varepsilon}$HCOCH_2), 2.22 (t, J = 7.6 Hz, 4H; CH_2CON$^{\alpha}$H, N$^{\alpha}$HCOCH_2), 3.23 (q, J = 6.3 Hz, 4H; NHCH_2), 4.19 (q, J = 7.3 Hz, 4H; OCH_2), 4.53–4.58 (m, 2H; CH), 5.75 (br, 2H; N^{α}H), 6.20 (d, J = 7.6 Hz, 2H; N^{ε}H); elemental analysis: calc. (%) for $C_{52}H_{98}N_4O_8$ (907.36): C, 68.83; H, 10.89; N, 6.17; found: C, 69.01; H, 11.00; N, 6.17.

N^{α},$N^{\alpha'}$-Oxalyl-bis(N^{ε}-lauroyl-L-lysine hexyl ester) (21). The same procedure as for **11** using N^{ε}-lauroyl-L-lysine hexyl ester (powder, 91%). IR (KBr): 3314 (νN–H, amide A), 1738 (νC=O, ester), 1662 cm^{-1}, 1641 (νC=O, amide I), 1540 cm^{-1} (δN–H, amide II); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 30 °C): δ 0.86–0.91 (m, 12H; CH_3), 1.72–1.97 (m, 4H; CHCH_2), 2.14 (t, J = 7.3 Hz, 4H; CH_2CON$^{\varepsilon}$H, N$^{\varepsilon}$HCOCH_2), 3.22 (q, J = 6.6 Hz, 4H; N$^{\varepsilon}$HCH_2, CH_2N$^{\varepsilon}$H), 4.15 (t, J = 6.3 Hz, 4H; OCH_2), 4.52–4.57 (m, 2H; CH), 5.67 (t, J = 5.5 Hz, 2H; N^{ε}H), 7.83 (d, J = 8.6 Hz, 1H; N^{α}H); elemental analysis: calc. (%) for $C_{50}H_{94}N_4O_8$ (879.30): C, 68.30; H, 10.78; N, 6.37; found: C, 68.33; H, 10.98; N, 6.38.

N^{α},$N^{\alpha'}$-Oxalyl-bis(N^{ε}-lauroyl-L-lysine decyl ester) (22). The same procedure as for **11** using N^{ε}-lauroyl-L-lysine decyl ester (powder, 93%). IR (KBr): 3319 cm^{-1}, 3276 (νN–H, amide A), 1741 (νC=O, ester), 1663 cm^{-1}, 1641 (νC=O, amide I), 1539 cm^{-1} (δN–H, amide II); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 30 °C): δ 0.86–0.89 (m, 12H; CH_3), 1.72–1.97 (m, 4H; CHCH_2), 2.14 (t, J = 7.6 Hz, 4H; CH_2CON$^{\varepsilon}$H, N$^{\varepsilon}$HCOCH_2), 3.22 (q, J = 6.6 Hz, 4H; N$^{\varepsilon}$HCH_2, CH_2N$^{\varepsilon}$H), 4.11–4.17 (m, 4H; OCH_2), 4.52–4.57 (m, 2H; CH), 5.59 (t, J = 5.6 Hz, 2H; N^{ε}H), 7.81 (d, J = 8.6 Hz, 2H; N^{α}H); elemental analysis: calc. (%) for $C_{58}H_{110}N_4O_8$ (991.52): C, 70.26; H, 11.18; N, 5.65; found: C, 70.33; H, 11.57; N, 5.67.

