Novel Low-Molecular-Weight Gelators Based on Azobenzene Containing L-Amino Acids

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A series of azobenzene derivatives containing glycine, L-alanine, L-valine, L-leucine, and L-isoleucine were synthesized and their gelation properties were examined. Although the azobenzene derivatives containing glycine, L-alanine, and L-leucine exhibited very low gelation abilities, other compounds of L-isoleucine and L-valine acted as good gelators that formed organogels in many organic solvents and oils at relatively low concentrations. The electron microscopic observation demonstrated that a three-dimensional network was created by entanglement of self-assembled nanofibers. Furthermore, the spectroscopic studies suggested that the gelator molecules self-assembled into the nanofibers through hydrogen bonding and π–π interactions, including the H-aggregation mode of the azobenzene segments.

Low molecular weight organogelators have received much attention because of their potential applications to viscoelastic materials, cosmetics, drug delivery system, and pharmacology.[1,2] Organogels consist of long nanofibers, which are self-assembled as a result of the usual array of supramolecular forces such as hydrogen bonding, π-stacking, electrostatic, and van der Waals interactions. Noncovalent cross-links among the nanofibers and mechanical entanglements create a three-dimensional network to entrap solvent molecules within the interstices. A large number of organogelators based on peptides,[3–5] fatty acids,[6] steroids,[7] and fluorinated alkenes[8] have been reported. In particular, the peptide-type compounds containing L-isoleucine and L-valine derivatives function as excellent gelators that can gel many organic solvents at low concentration.[3,9] Organogelators and organogels have been applied to gel electrolytes,[9] liquid crystalline gel,[10] and ionogels.[11] Furthermore, the superstructures formed by gelators have been used as organic templates for the fabrication of mesoporous polymer materials and nano-scaled designed inorganic materials.[12–14]

On the other hand, azobenzene is well-known as a photoresponsive compound that undergoes the trans-cis isomerization upon UV irradiation and returns to the initial state by heating or visible light irradiation.[15,16] Organogelators based on azobenzene derivatives have been reported. For example, Shinkai and coworkers reported photoresponsive cholesterol based organogelators having azobenzene moiety.[6] Kato et al. reported azobenzene derivatives that can gel liquid cryatals.[17]

In addition, azobenzene derivatives have a self-organization property in some solvents through π–π interaction: their aggregation modes are mainly classified into H-aggregation and J-aggregation.[16,18] Such self-organization properties of azobenzene derivatives should be useful for development of new gelators.

In this paper, we describe the synthesis of new gelators based on azobenzene derivatives with L-amino acids such as glycine, L-alanine, L-leucine, L-isoleucine, and L-valine. Their gelation abilities and aggregation modes of the gelator molecules in the organogel were studied.

Results and Discussion

Gelation Ability. Chart 1 and Table 1 show the chemical structure of **1**–**16** and the results of gelation test. All azobenzene derivatives containing glycine (**6**, **11**, **16**), L-alanine (**5**, **10**, **15**), and L-leucine (**4**, **9**, **14**) exhibited very low gelation abilities, while those of L-isoleucine and L-valine formed organogels in some organic solvents. These results are in agreement with the previous report.[19] Gelation ability strongly depends on the structure of the amino acid residue. Monosubstituted azobenzene derivatives **1**–**3** had good gelation abilities for aromatic solvents and oils; e.g., the MGC values of **2** for nitrobenzene and silicone oil were 5 mg/mL and 4 mg/mL. Gelator **2** has better gelation ability than **1**. This is because **2** has a long alkyl chain that provides more suitable hydrophilic–hydrophobic balance for gelation. On the other hand, 4-substituted benzoic acid derivatives **7** and **8** and disubstituted azobenzene derivatives **12** and **13** had better gelation abilities than **1**–**3**; they formed organogels in aromatic solvents, pyridine, and oils. It is noteworthy that these compounds can gel chloroform and THF, which are usually difficult to gel up. Compared with **1**–**3**, these compounds have more functional groups capable of forming hydrogen bonds. Namely, besides an amide segment, **7** and **8** have a carboxylic group, while **12** and **13** possess another amide. The carboxylic group of **7** and **8** and the other amide segment of **12** and **13** will result in the effective gelation.

TEM and FE-SEM Observations. Considering that the gelation mechanism by gelators is primary by self-aggregation of molecules, followed by the gathering of self-aggregates, one can reasonably assume that images of molecular aggregates

