Selected Papers

Supramolecular Helical Columnar Structures Formed by Hydrogen-Bonded Disk-Like (Phenylethynyl)benzene Derivatives with L-Alanine Pendant Groups: Helix Stability and Supramolecular Helical Sense Inversion

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To investigate the influence of the number of substituents on supramolecular assemblies of hydrogen-bonded disklike (phenylethynyl)benzene derivatives with chiral L-alanine dodecyl groups, a tris(phenylethynyl)benzene derivative 3and a tetrakis(phenylethynyl)benzene derivative 4 were synthesized. The behavior of these supramolecular assemblies was compared with that of the previously reported hexakis(phenylethynyl)benzene derivative 6. It is clearly shown that the stability of the supramolecular helical columnar structure is enhanced by increasing the number of substituents, namely the number of amide groups contributing to the hydrogen bonding. In addition, along with 6, 4 also exhibits a solvent-induced supramolecular helical sense inversion. Furthermore, 4 exhibits a thermally reversible supramolecular helical sense inversion at a critical solvent composition.

It is well-known that biological helices such as DNA and polypeptides adopt regular one-handed helical structures composed of homochiral components. Because the structures and properties of these biological helices are highly attractive, the development of various helical architectures has been accelerated.¹⁻⁴ Among them, supramolecular helical assemblies constructed using various types of noncovalent bonding interactions (such as π - π stacking, hydrogen-bonding, and hydrophobic interactions),⁴ as utilized in biological systems, are of great interest from fundamental and biological viewpoints and have potential applications in chiral materials science.^{1a,lb,le}

Recently, we reported the supramolecular assembly of the six-armed hydrogen-bonded disk-like molecule **6**, as shown in Figure 1 (left).^{5a} Compound **6** consists of a large hexakis-(phenylethynyl)benzene central core bearing chiral L-alanine



Figure 1. Molecular structures of 6, 4, and 3.

parts and peripheral hydrophobic dodecyl chains. The stacking among large central cores of **6** is enforced by six intermolecular hydrogen bonds, leading to an exceptionally stable supramolecular helical columnar structure that is maintained even at 100 °C in dilute nonpolar *n*-alkane solutions. The rigidity of the helical column also produces lyotropic liquid crystalline properties at a relatively low concentration (ca. 6 wt %) in *n*alkane. However, **6** is molecularly dispersed in relatively polar haloalkanes. Interestingly, we found a solvent-induced supramolecular helical sense inversion in a binary solvent system consisting of a helicogenic *n*-alkane and a nonhelicogenic haloalkane.^{5b}

Such a chirality inversion is a topic of particular interest.^{1c,1d,6} The majority of studies on this subject have involved polymers⁷ and host–guest complexes.⁸ There are, however, a few reports on supramolecular helical columns constructed using the noncovalent bonding interactions.⁹ With our system, it is easy to prepare various analogous compounds, which enables us to systematically examine the supramolecular chirality inversion of helical columnar structures and the stability of each helix.

In this study, we synthesized two new compounds to investigate the influence of the number of substituents on the supramolecular assembly of hydrogen-bonded disk-like (phenylethynyl)benzene derivatives with chiral L-alanine dodecyl groups, namely, the three-armed tris(phenylethynyl)benzene derivative **3** and the four-armed tetrakis(phenylethynyl)benzene derivative **4**, as shown in Figure 1. Herein, we report their helix



Figure 2. Temperature-dependent (a) UV-vis and (b) CD spectra of 4 in *n*-dodecane $(4.20 \times 10^{-5} \text{ M})$ at 25, 50, 70, 80, and 90 °C.

stabilities and helical sense inversion behaviors together with the results of UV–visible absorption (UV–vis), circular dichroism (CD) and fluorescence (FL) measurements.

