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Novel dumbbell-form low-molecular-weight gelators based on L-lysine: their hydrogelation and organogelation properties

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New L-lysine-based, dumbbell-form, low-molecular-weight gelators, in which two L-lysine derivatives are linked by alkylene spacers, were synthesized and their gelation abilities for aqueous solutions and organic solvents were examined. These gelators are amphiphilic gelators that function as not only hydrogelators but also as organogelators. In hydrogels, these gelators created a three-dimensional network by entanglement of self-assembled nanofibers *via* hydrogen bonding and van der Waals interactions. The hydrogel-broken temperatures (T_{gel}) depended on the carbon numbers of the alkylene spacers and showed an odd–even effect. The FT-IR and ^{1}H-NMR spectra demonstrated a difference in the intermolecular hydrogen bonding modes between the gelators of the even-numbered chains and odd-numbered chains.

Introduction

On the basis of supramolecular chemistry, functional low-molecular-weight compounds, which form supramolecular polymers, have been considerably investigated.[1] Supramolecular strategy is very useful for the design of polymeric materials based on low-molecular-weight molecules. Supramolecular polymers possessing nanoscale superstructures, such as nanofibers and nanoribbons, and helical structure have gained much attention.[1] Compared with common polymers (macromolecules), supramolecular polymers, consisting of arrays of the monomer units linked *via* non-covalent interactions (hydrogen bonding, van der Waals, π-stacking, coordination, and electrostatic interactions), show polymeric properties in solution and in the bulk and reversible self-assembling behavior that changes from polymer to monomer with external stimuli such as temperatures, pHs, light, and electricity.

Some compounds often form a supramolecular gel; they are an organogelator for organic solvents and oils[2] and a hydrogelator for aqueous solutions.[3] In supramolecular gels, the gelator molecules create a three-dimensional network formed by entanglement of supramolecular polymers; therefore, most supramolecular gels are physical gels that undergo thermally reversible gel-to-sol transition. Because of their unique properties, gelators and their supramolecular gels have been of interest as fascinating materials.

Recently, low-molecular-weight gelators have been of interest not only for their gelation abilities but also for their nanostructures formed in the supramolecular gels. The gelators form various nanostructures such as nanofibers, nanoribbons, nanoparticles, and helical structures.[2–4] In particular, dumbbell-form compounds show a good gelation ability and form a helical (twisted) nanostructure because they may have at least two intermolecular interaction sites on both sides.[4c,5] One of the applications is their use as an organic template for the fabrication of mesoporous polymer materials[6] and nanoscale designed inorganic materials.[7] The sol-gel polymerization of various metal alkoxides (Si, Ti, Ta, V, *etc.*), in solvents containing gelators, forms hollow nanofibers and helical nanofibers followed by calcinations.[7] Other applications are their use as gel electrolytes,[8] liquid crystallines,[9] and so on.[10] As wide applications, gelators that are simply synthesized and environmentally friendly are desired. In this paper, we describe the simple synthesis of new dumbbell-form gelators based on L-lysine and their gelation abilities in aqueous solutions and organic solvents. These dumbbell compounds are environmentally-friendly due to the use of L-lysine and their synthetic procedures are only two steps with relatively high reaction yields.

Results and discussion

Synthesis of gelators

Gelators **1–6** were prepared according to Scheme 1. Carboxylic acid-type compounds were prepared by acylation of N^{ε}-lauroyl-L-lysine (2.5 eq.) and corresponding diacid dichlorides (1 eq.), followed by addition of conc. HCl. Monosodium salt compounds, **1a–7a**, were obtained by reaction of **1–7** and 1 M NaOH in methanol. These compounds were obtained in relatively high yield (60–90% for **1–7** and >99% for **1a–7a**).

Hydrogelation and organogelation properties

We also synthesized disodium salt compounds and examined their hydrogelation and organogelation properties. Unfortunately, these compounds had no gelation abilities for aqueous solutions and organic solvents. The monosodium salt compounds, however, showed hydrogelation and organogelation properties. The gelation properties of **1a–7a** are listed in Table 1. In pure water, all gelators, except for **7a**, formed a hydrogel below 2.5 wt%, and the hydrogelation abilities increased with the decreasing length of the alkylene spacer. In contrast, the hydrogels were formed at the low concentrations when the spacer length increased for 0.1 M $NaCl_{(aq)}$ solution and the mixed solution of ethanol and water. It is noteworthy that **7a** forms the hydrogels in the presence of NaCl or ethanol in

