JOC Note
pubs.acs.org/joc

Chirality Organization of Aniline Oligomers through Hydrogen Bonds of Amino Acid Moieties

Satoshi D. Ohmura, Toshiyuki Moriuchi,* and Toshikazu Hirao*

Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Yamada-oka, Suita, Osaka 565-0871, Japan

moriuchi@chem.eng.osaka-u.ac.jp; hirao@chem.eng.osaka-u.ac.jp

Received May 8, 2010

Aniline oligomers bearing amino acid moieties were designed by the introduction of L/D-Ala-OMe into aniline oligomers to induce chirality organization of the π-conjugated aniline oligomer moieties, wherein the formation of intramolecular hydrogen bonds was demonstrated to play an important role to regulate the aniline oligomer moieties conformationally.

π-Conjugated polymers are of potential for the application to electronic materials. One of the most important π-conjugated polymers, polyaniline, is redox-active and present in various redox states.[1] Recently, there has been increased interest in chiral induction of polyanilines because of their use in diverse areas for surface-modified electrodes, molecular recognition, and chiral separation.[2] In previous papers, the introduction of chiral transition metal complexes into poly(*o*-toluidine) has been demonstrated to afford chiral d,π-conjugated complex systems.[3] Bioinspired architectural control of molecular self-organization is of importance for the development of functional materials.[4] The utilization of amino acid moieties, which possess chiral centers and hydrogen-bonding sites, is considered to be a relevant approach to highly ordered molecular assemblies. In this system, inter/intramolecular hydrogen bonds play a critical role in enforcing well-defined assembly structures. We herein report the synthesis and characterization of the chirality-organized aniline oligomers by introduction of the amino acid moieties.

Two types of aniline tetramers, **1** and **2**, bearing alanine moieties are designed to investigate the chirality-organized structures (Figure 1). **1** and **2** were synthesized from L/D-alanine methyl ester hydrochloride salt and the carboxylic acids which were prepared from the ethyl esters **3** and **4**. The thus-obtained aniline tetramers were fully characterized by spectral data and elemental analyses.

In the ^{1}H NMR spectra of **1-L** in CD_2Cl_2 (5.0×10^{-3} M), the central-amino NHs of the aniline moieties were hardly perturbed by the addition of an aliquot of DMSO-d_6 to CD_2Cl_2 (CD_2Cl_2: 9.26 ppm, CD_2Cl_2-DMSO-d_6 (9:1): 9.28 ppm) although the terminal-amino NHs showed a slight downfield shift (CD_2Cl_2: 8.02 ppm, CD_2Cl_2-DMSO-d_6 (9:1): 8.27 ppm). The FT-IR spectrum of **1-L** in dichloromethane (5.0×10^{-3} M) showed the hydrogen-bonded NHs stretching bands at 3293 and 3333 cm^{-1}. The central-amino NHs are indicated to be locked in strong intramolecular hydrogen bonds and the terminal-amino NHs might participate in weak intramolecular hydrogen bonds in a solution state. The ^{1}H NMR spectra of **2-L** in CD_2Cl_2 (5.0×10^{-3} M) indicate that the central-amino NHs of the aniline moieties were hardly perturbed by the addition of an aliquot of DMSO-d_6 to CD_2Cl_2 (CD_2Cl_2: 7.94 ppm, CD_2Cl_2-DMSO-d_6 (9:1): 8.17 ppm), although the terminal-amino NHs were perturbed decidedly (CD_2Cl_2: 5.70 ppm, CD_2Cl_2-DMSO-d_6 (9:1): 6.48 ppm). The FT-IR spectrum of **2-L** in CH_2Cl_2 (5.0×10^{-3} M) showed hydrogen-bonded NH and not hydrogen-bonded NH stretching bands at 3342 and 3423 cm^{-1} in a solution state, respectively. These results indicate that the central-amino NHs form the intramolecular hydrogen bonds although the terminal-amino NHs do not participate in hydrogen bonding.

The electronic spectrum of **1-L** in dichloromethane exhibited a broad absorption at around 450 nm, which is probably due to a low-energy charge-transfer transition of the π-conjugation moiety (Figure 2a).[3,5] It should be noted that **1-L** exhibits an induced circular dichroism (ICD) at the absorbance region of the π-conjugated moiety. This result

(1) (a) Pouget, J. P.; Laridjani, M.; Jozefowicz, M. E.; Epstain, A. J.; Scherr, E. M.; MacDiarmid, A. G. *Synth. Met.* **1992**, *51*, 95. (b) Lux, F. *Polymer* **1994**, *35*, 2915. (c) MacDiarmid, A. G. *Synth. Met.* **1997**, *84*, 27. (d) Malinauskas, A. *J. Power Sources* **2004**, *126*, 214. (e) Wang, Y.; Zhang, D. *Mater. Sci. Eng., B* **2006**, *134*, 9. (f) Miras, M. C.; Acevedo, D. F.; Monge, N.; Frontera, E.; Rivarola, C. R.; Barbero, C. A. *Open Macromol. J.* **2008**, *1*, 58.