Results and Discussion

Stability of the Supramolecular Helices. To investigate the self-assembly of 3 and 4, UV-vis and CD spectra were measured (4.20×10^{-5} M). Unfortunately, **3** did not dissolve in a pure helicogenic *n*-alkane. Although 3 was dissolved in *n*hexane (Hx) containing 5 vol % of chloroform (CHCl₃), a CD signal was not observed. As described in the next section, both 4 and 6 form helical columnar structures under these conditions. Consequently, it is concluded that the construction of the supramolecular chiral self-assembly is more difficult in 3 than in 4 and 6. On the other hand, an *n*-alkane solution of 4 showed an obvious CD signal. Hereinafter, the self-assembly behavior of 4 will be described in detail. Figures 2a and 2b show the temperature-dependent UV-vis and CD spectra of 4 in ndodecane (4.20 \times 10⁻⁵ M), respectively. Compound 4 shows a major absorption band at 316 nm ($\varepsilon = 1.34 \times 10^5 \,\mathrm{M^{-1} \, cm^{-1}}$) at 25 °C and a bisignate Cotton effect with the sign being negative at long wavelengths ($\Delta \varepsilon_1 = -763 \,\mathrm{M}^{-1} \,\mathrm{cm}^{-1}$ at 321



Figure 3. Temperature-dependent (a) UV-vis and (b) CD spectra of 4 in *n*-dodecane $(4.20 \times 10^{-6} \text{ M})$ at 25, 50, 70, 80, and 90 °C.

nm) and positive at short wavelengths ($\Delta \varepsilon_2 = 809 \text{ M}^{-1} \text{ cm}^{-1}$ at 306 nm) near this UV–vis absorption. The same spectra were also obtained in Hx solution ($4.20 \times 10^{-5} \text{ M}$), as shown in Figure S1 (see the Supporting Information). These profiles (so-called negative coupling) suggest the presence of a left-handed helical arrangement of **4** molecules.^{8b,8c,9b} An increase in temperature slightly decreased the UV–vis absorption. Correspondingly, there was a gradual decrease in the CD intensity with increasing temperature. Importantly, the apparent CD spectrum at 90 °C reveals that the helical structure of **4** is definitely maintained at this concentration. Subsequent cooling to 25 °C restored the original CD spectrum.

When the solution was more dilute $(4.20 \times 10^{-6} \text{ M})$, the thermal behavior of 4 changed. Figures 3a and 3b show the temperature-dependent UV-vis and CD spectra of 4 in *n*dodecane $(4.20 \times 10^{-6} \text{ M})$, respectively. In addition, to easily see its thermal behavior, the variation in Kuhn's anisotropy factor ($g = \Delta \varepsilon_1 / \varepsilon$) as a function of temperature are shown in Figure S2 (see the Supporting Information). Compound 4 shows a major absorption band at 316 nm ($\varepsilon = 1.18 \times 10^5$ $\text{M}^{-1} \text{ cm}^{-1}$) at 25 °C, which is at the same position as that in the spectrum of the 4.20×10^{-5} M solution. In addition, this CD



Figure 4. Temperature-dependent FL spectra of 4 in *n*-dodecane $(4.20 \times 10^{-6} \text{ M})$ at 25, 50, 60, and 70 °C. The FL spectrum in CHCl₃ at 25 °C is also shown.¹⁰ FL spectra were measured at excitations of 316 and 329 nm (corresponding to the absorption maxima) for *n*-dodecane and CHCl₃ solutions, respectively, and normalized using the corresponding absorption values.

spectrum also has the same features as those in the spectrum of the 4.20 × 10⁻⁵ M solution at 25 °C, namely a bisignate Cotton effect with the sign being negative at long wavelengths ($\Delta \varepsilon_1 = -665 \, \text{M}^{-1} \, \text{cm}^{-1}$ at 321 nm) and positive at short wavelengths ($\Delta \varepsilon_2 = 713 \, \text{M}^{-1} \, \text{cm}^{-1}$ at 306 nm) near this UV–vis absorption. This result indicates that **4** forms a left-handed supramolecular helical structure in a 4.20 × 10⁻⁶ M solution at 25 °C.