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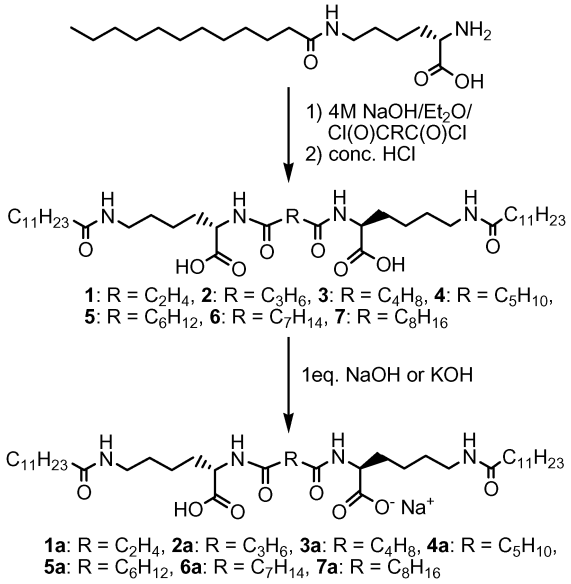


Scheme 1 Synthetic procedure of gelators.

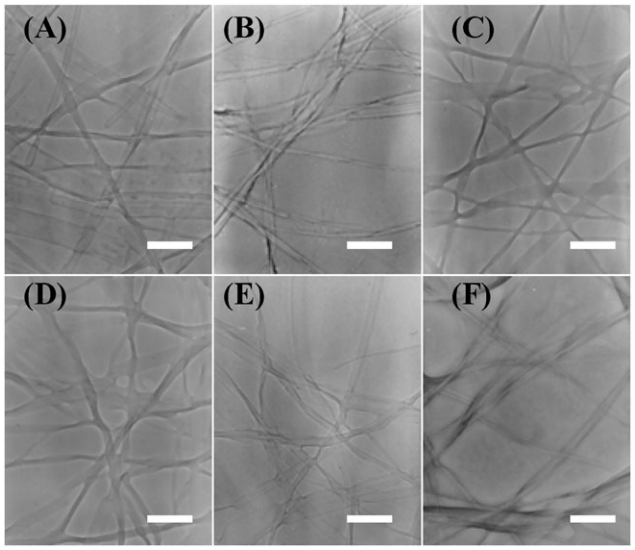


Fig. 1 TEM images of samples prepared from hydrogels and organogels. Hydrogels based on **2a** (A), **4a** (B), and **4a** (C) in 0.1 M NaCl. Chloroform gels based on **2a** (D) and **4a** (E), and a THF gel based on **4a** (F). Scale bars are 200 nm.

water, but not in pure water. Probably, such hydrogelation behavior is induced by the change of polarity in aqueous solutions.

On the other hand, these gelators are well-soluble in methanol and ethanol, while they form organogels in some organic solvents. It is noteworthy that most gelators are able to gel chloroform. In addition, **7a** was able to gel many organic solvents. Although **1a**, possessing a short alkylene spacer, is insoluble in PrOH, BuOH, cyclohexanone, and THF, it shows good organogelation abilities for aromatic solvents, DMSO, and $CHCl_3$. These results indicate that these gelators function as amphiphilic gelators that can form organogels and hydrogels.

Transmission electron microscopy (TEM)

To evaluate visual insights into the aggregation modes of the gelators in hydrogels and organogels, we took the TEM images. Fig. 1 shows the TEM images of dried gels prepared from hydrogels based on **2a** (A), **4a** (B), and **4a** in 0.1 M NaCl (C), as well as chloroform gels based on **2a** (D) and **4a** (E) and a THF gel based on **4a** (F). In organogels and hydrogels, all gelators form self-assembled nanofibers with a diameter of several tens of nanometres and create a three-dimensional network by entanglement of the nanofibers. Therefore, organogelation and hydrogelation occur because many nanospaces in the three-dimensional network structure absorb solvents.

Thermal stability of hydrogels

All hydrogels were thermoreversible; they turned into clear solutions upon heating and gelation returned after cooling. To evaluate the thermal stabilities of hydrogels, we measured the hydrogel-broken temperatures (T_{gel}). At 80 °C, all gelators were dissolved at 50 g L^{-1}. The T_{gel} value increased with the increasing concentration of gelators.[9] Especially, the saline and NaCl gels based on **3a** had good thermal stabilities; their T_{gel} values were 70 °C at 20 g L^{-1}.