N^{α},$N^{\alpha'}$-Oxalyl-bis(N^{ε}-lauroyl-L-lysine dodecyl ester) (23). The same procedure as for **11** using N^{ε}-lauroyl-L-lysine dodecyl ester (powder, 93%). IR (KBr): 3316 cm^{-1}, 3282 (νN–H, amide A), 1740 (νC=O, ester), 1661 cm^{-1}, 1640 (νC=O, amide I), 1545 cm^{-1} (δN–H, amide II); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 30 °C): δ 0.88 (t, J = 5.8 Hz, 12H; CH_3), 2.14 (t, J = 7.3 Hz, 4H; CH_2CON$^{\varepsilon}$H, N$^{\varepsilon}$HCOCH_2), 3.22 (q, J = 6.6 Hz, 4H; N$^{\varepsilon}$HCH_2, CH_2N$^{\varepsilon}$H), 4.12–4.16 (m, 4H; OCH_2), 4.52–4.57 (m, 2H; CH), 5.58 (t, J = 5.6 Hz, 2H; N^{ε}H), 7.81 (d, J = 8.6 Hz, 2H; N^{α}H); elemental analysis: calc. (%) for $C_{62}H_{118}N_4O_8$ (1047.62): C, 71.08; H, 11.35; N, 5.35; found: C, 71.11; H, 11.66; N, 5.35.

N^{α},$N^{\alpha'}$-Oxalyl-bis(N^{ε}-lauroyl-L-lysine 2-ethyl-1-hexyl ester) (24). The same procedure as for **11** using N^{ε}-lauroyl-L-lysine 2-ethyl-1-hexyl ester (powder, 94%). IR (KBr): 3319 cm^{-1}, 3277 (νN–H, amide A), 1741 (νC=O, ester), 1661 cm^{-1}, 1641 (νC=O, amide I), 1539 cm^{-1} (δN–H, amide II); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 30 °C): δ 0.86–0.91 (m, 18H; CH_3), 1.89–1.98 (m, 2H; $CH_2CH(C_2H_5)C_4H_9$), 2.14 (t, J = 7.3 Hz, 4H; CH_2CON$^{\varepsilon}$H, N$^{\varepsilon}$HCOCH_2), 3.22 (q, J = 6.6 Hz, 4H; N$^{\varepsilon}$HCH_2, CH_2N$^{\varepsilon}$H), 4.03–4.11 (m, 4H; OCH_2), 4.53–4.58 (m, 2H; CH), 5.59 (t, J = 5.6 Hz, 1H; N^{ε}H), 7.81 (d, J = 8.6 Hz, 1H; N^{α}H); elemental analysis: calc. (%) for $C_{54}H_{102}N_4O_8$ (935.41): C, 69.34; H, 10.99; N, 5.99; found: C, 69.41; H, 11.34; N, 6.01.

N^{α},$N^{\alpha'}$-Oxalyl-bis(N^{ε}-lauroyl-L-lysine 3,5,5-trimethylhexyl ester) (25). The same procedure as for **11** using N^{ε}-lauroyl-L-lysine 3,5,5-trimethylhexyl ester (powder, 93%). IR (KBr): 3319 cm^{-1}, 3278 (νN–H, amide A), 1741 (νC=O, ester), 1662 cm^{-1}, 1642 (νC=O, amide I), 1538 cm^{-1} (δN–H, amide II); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 30 °C): δ 0.83–0.90 (m, 24H; CH_3), 0.95 (t, J = 6.6 Hz, 6H; CH_3), 1.72–1.94 (m, 4H; CHCH_2, CH_2CH), 2.14 (t, J = 7.6 Hz, 4H; CH_2CON$^{\varepsilon}$H, N$^{\varepsilon}$HCOCH_2), 3.22 (q, J = 6.6 Hz, 4H; N$^{\varepsilon}$HCH_2, CH_2N$^{\varepsilon}$H), 4.17 (t, J = 6.6 Hz, 4H; OCH_2), 4.54 (q, J = 5.3 Hz, 2H; CH), 5.64 (t, J = 5.3 Hz, 2H; N^{ε}H), 7.81 (d, J = 8.4 Hz, 2H; N^{α}H); elemental analysis: calc. (%) for $C_{56}H_{106}N_4O_8$ (963.46): C, 69.81; H, 11.09; N, 5.82; found: C, 69.82; H, 11.47; N, 5.81.

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