An increase in temperature, however, gradually decreased the UV-vis absorption, CD intensities, and |g| value. At 80 °C, the main absorption band shifted bathochromically. At 90 °C, no CD signal was observed and the g value dropped to zero. Finally, the position of the UV-vis absorption band shifted to 326 nm ($\varepsilon = 1.11 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$). This wavelength is quite close to that ($\varepsilon = 1.45 \times 10^5 \,\mathrm{M^{-1}\,cm^{-1}}$ at 329 nm) in a CHCl₃ solution, as shown in Figure S1a (see the Supporting Information). In addition, 4 does not show any CD in CHCl₃, as can easily be seen in Figure S1b (see the Supporting Information). Therefore, 4 does not form a self-assembled structure but is molecularly dispersed at high temperature in this dilute 4.20×10^{-6} M solution. This transition was further confirmed by investigating the temperature dependence of the intermolecular interactions of **4** in the same 4.20×10^{-6} M solution. Figure 4 shows the FL spectra of 4 measured at excitations of 316 and 329 nm (corresponding to the absorption maxima) for *n*-dodecane and CHCl₃ solutions, respectively. The emission maximum in the CHCl₃ solution at 25 °C was observed at around 400 nm.¹⁰ In contrast to the blue fluorescence observed for this nonhelicogenic solution, the emission in the helicogenic *n*-dodecane solution was green, and this maximum was observed at around 517 nm at 25 °C. In addition, this broad peak for the helicogenic solution is weak with respect to the sharp emission peak for the nonhelicogenic solution. This behavior indicates that the molecules form columnar structures by strong π - π stacking in the helicogenic solvent. In fact, the broad emission in the helical columnar state is shifted by

approximately 5600 cm^{-1} to a lower energy compared to that of the monomer emission, considered to be an excimer emission, because this energy difference is comparable to those of other excimers generated among the phenylethynyl units.¹¹ With heating, the intensity of the excimer emission peak decreased gradually. Concomitantly, the monomer emission appeared at 395 nm above 50 °C, and its peak intensity gradually increased with temperature. This result indicates that the helical columnar structure of 4 collapses with an increase in temperature.

Furthermore, the stability of the helical column of **4** was evaluated on the basis of IR measurements. In a *n*-dodecane solution of **4** (4.20×10^{-4} M), the C=O stretching vibration of amide I was observed at 1637 cm⁻¹, whereas a higher wavenumber was observed (1662 cm^{-1}) for this vibration in a CHCl₃ solution of **4** (4.20×10^{-4} M). The combined results of the UV–vis, CD, FL, and IR analyses indicate that **4** forms a rigid helical columnar structure at lower temperature in nonpolar *n*-alkane solvents that is stabilized by strong hydrogen bonds among the large disk cores. With heating, the self-assembled helical columnar structure is deconstructed because of the breaking of the hydrogen bond.

Compound 6, on the other hand, forms a thermally stable supramolecular helical columnar structure without any free monomers even in a more dilute *n*-alkane solution (4.20×10^{-7} M).^{5a} Therefore, these results have given direct evidence that the stability of the supramolecular helical columnar structure is enhanced by increasing the number of substituents, namely the number of amide groups contributing to the hydrogen bonding.

Solvent-Induced Supramolecular Helical Sense Inversion. We previously reported that the six-armed disk-like molecule 6 exhibited a solvent-induced supramolecular helical sense inversion in a binary solvent system using helicogenic Hx and nonhelicogenic CHCl₃.^{5b} In the present study, we also investigated the supramolecular assembly state of 4 in mixed solvents of various CHCl₃/Hx ratios (v/v). The UV–vis and CD spectra of 4 (4.20×10^{-6} M) measured at 25 °C are shown in Figure S3 (see the Supporting Information) and Figure 5, respectively. In addition, to easily see the self-assembled behaviors, the variation in the maximal absorption wavelength (λ_{max}) and the $\Delta \varepsilon_1$ value, and the g value as a function of the CHCl₃ content are shown in Figure 6 and Figure S4 (see the Supporting Information), respectively.

In pure Hx, i.e., CHCl₃/Hx (0/100), 4 shows a major absorption band at 315 nm ($\varepsilon = 1.26 \times 10^5 \,\mathrm{M^{-1} \, cm^{-1}}$) and a bisignate Cotton effect with the sign being negative at long wavelengths ($\Delta \varepsilon_1 = -733 \,\mathrm{M}^{-1} \,\mathrm{cm}^{-1}$ at 319 nm) and positive at short wavelengths ($\Delta \varepsilon_2 = 752 \,\mathrm{M}^{-1} \,\mathrm{cm}^{-1}$ at 306 nm) near this UV-vis absorption. These spectra are essentially the same as those of the helical columnar assembly in *n*-dodecane. At CHCl₃/Hx (5/95), 4 also shows a major absorption band at 316 nm ($\varepsilon = 1.21 \times 10^5 \,\text{M}^{-1} \,\text{cm}^{-1}$) and a bisignate Cotton effect with the sign being negative at long wavelengths ($\Delta \varepsilon_1 =$ -694 M⁻¹ cm⁻¹ at 320 nm) and positive at short wavelengths $(\Delta \varepsilon_2 = 709 \,\mathrm{M}^{-1} \,\mathrm{cm}^{-1}$ at 306 nm) near this UV-vis absorption. These spectra are almost the same as those of the helical columnar assembly in CHCl₃/Hx (0/100). When the CHCl₃ content was higher than CHCl₃/Hx (5/95), however, the CD intensity and |g| value decreased drastically. Subsequently, at