Fig. 2 shows the dependence of the T_{gel} values, at 30 g L^{-1} of gelator, on the length of alkylene spacer and the T_{gel} values are listed in Table 2. Interestingly, an odd–even effect of the methylene spacer on the T_{gel} values was observed, and the effect varied between long spacer and short spacer (boundary

Table 1 Hydrogelation and organogelation properties at 25 °C[a]

	1a	2a	3a	4a	5a	6a	7a
H_2O	15	15	15	20	20	25	S
Saline	15	10	20	10	15	15	20
NaCl	20	20	15	20	30	15	15
EtOH–H_2O	25	20	25	30	20	15	15
MeOH	S	S	S	S	S	S	S
EtOH	S	S	S	S	S	S	S
^{1}PrOH	INS	VS	45	P	S	10	10
^{1}BuOH	INS	45	50	P	S	S	30
Cyclohexanone	INS	10	10	10	10	10	10
THF	INS	INS	INS	5	30	35	50
Ph–CH_3	10	VS	VS	7	VS	VS	45
Ph–Cl	7	10	45	20	10	50	15
Ph–NO_2	10	25	10	10	50	10	10
DMF	P	40	VS	40	20	VS	40
DMSO	10	30	VS	40	15	10	10
$CHCl_3$	10	5	VS	10	20	20	35

[a] Values denote minimum gel concentration (MGC, g L^{-1}) necessary for gelation. S: Solution at 5 wt%; VS: viscous fluid at 5 wt%; INS: almost insoluble; P: precipitate.

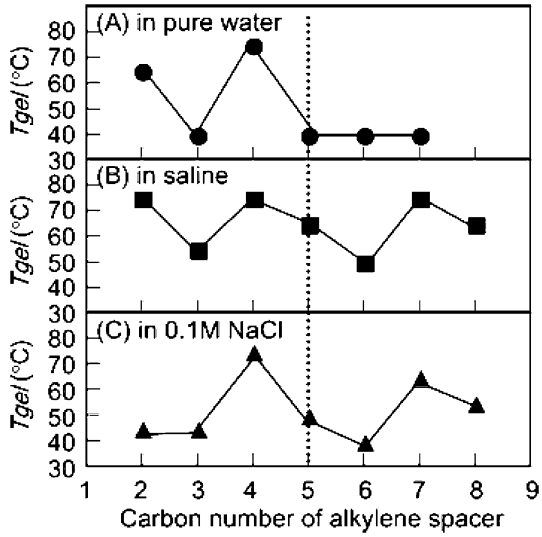


Fig. 2 Plots of T_{gel} for hydrogels against carbon number of alkylene spacer. (A): Pure water gels; (B): saline gels; (C): NaCl gels. [Gelator] = 30 g L^{-1}.

Table 2 T_{gel} values of hydrogels based on **1a–7a**[a]

	1a	2a	3a	4a	5a	6a	7a
H_2O	65 °C	40 °C	75 °C	40 °C	40 °C	40 °C	—
Saline	70 °C	55 °C	75 °C	65 °C	50 °C	75 °C	65 °C
NaCl	45 °C	45 °C	75 °C	50 °C	40 °C	65 °C	55 °C

[a] [Gelator] = 30 g L^{-1}.

number is 5). In pure water, the valley and top of T_{gel} were repeated alternately according to the even and odd numbers of the alkylene spacer up to a carbon number of 5 [top for **1a** (C2) and **3a** (C4), valley for **2a** (C3) and **4a** (C5)], and then T_{gel} values were independent of the alkylene spacer. The alternate valley and top were also observed in the T_{gel} values for saline gels and NaCl gels up to a carbon number of 5, while they varied for hydrogelators with the long alkylene spacer [top for **4a** (C5) and **6a** (C7), valley for **5a** (C6) and **7a** (C8)]. Considering that no differences in appearance of the self-assembled nanofibers were observed by the TEM, the phenomena may be attributable to structural differences in the self-assembly.

Variable temperature FT-IR study

It is well-known that hydrogen bonding and van der Waals interactions are main driving forces for the self-assembly of the gelators into nanofibers.[2,3] IR spectroscopy is a powerful tool for studying these interactions. Fig. 3 shows the temperature controlled FT-IR spectra of **5a** in D_2O. Up to 40 °C, the IR spectra hardly changed and showed absorption bands at 2919 cm^{-1} (ν_{as}C–H), 2849 cm^{-1} (ν_{s}C–H), 1726 cm^{-1} (νC=O, CO_2H), 1627 cm^{-1} (νC=O, amide I), and 1585 cm^{-1} (νC–O, CO_2^-). The absorption bands dramatically change over 40 °C; the absorption band of the amide I broadened and the absorbance decreased. In addition, the IR peaks of ν_{as}C–H, and ν_{s}C–H shifted to a higher frequency [2919 cm^{-1} → 2925 cm^{-1} (ν_{as}C–H) and 2849 cm^{-1} → 2856 cm^{-1} (ν_{s}C–H)]. The temperature is consistent with the T_{gel}; *i.e.*, the IR spectral change when the hydrogel is broken. In contrast, the absorption band of the carboxyl group showed a different temperature dependence; the IR peak dramatically changed over 55 °C. These results indicate that the gel-to-sol transition is induced by mainly breaking hydrogen bonds and van der Waals interactions.