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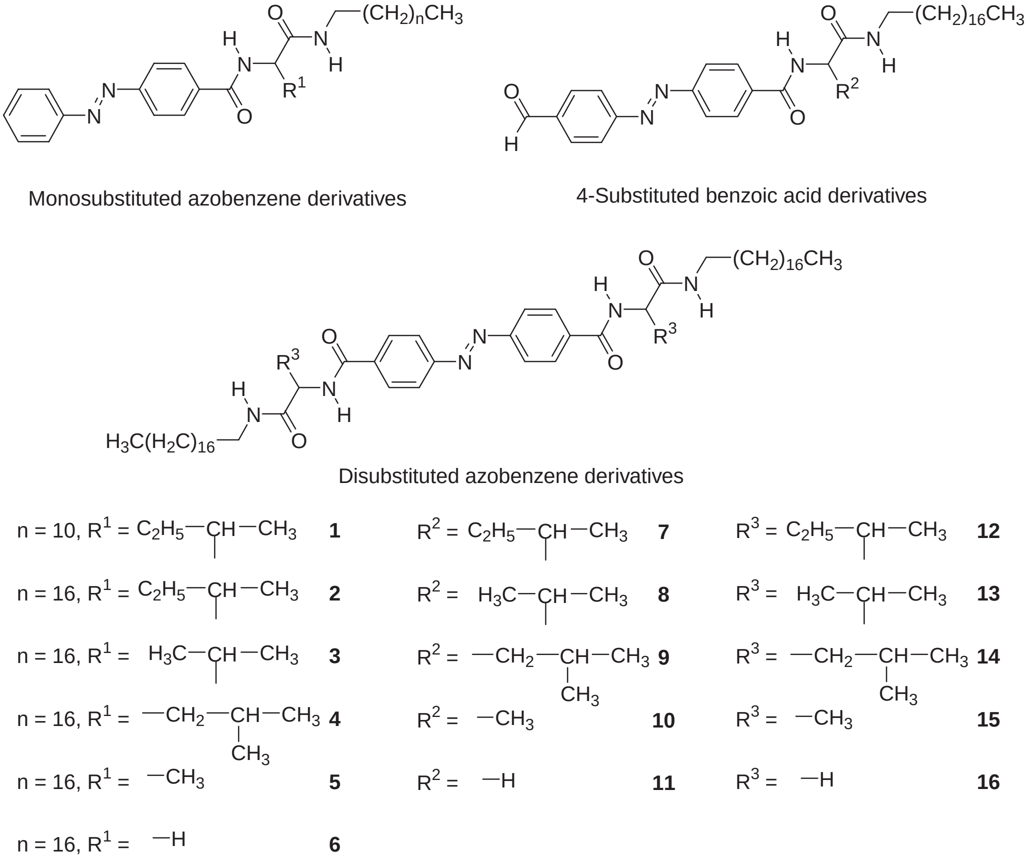

Chemical structure of **1-16**

Chart 1.

Table 1. Gelation Properties of **1**–**3**, **7**, **8**, **12**, and **13** at 25 °C

Solvent	**1**	**2**	**3**	**7**	**8**	**12**	**13**
Cyclohexane	C	C	C	I	I	I	I
Cyclohexanone	C	C	C	V.F.	V.F.	7	12
1-Propanol	C	C	C	7	7	S	S
2-Butanone	C	C	C	C	C	V.F.	V.F.
THF	C	C	C	20	22	15	10
Benzene	10	6	6	8	12	8	8
Nitrobenzene	15	6	5	8	8	8	8
Toluene	18	12	14	12	10	10	3
Chlorobenzene	15	5	C	9	13	9	13
Chloroform	S	S	S	32	30	32	30
CCl_4	C	C	C	C	C	V.F.	V.F.
DMF	C	C	C	C	C	C	C
Pyridine	S	S	S	17	22	17	8
Kerosene	5	2	2	3	5	3	5
Light oil	5	2	2	4	5	4	5
Silicone oil	8	4	2	7	7	7	5

Values means minimum gel concentration (MGC, mg/mL) necessary for gelation, C = crystallization, S = solution, I = almost insoluble, V.F. = viscous fluid.

can be observed by electron microscope. Actually, superstructures built up with **7**, **12**, and **13** in the organogels were observed by electron microscopy (TEM, FE-SEM). As expected, these gelators create a three-dimensional network by the entanglement of self-assembled nanofibers with a diameter of 20–50 nm (Fig. 1). Very interestingly, the electron micrographs reveal that gelator **7** self-assembled numerous intertwined helical fibers in the benzene gel. It is assumed that the gelation occurs by entrapping solvent molecules in the space of the three-dimensional networks, as shown in Fig. 1c.

FT-IR Spectroscopy. It is well-known that hydrogen bonding is one of the driving forces for the self-assembly of gelators in organic solvents.[1] The infrared spectroscopy is a powerful tool to study hydrogen bonding interactions. Figure 2 shows the FT-IR spectra of **12** in chloroform. At the low concentrations (1 mg/mL and 2 mg/mL), typical IR bands were observed at 1650 cm^{-1} and 3435 cm^{-1}, which are characteristic of non-hydrogen bonding amide I (νC=O) and amide A (νN–H), respectively. With the increasing concentration of **12**, new IR peaks appeared at 1628 cm^{-1} and 3292 cm^{-1}. It should be mentioned that these spectra were similar to the IR spectrum of KBr-pellet of solid **12**. Figure 3 shows the FT-IR spectra of **7** in chloroform. At the low concentrations, the IR bands were observed at 1651 cm^{-1} (νC=O) and 3438 cm^{-1} (νN–H), characteristics of non-hydrogen bonding amide groups. With the increasing concentration of **7**, new IR peaks appeared at 1630 cm^{-1} (νC=O) and 3297 cm^{-1} (νN–H), corresponding to hydrogen-bonded amide group. Thus, the amide groups of **7** play an important role for gelation. In contrast, the IR peak of the carboxyl group was observed at 1719 cm^{-1} (νC=O) and was independent of