Figure 5. CD spectra of 4 $(4.20 \times 10^{-6} \text{ M} \text{ at } 25 \,^{\circ}\text{C})$ measured in different solvent compositions (CHCl₃/Hx): (0/100), (5/95), (8.5/91.5), (9/91), (12.5/87.5), (20/80), and (25/75).



Figure 6. Variation in the maximal absorption wavelength (λ_{max}) (closed circles) and the $\Delta \varepsilon_1$ value (open circles) obtained from the UV-vis and CD spectra of 4 (4.20 × 10^{-6} M at 25 °C), respectively, as a function of the CHCl₃ content in CHCl₃/Hx mixtures.

CHCl₃/Hx (9/91), the CD sign inversion occurred without a change in the position of the UV-vis absorption band. At CHCl₃/Hx (12.5/87.5), the CD intensity with the opposite sign reached a maximum. It is noteworthy that these two types of CD spectra with opposite signs are exact mirror images. In the CHCl₃/Hx (12.5/87.5) solution of 4 (4.20×10^{-4} M), the C=O stretching vibration of amide I was observed at 1638 cm⁻¹. This value indicates that the inverted helical columns are also stabilized by hydrogen bonds between the large disk cores, as well as between the original left-handed helical columns. In addition, at 0–12.5 vol % of CHCl3, the λ_{max} values are almost independent of the nonhelicogenic CHCl3 content and nearly constant, as can be clearly seen in Figure 6. This result indicates that the supramolecular helical columns are robustly maintained in the range from 0 to approximately 12.5 vol % of nonhelicogenic CHCl₃. It should be noted that a small amount



Figure 7. FL spectra of 4 $(4.20 \times 10^{-6} \text{ M} \text{ at } 25 \,^{\circ}\text{C})$ measured in different solvent compositions ((CHCl₃/Hx): (5/95), (9/91), (12.5/87.5), (15/85), (20/80), and (25/75)) at an excitation of 316 nm and normalized using the absorption values.

of free monomer was observed at around 400 nm in the FL spectra at 0-12.5 vol % of CHCl₃, as shown in Figure 7.

On the contrary, free monomers of 6 were not observed under these conditions,^{5b} indicating that the inverted helical columnar structure of 6 is more stable than that of 4, as is the case for the original left-handed helices. Although a very minor monomer emission is observed at around 400 nm in the FL spectra of 4, these FL spectra are mainly constituted of a major excimer-like emission at around 510 nm. Therefore, it is concluded that 4 exhibits a solvent-induced supramolecular helical sense inversion from a left-handed to a right-handed helical columnar structure. When the CHCl₃ content was further increased in the solutions of 4, the CD intensity became significantly weaker again (correspondingly, the g value also decreased), and the value of $\lambda_{\rm max}$ was red-shifted toward 329 nm as observed in the molecularly dispersed state in CHCl₃/Hx (100/0). Concomitantly, the free monomer content drastically increased, as shown by the sharp increase in the intensity of the monomer emission, and the self-assembled helical columnar structure was deconstructed, as seen from the decrease in the excimer-like emission (Figure 7).

Interestingly, **6** also exhibited a solvent-induced supramolecular helical sense inversion at a similar solvent composition (CHCl₃/Hx (8/92)) as that for **4**. As previously reported, the solvent polarity, namely the dielectric constant of the solvents, seems to trigger the helical sense inversion.^{5b} Some polyacetylene derivatives bearing amino acid pendants also tend to exhibit a solvent-induced helical sense inversion depending on the solvent polarity.^{7c,7d} It is likely that the amino acid portion (alanyl groups in our materials) is sensitive to the environment and play a key role in changing the helicity.