^{1}H-NMR and FT-IR studies

In order to evaluate their structures in the self-assembly, we measured the FT-IR and ^{1}H-NMR spectra of their hydrogels at 25 °C. Fig. 4A shows the FT-IR spectra of **1a–7a** in D_2O. It is clear that the IR profiles significantly depend on the alkylene spacer. For **1a**, **3a**, **5a**, and **7a** with even alkylene spacers, the sharp IR peak, arising from the hydrogen bonded amide I, and broad IR peaks of carboxylic acid and carboxylate were observed at 1627 cm^{-1}, 1725 cm^{-1} and 1586 cm^{-1}, respectively. In contrast, the absorption bands arising from the carboxylic acid and carboxylate appeared clearly for **2a**, **4a**, and **6a** with the odd alkylene spacers, and the IR peak of the amide I slightly broadened. These results indicate that a difference in the IR profiles between both gelators corresponds to these different hydrogen bonding modes caused by the odd–even effect.

Fig. 4B shows the ^{1}H-NMR spectra of **1a–7a** in D_2O–H_2O (2 : 8, v/v). For gelators with even alkylene spacers (**1a**, **3a**, **5a**, and **7a**), two NMR signals, corresponding to the hydrogen-bonded amide protons, were observed. Because these gelators have the two different amide protons, these gelators self-assemble into nanofibers through two different hydrogen bonding modes. In contrast, one NMR signal corresponding to the hydrogen-bonded amide protons appeared for gelators with the odd alkylene spacers (**2a**, **4a**, and **6a**), indicating the presence of one hydrogen bonding mode in the self-assembly.

Hydrogen bonding modes

These results led us to assume the intermolecular hydrogen bonding modes as illustrated in Scheme 2. These gelators have two amides (two ε-amide groups and two α-amide groups) as the hydrogen-bonded sites. Because the two α-amide groups and ε-amide groups in the gelators of even-numbered chains are antiparallel (the opposite direction), it is possible for the gelators to undergo the four intermolecular hydrogen bonding interactions through two modes that are between α-amide groups and between ε-amide groups. In contrast, the amide groups in the gelators of odd-numbered chains are parallel (the

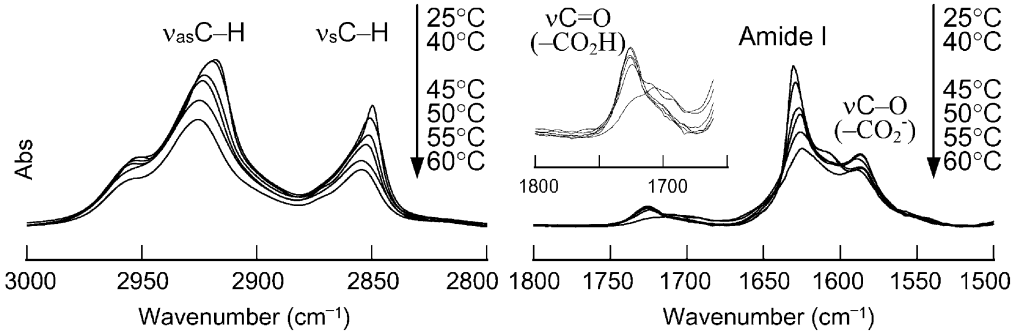


Fig. 3 Variable temperature FT-IR spectra of **5a** (30 mg mL^{-1}) in D_2O.