(2) (a) Majidi, M. R.; Kane-Maguire, L. A. P.; Wallace, G. G. *Polymer* **1994**, *35*, 3113. (b) Ashraf, S. A.; Kane-Maguire, L. A. P.; Majidi, M.-R.; Pyne, S. G.; Wallace, G. G. *Polymer* **1997**, *38*, 2627. (c) Uemura, S.; Kusabuka, K.; Nakahira, T.; Kobayashi, N. *J. Mater. Chem.* **2001**, *11*, 267. (d) Nagarajan, R.; Liu, W.; Kumar, J.; Tripathy, S. K.; Bruno, F. F.; Samuelson, L. A. *Macromolecules* **2001**, *34*, 3921. (e) Yuan, G.-L.; Kuramoto, N. *Chem. Lett.* **2002**, 544. (f) Yuan, G.-L.; Kuramoto, N. *Macromolecules* **2002**, *35*, 9773. (g) Li, W.; Wang, H.-L. *J. Am. Chem. Soc.* **2004**, *126*, 2278. (h) Zhang, X.; Song, W. *Polymer* **2007**, *48*, 5473.

(3) (a) Shen, X.; Moriuchi, T.; Hirao, T. *Tetrahedron Lett.* **2004**, *45*, 4733. (b) Moriuchi, T.; Shen, X.; Hirao, T. *Tetrahedron* **2006**, *62*, 12237.

(4) For recent reviews, see: (a) Hill, D. J.; Mio, M. J.; Prince, R. B.; Hughes, T. S.; Moore, J. S. *Chem. Rev.* **2001**, *101*, 3893. (b) Archer, E. A.; Gong, H.; Krische, M. J. *Tetrahedron* **2001**, *57*, 1139. (c) Huc, I. *Eur. J. Org. Chem.* **2004**, 17. (d) Moriuchi, T.; Hirao, T. *Chem. Soc. Rev.* **2004**, *33*, 294. (e) Sanford, A. R.; Yamato, K.; Yang, X.; Yuan, L.; Han, Y.; Gong, B. *Eur. J. Biochem.* **2004**, *271*, 1416. (f) Goodman, C. M.; Choi, S.; Shandler, S.; DeGrado, W. F. *Nat. Chem. Biol.* **2007**, *3*, 252. (g) Gong, B. *Acc. Chem. Res.* **2007**, *41*, 1736. (h) Kim, H.-J.; Lim, Y.-B.; Lee, M. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 1925. (i) Yashima, E.; Maeda, K.; Iida, H.; Furusho, Y.; Nagai, K. *Chem. Rev.* **2009**, *109*, 6102. (j) Saraogi, I.; Hamilton, A. D. *Chem. Soc. Rev.* **2009**, *38*, 1726.

(5) Moriuchi, T.; Kikushima-Honda, N.; Ohmura, S. D.; Hirao, T. *Tetrahedron Lett.* **2010**, *51*, 4530.

DOI: 10.1021/jo100853b Published on Web 10/19/2010

indicates that the chirality induction of a π-conjugated backbone aniline oligomer is achieved by the chirality organization based on the intramolecular hydrogen bonding. The mirror image of the CD signals observed with **1-L** was obtained in the CD spectrum of **1-D** as shown in Figure 2b, indicating that a chiral molecular arrangement based on the regulated structures via intramolecular hydrogen bonding is formed. ICD and the mirror-imaged CD signals were also observed in the case of **2**.

The CD signals of **1-L** were changed at around 360 nm by the addition of DMSO (Figure 2c). On the contrary, only a little change of the CD signals was observed in the case of **2-L**. The shape of the CD signal of **1** in CH_2Cl_2−DMSO (1:1) is similar to that of **2** in CH_2Cl_2−DMSO (1:1). From the above-mentioned results of the ^{1}H NMR and FT-IR experiments, the chirality-organized structure is considered to be preserved through the intramolecular hydrogen bonding of the central-amino NHs in CH_2Cl_2−DMSO (1:1).