Thermally Reversible Supramolecular Helical Sense Inversion. It is well known that the dielectric constant depends on the temperature.¹² Generally, the dielectric constants of solvents decrease with an increase in temperature. This behavior suggests that solvents become relatively polar



Figure 8. Temperature-dependent (a) UV-vis and (b) CD spectra of 4 in (CHCl₃/Hx): (8.5/91.5) (4.20 × 10⁻⁶ M) at 20, 25, 40, and 55 °C.

and nonpolar at low and high temperatures, respectively. At a critical solvent composition, where 4 and 6 exhibit a helical sense inversion, one therefore could expect that such a transition is also thermally induced. Although the reason has not yet been clearly identified, only the thermally induced helical sense inversion of 4 has been observed, as described below.

A CHCl₃/Hx (8.5/91.5) solution of 4 was selected as the critical sample solution because the CD intensity was significantly decreased at this solvent composition, and then, the helical sense inversion occurred at CHCl₃/Hx (9/91) by further addition of a small quantity of CHCl₃. As expected, a decrease in the temperature to 20 °C (corresponding to an increase in the solvent polarity) gave rise to the inversion of the CD sign, as shown in Figure 8b. Here, the UV-vis and FL spectra at 20 °C are almost the same as those at 25 °C (Figures 8a and 9, respectively). Consequently, these results indicate that 4 exhibited a thermally induced supramolecular helical sense inversion. On the contrary, an increase in the temperature to 40 °C led to an increase in the CD intensity. This result is surprising because an increase in temperature generally disrupts a helical columnar assembly and decreases the CD intensity. It is true that the free monomer content increased at 40 °C, as can be



Figure 9. Temperature-dependent FL spectra of 4 in $(CHCl_3/Hx)$: (8.5/91.5) $(4.20 \times 10^{-6} \text{ M})$ at 20, 25, 40, and 55 °C. The FL spectra were measured at an excitation of 316 nm and normalized using the absorption values.

seen by the increase in the monomer emission (Figure 9). Under this condition, the supramolecular helical columns partially dissociate into monomers and these are at equilibrium. Nevertheless, the CD intensity was enhanced. This suggests that the helix has greater excess one-handedness than those of helices with no monomers dissociated. In other words, it is possible that a decrease in the solvent polarity with the increase in temperature stabilized the original left-handed helical columnar structure. When the temperature was increased to 55 °C, however, the CD intensity decreased. In addition, the main absorption was slightly red-shifted, and the monomer emission was dominant (Figures 8a and 9, respectively). These results indicate that the helical columnar structures were being disrupted into smaller assemblies and free monomers. This temperature dependence of the self-assembled behavior is in good correspondence with the change of the g value as shown in Figure S5 (see the Supporting Information).

A CHCl₃/Hx (12.5/87.5) solution of **4** was also investigated as another example. Compound 4 in this solvent composition forms an inverted right-handed helical columnar structure at 25 °C. An increase in the temperature to 55 °C (corresponding to a decrease in the solvent polarity) gave rise to the inversion of the CD sign, as shown in Figure S6b (see the Supporting Information). Although disruption into smaller assemblies and free monomers is accompanied at this CHCl₃ content (Figures 7 and S6a in the Supporting Information), it is evident that 4 also retransforms from an inverted right-handed to the original left-handed helical regime. Moreover, it was confirmed that all of the transitions were thermally reversible. This result indicates that both of these opposite helical regimes are thermodynamically stable9c and the transition in this system is essentially different from the kinetically controllable transition (from metastable to thermodynamically stable helical regimes).^{9a,9b} Although the reversible supramolecular helical sense inversion was recently reported in a helical tubule formed from hexameric macrocycles,9c our material could be a valuable example exhibiting such a phenomenon in typical disk-like molecular systems.

Conclusion

To investigate the influence of the number of substituents on the supramolecular assembly of hydrogen-bonded disklike (phenylethynyl)benzene derivatives with chiral L-alanine dodecyl groups, 3 and 4 were synthesized, and these supramolecular assemblies were compared with that of the previously reported 6. The combined results showed that the number of substituents, namely the number of amide groups contributing to the hydrogen bonding, is important for the stabilization of supramolecular helical columns. In addition, 4 exhibited a solvent-induced supramolecular helical sense inversion at a similar solvent composition as that observed for 6, indicating that the amino acid group may be sensitive to the solvent polarity and play a key role in changing the helicity. Furthermore, 4 exhibited a thermally reversible supramolecular helical sense inversion at a critical solvent composition. These behaviors have not been found in typical disk-like molecules.⁹ To further understand the mechanism and the driving force of such a transition, a systematic study including other analogous compounds (for example, with different amino acid groups) will be continued, together with detailed structural analyses of these compounds.