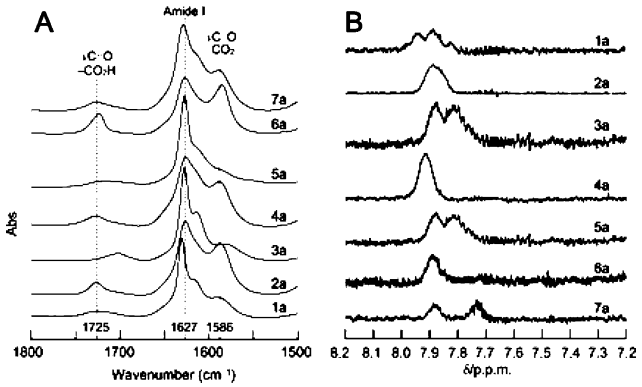


Fig. 4 FT-IR (A) and ^{1}H-NMR (B) spectra of **1a–7a** at 25 °C. A: In D_2O, [**1a–7a**] = 20 mg mL^{-1}; B: in D_2O–H_2O (2 : 8, v/v), [**1a–7a**] = 15 mg mL^{-1}.

same direction) and they have four hydrogen bonding interactions with one binding mode that are between α-amides and between ε-amides. The gelators of the even-numbered chains have strong interactions through the hydrogen bonding at the center sites (α-amides) and in both sides (ε-amides), which leads to the formation of thermally stable hydrogels.

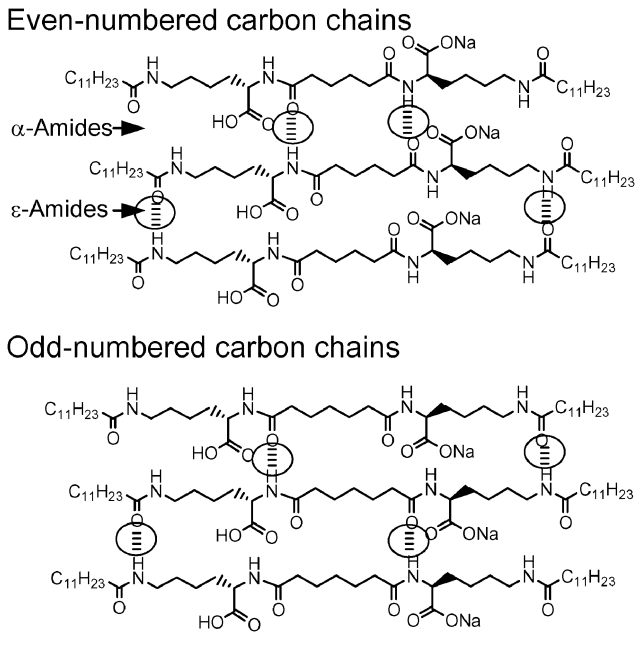
Conclusion

In conclusion, we revealed that the synthesis of novel dumbbell-form amphiphilic gelators based on L-lysine derivatives and their gelation abilities were investigated. They function as amphiphilic gelators that can gel not only aqueous solutions but also organic solvents. In the hydrogels, the hydrogel-broken temperatures (T_{gel}) depend on the carbon number of the alkylene spacer and the gelators of the even-numbered chains form a thermally stable hydrogel. This can be explained by different hydrogen bonding modes.

Experimental section

Materials

N^{ε}-Lauroyl-L-lysine was supplied from the Ajinomoto Co., Inc. All acid chlorides were purified by distillation just before use. The other chemicals were of the highest commercially available grade and used without further purification. All solvents used in the syntheses were purified, dried, or freshly distilled as required.



Scheme 2 Tentative illustration of hydrogen bonding modes.

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. TEM images were obtained using a JEOL JEM-2010 electron microscope at 200 kV. ^{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 water (1 mL) in a sealed test tube was heated 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.

TEM

Samples were prepared as follows: the aqueous or organic solutions of the gelators were dropped on a collodion and carbon coated 400 mesh copper grid and dried in a vacuum for 24 h. After dropping a 2 wt% phosphotungstic acid solution, the grids were dried under reduced pressure for 24 h.

FT-IR study

FT-IR spectroscopy was performed in D_2O (15 mg mL^{-1} of gelators) operating at a 2 cm^{-1} resolution with 32 scans. The spectroscopic cell with a CaF_2 window and 25 μm spacers was used for the measurements. The various temperature FT-IR spectra were measured using an automatic temperature-control cell unit (Specac Inc., P/N 20730) with a vacuum-tight liquid cell (Specac Inc., P/N 20502, path length 50 μm) fitted with CaF_2 windows.

^{1}H-NMR study

Solutions of gelators (15 mg mL^{-1}) were prepared in D_2O–H_2O (2 : 8, v/v).

General procedure for the synthesis of bis(N^{ε}-lauroyl-L-lysine) alkanedioyl amides

N^{ε}-Lauroyl-L-lysine (60 mmol) was dissolved in water (600 mL) containing NaOH (0.3 mol) and diethyl ether was added. Freshly distilled alkanedioyl chloride (30 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 with 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.