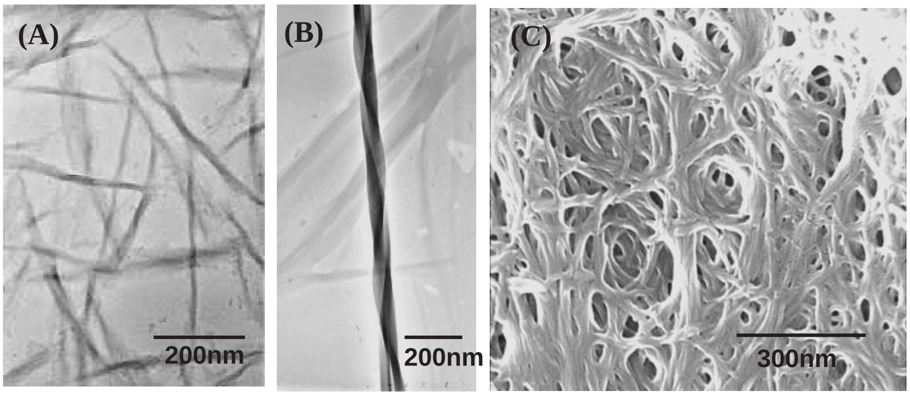

Fig. 1. Electron micrographs of dried gels. (A) toluene gel by **13** (TEM), (B) benzene gel by **12** (TEM), and (C) chloroform gel by **12** (FE-SEM).

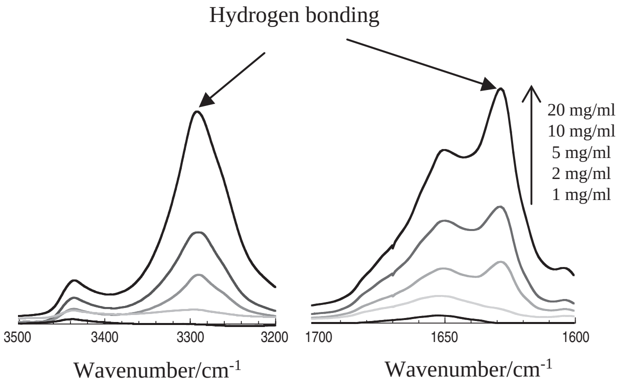

Fig. 2. FT-IR spectra of chloroform solution of **12** at various concentrations.

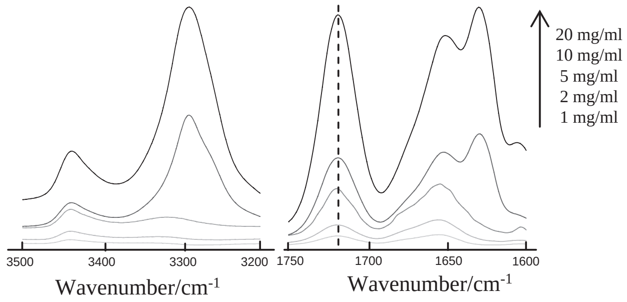

Fig. 3. FT-IR spectra of **7** in chloroform at various concentrations.

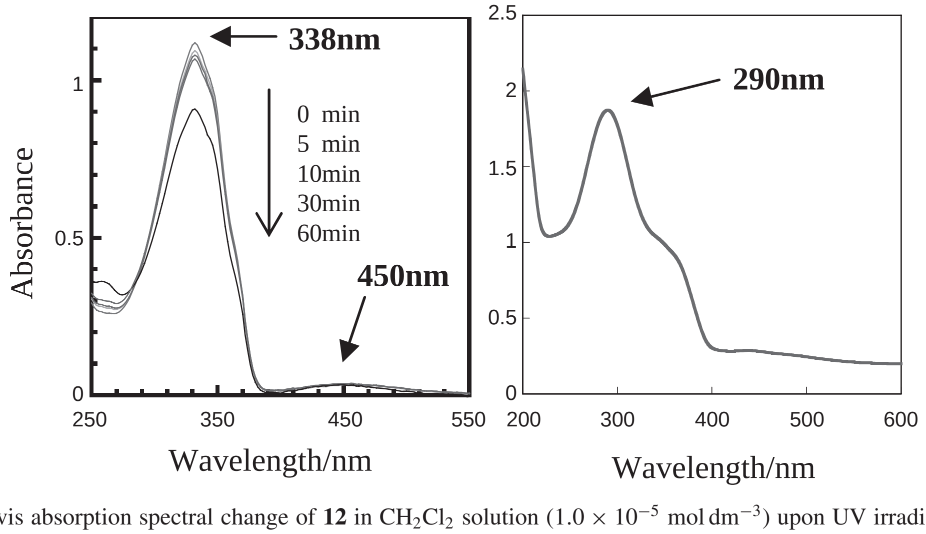

Fig. 4. (A) UV–vis absorption spectral change of **12** in CH_2Cl_2 solution (1.0×10^{-5} mol dm^{-3}) upon UV irradiation. (B) UV–vis absorption spectra of cyclohexanone gel based on **12** (1.0×10^{-2} mol dm^{-3}, 10 mg/mL) before and after UV irradiation (60 min).

the gelator concentration. In general, the IR band of hydrogen-bonded carboxyl group appears around 1720 cm^{-1}. The fact indicates that the carboxyl group undergoes hydrogen bonded interaction even in the solution. These results imply that the gelator molecules self-assemble into nanofibers through intermolecular hydrogen bonding interactions mainly between the amide groups as well as complementarily between the carboxylic acid groups. One of the driving forces for the formation of organogel is the intermolecular hydrogen bonding between the amide groups and the carboxyl group.