Experimental

Instruments. ¹H NMR and ¹³C NMR spectra were recorded on a JEOL JNM-A400 (400, 100 MHz) in CDCl₃. Chemical shifts of ¹H and ¹³C are reported in δ values referred respectively to tetramethylsilane and CDCl₃ as internal standards. Elemental analyses were carried out by Elemental Analysis Center of Kyoto University. IR spectra were recorded with a Jasco FT-IR-460 Plus/IRT-30 spectrophotometer. UV-visible absorption (UV-vis) and circular dichroism (CD) spectra were measured using a Hitachi U-4000S spectrophotometer and a Jasco J-820P spectropolarimeter, respectively. The temperature was controlled with a Komatsu Electronics SPR-7 for UV-vis spectral measurements and a Jasco PTC-423L apparatus for CD spectral measurements. Fluorescence (FL) spectra were measured using a Hitachi F-4500 fluorescence spectrophotometer. The temperature was controlled with a Komatsu Electronics CTE32 apparatus.

Materials. Unless otherwise noted, reagents were commercially available and used without purification. Triethylamine (TEA) was obtained from Kishida Chemical Co., Ltd. 1,3,5-Tribromobenzene, 1,2,4,5-tetrabromobenzene, bis(triphenylphosphine)palladium dichloride ([Pd(PPh₃)₂Cl₂]), copper(I) iodide (CuI), and triphenylphosphine (PPh₃) were obtained from Tokyo Chemical Industry Co., Ltd. Silica gel used for column chromatography was Silica gel C-200 from Wako. 4-Ethynylbenzoyl-L-alanine dodecyl ester and the six-armed *C*₆-symmetric hexakis(phenylethynyl)benzene derivatives were prepared according to a previously reported method.^{5a} The new three-armed *C*₃-symmetric tris(phenylethynyl)benzene and four-armed *C*₂-symmetric tetrakis(phenylethynyl)benzene analogous compounds, **3** and **4**, respectively, were also synthesized by the similar method described below.

1,3,5-Tris{**4-**[(*S*)-**1-**(dodecyloxycarbonyl)ethylcarbamoyl]phenylethynyl}benzene (3):^{5a} A mixture of 4-ethynylbenzoyl-L-alanine dodecyl ester (1.16 g, 3.01 mmol), 1,3,5-tribromo-

benzene (277 mg, 0.879 mmol), [Pd(PPh₃)₂Cl₂] (111 mg, 0.158 mmol), CuI (111 mg, 0.582 mmol) and PPh₃ (221 mg, 0.843 mmol) in TEA (40 mL) was refluxed under nitrogen for 1 week. After the reaction mixture was evaporated under reduced pressure, the residue was dissolved in CHCl₂ (30 mL) and then the dark brown solution was washed twice with 0.2 M HCl (50 mL), three times with water (150 mL), dried over MgSO₄, filtered and evaporated to dryness. The residue was purified by silica gel chromatography with CHCl₃ as the eluent and recrystallization several times from methanol to give a white powder (48 mg, 4.4%). Mp 107.8 °C. ¹H NMR (400 MHz, 45 °C): $\delta_{\rm H}$ 0.88 (t, J = 6.8 Hz, 3 × 3H, 3 × CH₃), 1.26–1.38 (m, 3×18 H, $3 \times 9 \times C$ H₂), 1.53 (d, J = 7.6 Hz, 3×3 H, 3×3 $C^{\alpha}CH_3$), 1.64–1.71 (m, 3 × 2H, 3 × OCH₂CH₂), 4.14–4.24 (m, $3 \times 2H$, $3 \times OCH_2$), 4.75–4.82 (m. $3 \times 1H$, $3 \times C^{\alpha}H$), 6.78 $(d, J = 6.8 \text{ Hz}, 3 \times 1\text{H}, 3 \times \text{NH}), 7.58 (d, J = 8.4 \text{ Hz}, 3 \times 2\text{H}),$ peripheral aromatic protons), 7.68 (s, 3H, central aromatic protons), 7.80 (d, J = 8.4 Hz, 3×2 H, peripheral aromatic protons). ¹³C NMR (100 MHz, 45 °C): $\delta_{\rm C}$ 14.02, 18.70, 22.65, 25.83, 28.59, 29.18, 29.30, 29.47, 29.53, 29.60, 31.89, 48.75, 65.86, 89.91 (C=C), 89.97 (C=C), 123.89, 126.20, 127.16, 131.84, 133.93, 134.50, 165.93, 173.21. Anal. Calcd (%) for C₇₈H₁₀₅N₃O₉: C, 76.25; H, 8.61; N, 3.42%. Found: C, 76.51; H, 8.90; N, 3.20%.