On the basis of these observations, the structural elucidation of **1** and **2** was investigated by crystal structural analysis of the ethyl esters **3** and **4**. The crystal structure of the tetraethyl ester **3** revealed the formation of the intramolecular hydrogen bonds between the amino NH and CO, resulting in an *anti*−*anti*−*anti*-conformation of the π-conjugated moieties. The orientation of the benzene rings has the dihedral angles of 149.5(2)° (central) and 125.4(1)° (terminal) as shown in Figure 3a. A similar structure is considered to be formed with **1** to permit chirality organization of the aniline oligomers through hydrogen bonding of the amino acid moieties. The packing structure of the tetraethyl ester **3** exhibited the ordered-layer structure through π−π stacking (Figure 3b). Contrary to the molecular structure of **3**, a *syn*−*anti*−*syn*-conformation of the π-conjugated moieties based on intramolecular hydrogen bonding was observed in the crystal structure of the diethyl ester **4** (Figure 4a).This difference might arise from the existence of the hydrogen bonds. While all NHs of **3** participated in the intramolecular hydrogen bonds to regulate the conformation of the π-conjugated moieties, the terminal moieties of **4** were not regulated because of the absence of the hydrogen bonds in the terminal-amino NHs. The formation of the intramolecular hydrogen bonds was found to play an important role in the structural regulation of the π-conjugated moieties. The orientation of the benzene rings of **4** has the dihedral angles of 98.15(4)° (central) and 62.52(6)° (terminal). Contrary to the packing structure of **3**, the diethyl ester **4** exhibited the sheet-like self-assembly through the intermolecular hydrogen-bonding networks, wherein each molecule is bonded to two neighboring

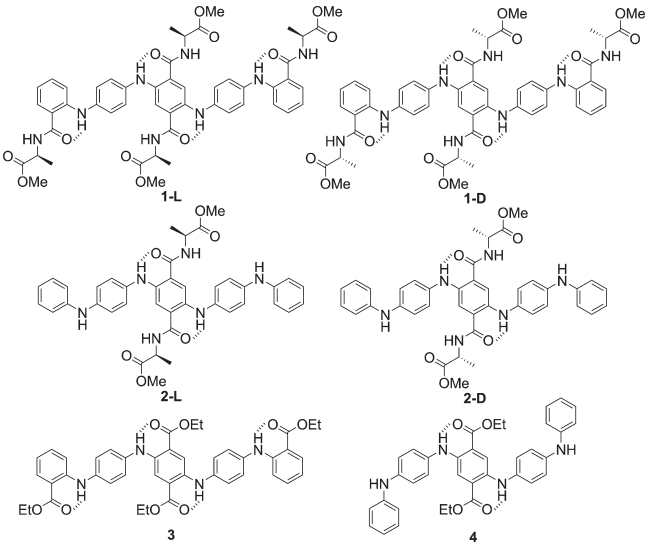

FIGURE 1. Structures of aniline tetramer derivatives.

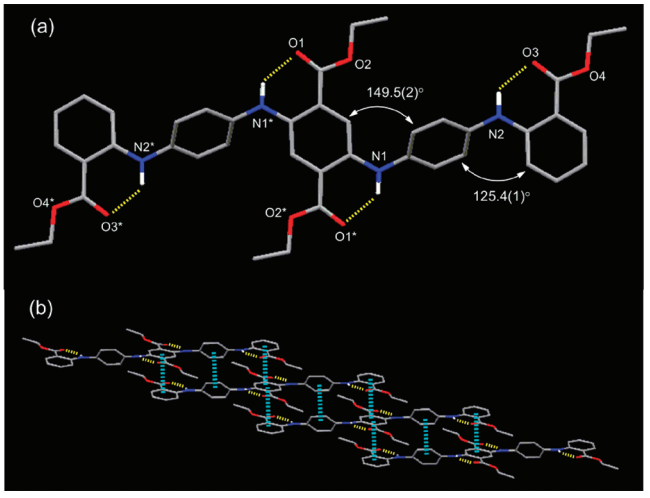

FIGURE 3. (a) Crystal structure of **3**. (b) Portion of a layer containing the ordered-layer structure through π−π stacking in the crystal packing of **3**.