UV–Vis Spectroscopy. Figure 4 shows the UV–vis absorption spectra of a CH_2Cl_2 solution of **12** (a) and a cyclohexanone gel of **12** (b) at room temperature. In CH_2Cl_2, the π–π^* transition band, arising from the trans-formed azobenzene, was

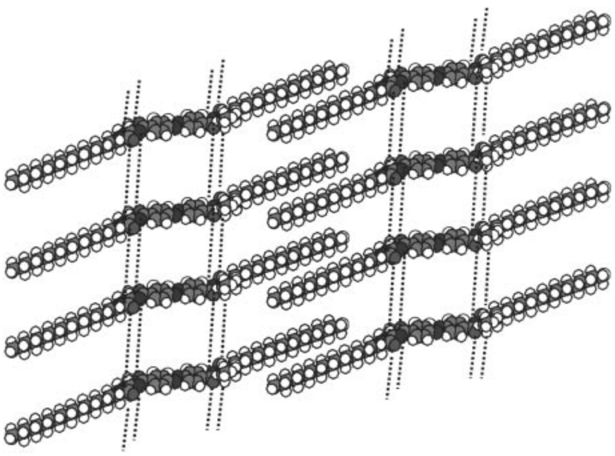

Fig. 5. Possible molecular ordering of **12** in gel state.

observed at 338 nm. Under UV irradiation of 360 nm, the absorbance at 338 nm decreased and a new absorption appeared at 450 nm. This result indicates that isomerization of trans to cis of azobenzene segment in CH_2Cl_2 solution of **12** occurs by UV irradiation. In contrast, the UV–vis spectra of cyclohexanone gel of **12** showed the absorption band at 290 nm, and no spectroscopic change was observed upon UV irradiation. Compared with the isolated azobenzene in CH_2Cl_2 solution, the absorption maximum blue-shift of cyclohexanone gel was ca. 50 nm. Such phenomena suggest the presence of strong interactions between the azobenzene segments. Indeed, the analysis using the molecular exciton model of Kasha shows that the azobenzene segments in the cyclohexanone gel follow a parallel orientation of neighboring transition dipoles:[20] namely, the existence of interdigitated H-aggregation is indicated (Fig. 5).[21] The present results suggest that interdigitated H-aggregation accompanied by intermolecular hydrogen bonding among two amide segments is too robust to cause photoisomerization of azobenzene segment by UV irradiation.

Conclusion

We synthesized new low-molecular-weight gelators containing azobenzene with L-amino acids and studied their gelation abilities. Although the azobenzene derivatives with glycine, L-alanine, and L-leucine show very low organogelation abilities, those of L-valine and L-isoleucine can gel many organic solvents. Especially, **7**, **8**, **12**, and **13** are good gelators that can gel not only aromatic solvents and oils but also THF and chloroform. Electron microscope observations demonstrate that the gelators create a three-dimensional network by entanglement of self-assembled nanofibers. The FT-IR and UV–vis studies show the presence of intermolecular hydrogen bonding and the interdigitated H-aggregation of the π-stacked azobenzene segments. The gelation occurs by gathering of self-assembled nanofibers formed through hydrogen bonding between the amide groups and π-stacking interaction between the azobenzene segments.

Experimental

Apparatus for Measurements. The elemental analysis was performed using a Perkin-Elmer series II CHNS/O analyzer 2400. The FT-IR spectra were recorded on a JASCO FS-420 spectrometer. The ^{1}H NMR and ^{13}C NMR spectra were obtained with a Bruker AVANCE 400 spectrometer with TMS as the standard. 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 MALDI-TOF spectra were obtained using a Perseptive Biosystems Voyager VE-Pro with a dithranol matrix.

Gelation Test. A mixture of a weighed gelator in solvent (1 mL) in a sealed test tube was heated around its boiling point until a clear solution was formed. After allowing the solutions to stand at 25 °C for 2 h, we evaluated the state of the solution by the "upside-down test tube method".

Transmission Electron Microscopy (TEM). Samples were prepared as follows: the benzene solutions of the gelators were dropped on collodion- and carbon-coated 400 mesh copper grid and immediately dried in a vacuum for 24 h. The samples were negatively stained by osmic acid.

Field Emission Scanning Electron Microscopy (FE-SEM). Samples were prepared and dried overnight in a vacuum before the observation. The dried gels were sputtered using a platinum target.

FT-IR Study. The FT-IR spectroscopy was performed in $CHCl_3$ (1 mg/mL, 2 mg/mL, 5 mg/mL, 10 mg/mL, and 20 mg/mL of gelators) and operation at a 4 cm^{-1} resolution for 16 scans. The spectroscopic cell with a KRS-5 window and 1 mm spacer was used for the measurements.

UV–Vis Study. A Cylindrical quartz cell (0.1- or 0.2 mm) or demountable quartz cell (0.1 mm) was used, depending on the concentration of the gelators. UV irradiation was performed using a Xenon lamp (Wacom KXL-500F, 500W).