1,2,4,5-Tetrakis{4-[(S)-1-(dodecyloxycarbonyl)ethylcarbamoyl]phenylethynyl}benzene (4):^{5a} A mixture of 4ethynylbenzoyl-L-alanine dodecyl ester (1.59 g, 4.12 mmol), 1,2,4,5-tetrabromobenzene (330 mg, 0.838 mmol), [Pd(PPh₃)₂-Cl₂] (116 mg, 0.166 mmol), CuI (107 mg, 0.560 mmol) and PPh₃ (216 mg, 0.824 mmol) in TEA (40 mL) was refluxed under nitrogen for 8 days. After the reaction mixture was evaporated under reduced pressure, the residue was dissolved in CHCl₃ (50 mL) and then the dark brown solution was washed twice with 0.2 M HCl (100 mL), four times with water (150 mL), dried over MgSO₄, filtered and evaporated to dryness. The residue was purified by silica gel chromatography with CHCl₃ as the eluent, and then the crude product was recrystallized several times from 1,2-dichloroethane, ethyl acetate, and acetone to give a yellowish white powder (0.30 g, 22%). Mp 178.9 °C. ¹H NMR (400 MHz, rt): $\delta_{\rm H}$ 0.88 (t, J = 6.8 Hz, 4 × 3H, 4 × CH₃), 1.22– 1.40 (m, 4×18 H, $4 \times 9 \times C$ H₂), 1.55 (d, J = 7.1Hz, 4×3 H, $4 \times C^{\alpha}CH_3$, 1.64–1.71 (m, $4 \times 2H$, $4 \times OCH_2CH_2$), 4.14–4.24 $(m, 4 \times 2H, 4 \times OCH_2), 4.76-4.83 (m, 4 \times 1H, 4 \times C^{\alpha}H), 6.93$ (broad, 4×1 H, $4 \times$ NH), 7.56 (d, J = 7.8 Hz, 4×2 H, peripheral aromatic protons), 7.76 (s, 2H, central aromatic protons), 7.78 (d, J = 8.1 Hz, 4×2 H, peripheral aromatic protons). ¹³C NMR (100 MHz, rt): $\delta_{\rm C}$ 14.09, 18.52, 22.66, 25.80, 28.52, 29.20, 29.32, 29.49, 29.55, 29.60, 29.62, 31.88, 48.71, 65.79, 89.48 (C=C), 94.93 (C=C), 125.28, 126.10, 127.27, 131.70, 133.91, 135.10, 166.13, 173.20. Anal. Calcd (%) for C₁₀₂H₁₃₈N₄O₁₂: C, 75.99; H, 8.63; N, 3.48%. Found: C, 76.09; H, 8.67; N, 3.44%.

UV-vis, CD, FL, and IR Spectra Measurements. 4.20×10^{-5} M solutions were prepared in 100-mL flasks equipped with stopcocks, and UV-vis and CD spectra were measured in a 1-mm cell. Aliquots (2.5 mL) of the solutions were transferred to 25-mL flasks equipped with stopcocks and diluted, and then UV-vis, CD, and FL spectra of the solutions (4.20 $\times 10^{-6}$ M) were measured in a 1-cm cell. Here, only the FL

spectrum in CHCl₃ was measured at more dilute 4.20×10^{-7} M because the FL intensity saturated at 4.20×10^{-6} M solution. IR spectral measurements of 4.20×10^{-4} M solutions were performed at about 25 °C in a 1-mm cell.

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Supporting Information

Characterization of new compounds. Figures S1–S6. This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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