Bis(N^{ε}-lauroyl-L-lysine) succinyl amide (1)

88%. IR (KBr): 3310 cm^{-1} (amide A), 1728 cm^{-1} (ν C=O, CO_2H), 1640 cm^{-1} (amide I), 1547 cm^{-1} (amide II); ^{1}H-NMR [400 MHz, $CDCl_3$–DMSO-d_6 (5 : 5), 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 calcd (%) 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.

Bis(N^{ε}-lauroyl-L-lysine) glutaryl amide (2)

93%. IR (KBr): 3308 cm^{-1} (amide A), 1732 cm^{-1} (νC=O, CO_2H), 1640 cm^{-1} (amide I), 1555 cm^{-1} (amide II); ^{1}H-NMR [400 MHz, $CDCl_3$–DMSO-d_6 (8 : 2), TMS, 30 °C]: $\delta = 0.88$ (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 calcd (%) 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.

Bis(N^{ε}-lauroyl-L-lysine) adipoyl amide (3)

90%. IR (KBr): 3310 cm^{-1} (amide A), 1724 cm^{-1} (νC=O, CO_2H), 1641 cm^{-1} (amide I), 1544 cm^{-1} (amide II); ^{1}H-NMR [400 MHz, $CDCl_3$–DMSO-d_6 (6 : 4), TMS, 25 °C]: $\delta = 0.88$ (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 calcd (%) 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.

Bis(N^{ε}-lauroyl-L-lysine) pimeloyl amide (4)

92%. IR (KBr): 3309 cm^{-1} (amide A), 1731 cm^{-1} (νC=O, CO_2H), 1641 cm^{-1} (amide I), 1550 cm^{-1} (amide II); ^{1}H-NMR [400 MHz, $CDCl_3$–DMSO-d_6 (6 : 4), TMS, 25 °C]: $\delta = 0.88$ (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, $J = 6.1$, 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 calcd (%) 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.

Bis(N^{ε}-lauroyl-L-lysine) suberoyl amide (5)

96%. IR (KBr): 3312 cm^{-1} (amide A), 1723 cm^{-1} (νC=O, CO_2H), 1642 cm^{-1} (amide I), 1543 cm^{-1} (amide II); ^{1}H-NMR [400 MHz, $CDCl_3$–DMSO-d_6 (5 : 5), TMS, 25 °C]: $\delta = 0.87$ (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 calcd (%) 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.

Bis(N^{ε}-lauroyl-L-lysine) azelaoyl amide (6)

92%. IR (KBr): 3309 cm^{-1} (amide A), 1731 cm^{-1} (νC=O, CO_2H), 1639 cm^{-1} (amide I), 1548 cm^{-1} (amide II); ^{1}H-NMR [400 MHz, $CDCl_3$–DMSO-d_6 (8 : 2), TMS, 25 °C]: $\delta = 0.88$ (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 calcd (%) 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.

Bis(N^{ε}-lauroyl-L-lysine) sebacoyl amide (7)

93%. IR (KBr): 3313 cm^{-1} (amide A), 1727 cm^{-1} (νC=O, CO_2H), 1641 cm^{-1} (amide I), 1545 cm^{-1} (amide II); ^{1}H-NMR [400 MHz, $CDCl_3$–DMSO-d_6 (5 : 5), TMS, 25 °C]: $\delta = 0.87$ (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 calcd (%) 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.

General procedure for the synthesis of bis(N^{ε}-lauroyl-L-lysine) alkanedioyl amide monosodium salts

Diacid compound (10 mmol) was dissolved in MeOH (300 mL) and 1 M NaOH solution (10 mL) was added. The resulting solution was evaporated to dryness. The monosodium compound was obtained by recrystallization from MeOH–ether.

Bis(N^{ε}-lauroyl-L-lysine) succinyl amide monosodium salt (1a)