Materials. 4,4′-Bis(chlorocarbonyl)azobenzene was prepared according to the literature.[19] L-Isoleucine-*N*-dodecylamide, L-isoleucine-*N*-octadecylamide, L-valine-*N*-octadecylamide, L-alanine-*N*-octadecylamide, and glycine-*N*-octadecylamide were prepared by the methods described elsewhere.[2,3] The other chemicals were of the highest commercial grade available and were used without further purification. All solvents used in the synthesis were purified, dried, or freshly distilled as required.

L-[*N*-(4-Phenylazobenzoyl)isoleucine]-*N*-dodecylamide (1). To a dry THF solution (20 mL) of L-isoleucine-*N*-dodecylamide (1.0 mmol), 4-(phenylazo)benzoyl chloride (1.0 mmol), and dry triethylamine (1.5 mmol) was added at 0 °C. The solution was stirred at 0 °C for 1 h and then at room temperature for 12 h. The resulting suspension was filtered, and the filtrate was evaporated and dried. The product was recrystallized from ethyl acetate (orange powder, 65%). MALDI-TOF spectrum m/z calculated for ($C_{31}H_{46}N_4O_2$): 506.72. Found: 507.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (m, 4H), 7.56 (m, 5H), 6.20 (d, 1H), 5.91 (t, 1H), 4.22 (t, 1H), 3.33 (m, 2H), 2.01 (m, 1H), 1.62 (s, 2H), 1.55 (m, 2H), 1.25 (s, 18H), 0.96 (q, 6H), 0.87 (t, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 166.4, 155.0, 130.7, 123.2, 58.5, 39.7, 37.2, 31.9, 29.7, 29.5, 27.0, 22.7, 14.1. Elemental analysis calculated for $C_{31}H_{46}N_4O_2$: C, 73.48; H, 9.15; N, 11.06%. Found: C, 73.21; H, 9.32; N, 10.96%. FT-IR (KBr pellet, cm^{-1}) 3294, 2920, 2850, 1628, 1575, 1531, 1466, 1311, 1244, 1152.

L-[*N*-(4-Phenylazobenzoyl)isoleucine]-*N*-octadecylamide (2). The compound was prepared from L-isoleucyl-*N*-octadecylamide by the method described for **1** (powder, 60%). MALDI-TOF spectrum m/z calculated for ($C_{37}H_{58}N_4O_2$): 590.88. Found: 592.0. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (m, 4H), 7.62 (m, 5H), 6.19

(d, 1H), 5.96 (t, 1H), 4.27 (t, 1H), 3.30 (m, 2H), 2.09 (m, 1H), 1.59 (s, 2H), 1.55 (m, 2H), 1.20 (s, 30H), 0.96 (q, 6H), 0.88 (t, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 166.8, 127.4, 123.2, 58.5, 39.6, 37.2, 31.2, 29.7, 28.9, 27.0, 23.0, 14.1. Elemental analysis calculated for $C_{37}H_{58}N_4O_2$: C, 75.21; H, 9.89; N, 9.48%. Found: C, 74.89; H, 9.96; N, 9.78%. FT-IR (KBr pellet, cm^{-1}) 3289, 2821, 2851, 1629, 1559, 1540, 1457.

L-[*N*-(4-Phenylazobenzoyl)valine]-*N*-octadecylamide (3). The compound was prepared from L-valine-*N*-octadecylamide by the method described for **1** (powder, 70%). MALDI-TOF spectrum *m*/*z* calculated for ($C_{36}H_{56}N_4O_2$): 576.86. Found: 577.44. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (m, 4H), 7.52 (m, 5H), 6.21 (d, 1H), 5.60 (t, 1H), 4.24 (t, 1H), 3.37 (m, 2H), 2.10 (m, 1H), 1.62 (s, 2H), 1.25 (s, 30H), 1.01 (q, 6H), 0.87 (t, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 166.9, 128.3, 123.1, 58.4, 39.7, 37.2, 31.9, 29.7, 29.3, 26.9, 22.7, 15.5, 14.1. Elemental analysis calculated for $C_{36}H_{56}N_4O_2$: C, 74.96; H, 9.78; N, 9.71%. Found: C, 75.09; H, 9.47; N, 10.02%. FT-IR (KBr pellet, cm^{-1}) 3285, 2820, 2849, 1628, 1554, 1540, 1459.

L-[*N*-(4-Phenylazobenzoyl)leucine]-*N*-octadecylamide (4). The compound was prepared from L-leucine-*N*-octadecylamine by the method described for **1** (powder, 78%). MALDI-TOF spectrum *m*/*z* calculated for ($C_{37}H_{58}N_4O_2$): 590.88. Found: 591.78. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (m, 4H), 7.56 (m, 5H), 6.22 (d, 1H), 5.91 (t, 1H), 4.20 (t, 1H), 3.24 (m, 2H), 1.85 (t, 1H), 1.81(m, 2H), 1.62 (s, 2H), 1.25 (s, 30H), 0.96 (q, 6H), 0.87 (t, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 166.9, 128.3, 123.1, 58.4, 39.7, 37.2, 31.9, 29.7, 29.3, 26.9, 22.7, 15.5, 14.1. Elemental analysis calculated for $C_{37}H_{58}N_4O_2$: C, 75.21; H, 9.89; N, 9.48%. Found: C, 75.02; H, 9.53; N, 9.22%. FT-IR (KBr pellet, cm^{-1}) 3290, 2820, 2849, 1628, 1559, 1542, 1459.

L-[*N*-(4-Phenylazobenzoyl)alanine]-*N*-octadecylamide (5). The compound was prepared from L-alanine-*N*-octadecylamide by the method described for **1** (powder, 78%). MALDI-TOF spectrum *m*/*z* calculated for ($C_{34}H_{52}N_4O_2$): 540.80. Found: 541.88. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (m, 4H), 7.59 (m, 5H), 6.20 (d, 1H), 5.94 (t, 1H), 4.21 (t, 1H), 3.24 (m, 2H), 1.60 (s, 2H), 1.48 (t, 3H), 1.25 (s, 30H), 0.87 (t, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 167.1, 128.4, 122.8, 58.0, 39.6, 37.0, 31.9, 29.4, 29.3, 27.1, 23.4, 22.7, 14.1. Elemental analysis calculated for $C_{34}H_{52}N_4O_2$: C, 74.41; H, 9.56; N, 10.21%. Found: C, 73.90; H, 9.56; N, 10.10%. FT-IR (KBr pellet, cm^{-1}) 3284, 2820, 2851, 1626, 1556, 1542, 1458.

L-[*N*-(4-Phenylazobenzoyl)glycine]-*N*-octadecylamide (6). The compound was prepared from glycine-*N*-octadecylamide by the method described for **1** (powder, 71%). MALDI-TOF spectrum *m*/*z* calculated for ($C_{33}H_{50}N_4O_2$): 534.78. Found: 534.78. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (m, 4H), 7.55 (m, 5H), 6.19 (d, 1H), 5.96 (t, 1H), 4.21 (m, 2H), 3.26 (m, 2H), 1.61 (s, 2H), 1.24 (s, 30H), 0.90 (t, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 166.8, 154.0, 123.2, 58.5, 39.5, 37.2, 31.2, 28.9, 29.3, 27.0, 23.0, 14.1. Elemental analysis calculated for $C_{33}H_{50}N_4O_2$: C, 74.12; H, 9.42; N, 8.41%. Found: C, 74.03; H, 9.72; N, 8.56%. FT-IR (KBr pellet, cm^{-1}) 3289, 2820, 2852, 1627, 1555, 1538, 1456.

4′-{*N*-[(1*S*,2*S*)-2-Methyl-1-(*N*-octadecylcarbamoyl)butyl]carbamoyl}azobenzene-4-carboxylic Acid (7). Jayaraman's method was applied.[22] To a dry THF solution (30 mL) of L-isoleucine-*N*-octadecylamide (8 mmol) and triethylamine (16 mmol), a dry THF solution (20 mL) of 4,4′-Bis(chlorocarbonyl)azobenzene (10 mmol) was slowly added at 0 °C under a nitrogen atmosphere. The reaction mixture was stirred at room temperature for 24 h, and then filtered. The filtrate was evaporated, and the resulting orange residue was redissolved in ethyl acetate, and washed with aqueous HCl (5%) and H_2O. The orange portion was dried over Na_2SO_4, filtered, and concentrated in vacuum. The suspension of the resulting residue in EtOH was admixed with NaOEt/EtOH (0.5 mol/L, 50 mL) and stirred for 12 h, then neutralized with HCl, filtered; finally the filtrate was concentrated in vacuum. The product was obtained by recrystallization from MeOH/$CHCl_3$ (powder, 65%). MALDI-TOF spectrum *m*/*z* calculated for ($C_{38}H_{58}N_4O_4$): 634.45. Found: 634.55. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (m, 4H), 7.68 (m, 4H), 6.22 (d, 1H), 5.94 (t, 1H), 4.27 (t, 1H), 3.96 (m, 1H), 3.33 (m, 2H), 2.12 (m, 1H), 1.65 (s, 2H), 1.53 (m, 2H), 1.21 (s, 30H), 0.98 (q, 6H), 0.89 (t, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 166.9, 128.4, 123.3, 58.5, 39.7, 37.2, 31.9, 29.6, 29.3, 27.0, 22.7, 15.5, 14.1, 11.2. Elemental analysis calculated for $C_{38}H_{58}N_4O_4$: C, 71.89; H, 9.21; N, 8.82%. Found: C, 71.99; H, 8.91; N, 8.92%. FT-IR (KBr pellet, cm^{-1}) 3290, 2821, 2852, 1721, 1630, 1554, 1538, 1451.