99%. IR (KBr): 3307 cm^{-1} (amide A), 1716 cm^{-1} (νC=O, CO_2H), 1645 cm^{-1} (amide I), 1549 cm^{-1} (amide II); ^{1}H-NMR [400 MHz, $CDCl_3$–DMSO-d_6 (2 : 8), TMS, 30 °C]: $\delta = 0.87$ (t, $J = 6.6$ Hz, 6H; CH_3), 1.67–1.73 (m, 2H; $COCH_2CH_2CH_2CO$), 2.05 (t, $J = 7.6$ Hz, 4H; $CH_2CON^{\varepsilon}H$, $N^{\varepsilon}HCOCH_2$), 2.12 (t, $J = 6.8$ Hz, 4H; $N^{\alpha}HCOCH_2$, $CH_2CON^{\alpha}H$), 3.01 (q, $J = 6.3$ Hz, 4H; $NHCH_2$), 4.06 (q, $J = 5.3$ Hz, 2H; CH), 7.55 (d, $J = 7.6$ Hz, 2H; $N^{\alpha}H$), 7.69 (t, $J = 5.3$ Hz, 2H; $N^{\varepsilon}H$); elemental analysis calcd (%) for $C_{40}H_{73}N_4O_8Na$ (761.02): C, 63.13; H, 9.67; N, 7.36. Found: C, 63.21; H, 9.77; N, 7.36.

Bis(N^{ε}-lauroyl-L-lysine) glutaryl amide monosodium salt (2a)

99%. IR (KBr): 3304 cm^{-1} (νN–H, amide A), 1716 cm^{-1} (νC=O, CO_2H), 1645 cm^{-1} (νC=O, amide I), 1549 cm^{-1} (δN–H, amide II); ^{1}H-NMR [400 MHz, $CDCl_3$–DMSO-d_6 (2 : 8), TMS, 30 °C]: $\delta = 0.87$ (t, $J = 6.6$ Hz, 6H; CH_3), 1.67–1.73 (m, 2H; $COCH_2CH_2CH_2CO$), 2.05 (t, $J = 7.6$ Hz, 4H; $CH_2CON^{\varepsilon}H$, $N^{\varepsilon}HCOCH_2$), 2.12 (t, $J = 6.8$ Hz, 4H; $CH_2CON^{\alpha}H$, $N^{\alpha}HCOCH_2$), 3.01 (q, $J = 6.3$ Hz, 4H; $NHCH_2$), 4.06 (q, $J = 5.3$ Hz, 2H; CH), 7.55 (d, $J = 7.6$ Hz, 2H; $N^{\alpha}H$), 7.69 (t, $J = 5.3$ Hz, 2H; $N^{\varepsilon}H$); elemental analysis calcd (%) for $C_{41}H_{75}N_4O_8Na$ (775.05): C, 63.54; H, 9.75; N, 7.23. Found: C, 63.61; H, 10.05; N, 7.23.

Bis(N^{ε}-lauroyl-L-lysine) adipoyl amide monosodium salt (3a)

99%. IR (KBr): 3311 cm^{-1} (νN–H, amide A), 1715 cm^{-1} (νC=O, CO_2H), 1644 cm^{-1} (νC=O, amide I), 1549 cm^{-1} (δN–H, amide II); ^{1}H-NMR [400 MHz, $CDCl_3$–DMSO-d_6 (2 : 8), TMS, 25 °C]: $\delta = 0.87$ (t, $J = 6.6$ Hz, 6H; CH_3), 2.07 (t, $J = 7.6$ Hz, 4H; $CH_2CON^{\varepsilon}H$, $N^{\varepsilon}HCOCH_2$), 2.18 (br, 4H; $CH_2CON^{\alpha}H$, $N^{\alpha}HCOCH_2$), 3.05 (br, 4H; $NHCH_2$), 4.16 (q, $J = 5.0$ Hz, 2H; CH), 7.64–7.66 (m, 2H; $N^{\alpha}H$, $N^{\varepsilon}H$); elemental analysis calcd (%) for $C_{42}H_{77}N_4O_8Na$ (789.07): C, 63.93; H, 9.84; N, 7.10. Found: C, 63.99; H, 9.99; N, 7.11.

Bis(N^{ε}-lauroyl-L-lysine) pimeloyl amide monosodium salt (4a)

98%. IR (KBr): 3304 cm^{-1} (νN–H, amide A), 1739 cm^{-1} (νC=O, CO_2H), 1644 cm^{-1} (νC=O, amide I), 1548 cm^{-1} (δN–H, amide II); ^{1}H-NMR [400 MHz, $CDCl_3$–DMSO-d_6 (2 : 8), TMS, 25 °C]: $\delta = 0.87$ (t, $J = 6.6$ Hz, 6H; CH_3), 2.07 (t, $J = 7.6$ Hz, 4H; $CH_2CON^{\varepsilon}H$, $N^{\varepsilon}HCOCH_2$), 2.11–2.17 (m, 4H; $N^{\alpha}HCOCH_2$, $CH_2CON^{\alpha}H$), 3.04 (q, $J = 6.3$ Hz, 4H; $NHCH_2$), 4.11 (q, $J = 5.0$ Hz, 2H; CH), 7.52 (d, $J = 7.3$ Hz, 2H; $N^{\alpha}H$), 7.64 (t, $J = 5.3$ Hz, 2H; $N^{\varepsilon}H$); elemental analysis calcd (%) for $C_{43}H_{79}N_4O_8Na$ (803.10): C, 64.31; H, 9.91; N, 6.98. Found: C, 64.35; H, 10.18; N, 7.00.