4′-{*N*-[(*S*)-2-Methyl-1-(*N*-octadecylcarbamoyl)propyl]carbamoyl}azobenzene-4-carboxylic Acid (8). The compound was prepared from L-valine-*N*-octadecylamide by the method described for **7** (powder, 62%). MALDI-TOF spectrum *m*/*z* calculated for ($C_{37}H_{56}N_4O_4$): 620.87. Found: 621.71. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (m, 4H), 7.66 (m, 4H), 6.22 (d, 1H), 5.67 (t, 1H), 4.23 (t, 1H), 3.92 (m, 1H), 3.37 (m, 2H), 2.10 (m, 1H), 1.60 (s, 2H), 1.21 (s, 30H), 0.99 (q, 6H), 0.87 (t, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 167.1, 128.4, 123.0, 59.1, 39.7, 31.9, 29.7, 29.4, 27.0, 22.7, 19.4, 18.9, 14.1. Elemental analysis calculated for $C_{37}H_{56}N_4O_4$: C, 71.58; H, 9.09; N, 9.02%. Found: C, 71.86; H, 9.21; N, 8.88%. FT-IR (KBr pellet, cm^{-1}) 3288, 2823, 2849, 1720, 1630, 1553, 1532, 1449.

4′-{*N*-[(*S*)-3-Methyl-1-(*N*-octadecylcarbamoyl)butyl]carbamoyl}azobenzene-4-carboxylic Acid (9). The compound was prepared from L-leucine-*N*-octadecylamide by the method described for **7** (powder, 55%). MALDI-TOF spectrum *m*/*z* calculated for ($C_{38}H_{58}N_4O_4$): 634.45. Found: 634.51. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (m, 4H), 7.60 (m, 4H), 6.21 (d, 1H), 5.93 (t, 1H), 4.21 (t, 1H), 3.97 (m, 1H), 3.30 (m, 2H), 1.79 (t, 1H), 1.70 (m, 2H), 1.60 (s, 2H), 1.24 (s, 30H), 1.02 (q, 6H), 0.89 (t, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 128.6, 128.1, 43.8, 39.9, 39.6, 31.9, 29.6, 29.5, 29.3, 26.9, 22.7, 14.1. Elemental analysis calculated for $C_{38}H_{58}N_4O_4$: C, 71.89; H, 9.21; N, 8.82%. Found: C, 72.00; H, 9.09; N, 8.91%. FT-IR (KBr pellet, cm^{-1}) 3292, 2820, 2850, 1718, 1627, 1553, 1529, 1448.

4′-{*N*-[(*S*)-1-(*N*-Octadecylcarbamoyl)ethyl]carbamoyl}azobenzene-4-carboxylic Acid (10). The compound was prepared from L-alanine-*N*-octadecylamide by the method described for **7** (powder, 68%). MALDI-TOF spectrum *m*/*z* calculated for ($C_{35}H_{52}N_4O_4$): 592.81. Found: 593.01. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (m, 4H), 7.66 (m, 4H), 6.19 (d, 1H), 5.98 (t, 1H), 4.24 (t, 1H), 3.98 (m, 1H), 3.240 (m, 2H), 1.58 (s, 2H), 1.47 (t, 3H), 0.97 (s, 30H), 0.91 (t, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 166.9, 128.3, 122.6, 59.5, 39.7, 31.3, 29.7, 29.5, 29.3, 22.7, 19.4, 18.7, 14.1. Elemental analysis calculated for $C_{35}H_{52}N_4O_4$: C, 70.81; H, 8.84; N, 9.45%. Found: C, 70.88; H, 8.64; N, 9.44%. FT-IR (KBr pellet, cm^{-1}) 3290, 2826, 2850, 1720, 1632, 1553, 1526, 1453.

4′-{*N*-(*N*-Octadecylcarbamoyl)methyl]carbamoyl}azobenzene-4-carboxylic Acid (11). The compound was prepared from glycine-*N*-octadecylamide by the method described for **7** (powder, 70%). MALDI-TOF spectrum *m*/*z* calculated for ($C_{34}H_{50}N_4O_4$): 578.78. Found: 579.66. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (m, 4H), 7.62 (m, 4H), 6.18 (d, 1H), 5.97 (t, 1H), 4.18 (m, 2H), 3.90 (m, 1H), 3.27 (m, 2H), 1.66 (s, 2H), 1.31 (s, 30H), 0.98 (t, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 171.3, 166.5, 128.4, 123.0, 59.5, 39.7, 31.2, 29.7, 29.5, 29.3, 22.7, 19.4, 18.9, 14.1. Elemental analysis calculated for $C_{34}H_{50}N_4O_4$: C, 70.56; H, 8.71; N, 9.68%. Found: C, 70.45; H, 9.01; N, 9.77%. FT-IR (KBr pellet, cm^{-1}) 3298, 2923, 2852, 1632, 1535, 1466, 1322, 1258, 115. FT-IR (KBr pellet, cm^{-1}) 3290, 2824, 2854, 1722, 1628, 1553, 1530, 1447.

***N*,*N*′-Bis[(1*S*,2*S*)-2-methyl-1-(*N*-octadecylcarbamoyl)butyl]-4,4′-azodibenzamide (12).** The compound was prepared from 22 mmol of L-isoleucyine-*N*-octadecylamide by the method described for **7** (powder, 68%). MALDI-TOF spectrum *m*/*z* calculated for ($C_{62}H_{106}N_6O_4$): 999.54. Found: 1000.1. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.10 (m, 8H), 6.26 (d, 2H), 5.90 (t, 2H), 4.25 (t, 2H), 3.42 (m, 4H), 2.09 (m, 2H), 1.60 (s, 4H), 1.55 (m, 4H), 1.17 (s, 60H), 1.01 (q, 12H), 0.92 (t, 6H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 171.0, 166.7, 128.6, 122.6, 59.4, 39.8, 31.9, 29.7, 29.6, 29.4, 22.7, 14.1. Elemental analysis calculated for $C_{62}H_{106}N_6O_4$: C, 74.50; H, 10.69; N, 8.41%. Found: C, 74.98; H, 11.00; N, 8.51%. FT-IR (KBr pellet, cm^{-1}) 3298, 2960, 2923, 2852, 1632, 1535, 1446, 1258.

***N*,*N*′-Bis[(*S*)-2-methyl-1-(*N*-octadecylcarbamoyl)propyl]-4,4′-azodibenzamide (13).** The compound was prepared from 22 mmol of L-valyine-*N*-octadecylamide by the method described for **8** (powder, 60%). MALDI-TOF spectrum *m*/*z* calculated for ($C_{60}H_{102}N_6O_4$): 971.43. Found: 972.31. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.09 (m, 8H), 6.24 (d, 2H), 5.62 (t, 2H), 4.23 (t, 2H), 3.31 (m, 4H), 2.06 (m, 2H), 1.58 (s, 4H), 1.24 (s, 60H), 1.02 (q, 12H), 0.92 (t, 6H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 171.3, 166.5, 128.4, 123.0, 59.5, 39.7, 31.2, 29.7, 29.5, 29.3, 22.7, 19.4, 18.9, 14.1. Elemental analysis calculated for $C_{60}H_{102}N_6O_4$: C, 74.18; H, 10.58; N, 8.65%. Found: C, 74.44; H, 10.90; N, 8.77%. FT-IR (KBr pellet, cm^{-1}) 3290, 2964, 2920, 2849, 1631, 1535, 1440, 1264.

***N*,*N*′-Bis[(*S*)-3-(*N*-octadecylcarbamoyl)butyl]-4,4′-azodibenzamide (14).** The compound was prepared from 22 mmol of L-leucyine-*N*-octadecylamide by the method described for **9** (powder, 55%). MALDI-TOF spectrum *m*/*z* calculated for ($C_{62}H_{106}N_6O_4$): 999.54. Found: 1000.2. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.13 (m, 8H), 6.25 (d, 2H), 5.90 (t, 2H), 4.23 (t, 2H), 3.17 (m, 4H), 1.95 (t, 2H), 1.79 (m, 4H), 1.64 (s, 4H), 1.27 (s, 60H), 1.03 (q, 12H), 0.92 (t, 6H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 71.0, 166.7, 128.6, 122.6, 59.4, 39.8, 31.9, 29.7, 29.6, 29.4, 22.7, 14.1. Elemental analysis calculated for $C_{62}H_{106}N_6O_4$: C, 74.50; H, 10.69; N, 8.41%. Found: C, 74.56; H, 10.89; N, 8.43%. FT-IR (KBr pellet, cm^{-1}) 3294, 2964, 2919, 2848, 1630, 1535, 1441, 1247.

***N*,*N*′-Bis[(1*S*)-1-(*N*-octadecylcarbamoyl)ethyl]-4,4′-azodibenzamide (15).** The compound was prepared from 22 mmol of L-alanyine-*N*-octadecylamide by the method described for **10** (powder, 66%). MALDI-TOF spectrum *m*/*z* calculated for ($C_{56}H_{94}N_6O_4$): 915.38. Found: 916.33. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.17 (m, 8H), 6.24 (d, 2H), 5.92 (t, 2H), 4.34 (t, 2H), 3.29 (m, 4H), 1.63 (s, 4H), 1.52 (t, 6H), 1.22 (s, 60H), 0.92 (t, 6H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 171.1, 166.9, 128.3, 122.6, 59.3, 39.6, 31.3, 29.7, 29.5, 29.3, 22.5, 14.1. Elemental analysis calculated for $C_{56}H_{94}N_6O_4$: C, 73.48; H, 10.35; N, 9.18%. Found: C, 73.65; H, 10.45; N, 9.43%. FT-IR (KBr pellet, cm^{-1}) 3290, 2961, 2918, 2849, 1630, 1533, 1449, 1253.

***N*,*N*′-Bis[(*N*-octadecylcarbamoyl)]methyl]-4,4′-azodibenzamide (16).** The compound was prepared from 22 mmol of glycine-*N*-octadecylamide by the method described for **11** (powder, 70%). MALDI-TOF spectrum *m*/*z* calculated for ($C_{54}H_{90}N_6O_4$): 887.33. Found: 888.02. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.17 (m, 8H), 6.22 (d, 2H), 5.97 (t, 2H), 4.27 (m, 4H), 3.33 (m, 4H), 1.59 (s, 4H), 1.21 (s, 60H), 0.99 (t, 6H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 171.3, 166.8, 155.0, 127.9, 123.2, 58.5, 39.6, 31.2, 29.7, 28.9, 24.5, 23.0, 22.7, 14.1. Elemental analysis calculated for $C_{54}H_{90}N_6O_4$: C, 73.09; H, 10.22; N, 9.47%. Found: C, 73.33; H, 10.35; N, 9.43%. FT-IR (KBr pellet, cm^{-1}) 3295, 2964, 2924, 2847, 1629, 1533, 1441, 1251.

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