Bis(N^{ε}-lauroyl-L-lysine) suberoyl amide monosodium salt (5a)

98%. IR (KBr): 3306 cm^{-1} (νN–H, amide A), 1712 cm^{-1} (νC=O, CO_2H), 1643 cm^{-1} (νC=O, amide I), 1551 cm^{-1} (δN–H, amide II); ^{1}H-NMR [400 MHz, $CDCl_3$–DMSO-d_6 (2 : 8), TMS, 25 °C]: $\delta = 0.87$ (t, $J = 6.6$ Hz, 6H; CH_3), 2.06 (t, $J = 7.6$ Hz, 4H; $CH_2CON^{\varepsilon}H$, $N^{\varepsilon}HCOCH_2$), 2.13 (t, $J = 6.8$ Hz, 4H; $CH_2CON^{\alpha}H$, $N^{\alpha}HCOCH_2$), 2.99–3.09 (m, 4H; $NHCH_2$), 4.09–4.14 (m, 2H; CH), 7.68 (t, $J = 5.3$ Hz, 2H; $N^{\varepsilon}H$), 7.75 (d, $J = 7.8$ Hz, 2H; $N^{\alpha}H$); elemental analysis calcd (%)

for $C_{44}H_{81}N_4O_8Na$ (817.13): C, 64.67; H, 9.99; N, 6.86. Found: C, 64.69; H, 10.24; N, 6.87.

Bis(N^{ε}-lauroyl-L-lysine) azelaoyl amide monosodium salt (6a)

98%. IR (KBr): 3307 cm^{-1} (νN–H, amide A), 1715 cm^{-1} (νC=O, CO_2H), 1642 cm^{-1} (νC=O, amide I), 1550 cm^{-1} (δN–H, amide II); ^{1}H-NMR [400 MHz, $CDCl_3$–DMSO-d_6 (2 : 8), TMS, 25 °C]: $\delta = 0.86$ (t, $J = 6.6$ Hz, 6H; CH_3), 2.03 (t, $J = 7.3$ Hz, 4H; $CH_2CON^{\varepsilon}H$, $N^{\varepsilon}HCOCH_2$), 2.10 (t, $J = 7.1$ Hz, 4H; $CH_2CON^{\alpha}H$, $N^{\alpha}HCOCH_2$), 3.00 (q, $J = 6.6$ Hz, 4H; $NHCH_2$), 4.07 (q, $J = 5.1$ Hz, 2H; CH), 7.67–7.71 (m, 4H; $N^{\varepsilon}H$, $N^{\alpha}H$); elemental analysis calcd (%) for $C_{45}H_{83}N_4O_8Na$ (831.15): C, 65.03; H, 10.07; N, 6.74. Found: C, 65.10; H, 10.47; N, 6.74.

Bis(N^{ε}-lauroyl-L-lysine) sebacoyl amide monosodium salt (7a)

98%. IR (KBr): 3309 cm^{-1} (νN–H, amide A), 1715 cm^{-1} (νC=O, CO_2H), 1643 cm^{-1} (νC=O, amide I), 1550 cm^{-1} (δN–H, amide II); ^{1}H–NMR [400 MHz, $CDCl_3$–DMSO-d_6 (2 : 8), TMS, 25 °C]: $\delta = 0.86$ (t, $J = 7.1$ Hz, 6H; CH_3), 2.04 (t, $J = 7.3$ Hz, 4H; $CH_2CON^{\varepsilon}H$, $N^{\varepsilon}HCOCH_2$), 2.11 (t, $J = 7.1$ Hz 4H; $CH_2CON^{\alpha}H$, $N^{\alpha}HCOCH_2$), 3.01 (q, $J = 6.6$ Hz, 4H; $NHCH_2$), 4.04–4.10 (m, 2H; CH), 7.63–7.67 (m, 4H; $N^{\varepsilon}H$, $N^{\alpha}H$); elemental analysis calcd (%) for $C_{46}H_{85}N_4O_8Na$ (845.18): C, 65.37; H, 10.14; N, 6.63. Found: C, 65.38; H, 10.34; N, 6.64.

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