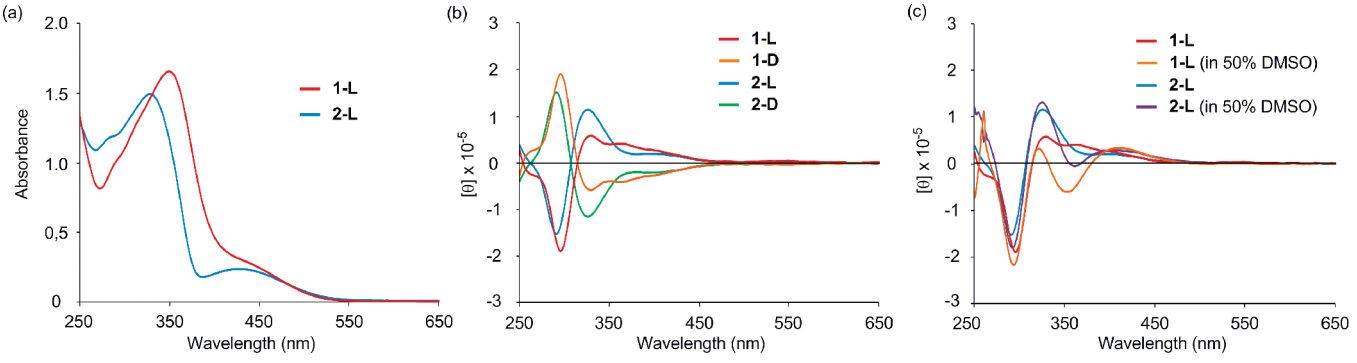

FIGURE 2. (a) Absorption spectra of **1-L** and **2-L**. (b) CD spectra of **1** and **2** in CH_2Cl_2 (5.0×10^{-5} M) and (c) **1-L** and **2-L** in CH_2Cl_2-DMSO (1:1) (5.0×10^{-5} M) at 25 °C under nitrogen atmosphere.

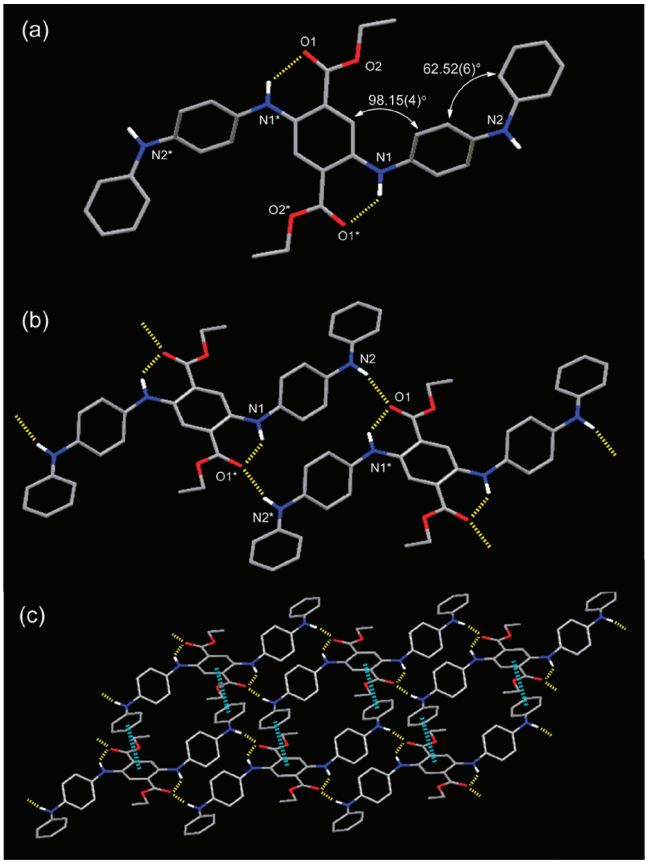

FIGURE 4. (a) Crystal structure of **4**. (b) Portion of a layer containing the sheet-like self-assembly through intermolecular hydrogen-bonding networks and (c) the $\pi-\pi$ stacking between the hydrogen-bonded sheets in the crystal packing of **4**.

molecules by an 18-membered hydrogen-bonded ring (O(1)···N(2), 2.19 Å; O(1*)···N(2*), 2.19 Å) (Figure 4b). Furthermore, each hydrogen-bonded sheet was connected through the $\pi-\pi$ stacking (Figure 4c).

The redox properties of **1**−**4** were disclosed by cyclic voltammetry (see Figure S2, Supporting Information). Tetraalanyl oligomer **1** in dichloromethane showed three consecutive redox waves (E^0 = 0.24, 0.44, and 0.76 V vs Fc/Fc^+). The waves at 0.24 and 0.44 V were assigned to consecutive one-electron oxidation of the phenylenediamine moieties to give the corresponding oxidized species. The most positive anodic peak with twice the height ($E^0{}_3$ = 0.76 V) is attributable to successive one-electron oxidation processes of the two terminal phenylenediamine moieties. The three successive redox waves (E^0 = −0.06, 0.09, and 0.48 V vs Fc/Fc^+) were also observed in the cyclic voltammogram of the oligomer **2**. All of the redox waves were more cathodic than those of **1**. The shift is probably due to the absence of the electron-withdrawing substituent at the terminal benzene rings.

In conclusion, the formation of the hydrogen bonds was found to play an important role in the conformational regulation of the oligoanilines by the introduction of L/D-alanine moieties. The hydrogen-bond regulated chirality organization of the π-conjugated moieties has been achieved. Studies on the application of the chirality-organized aniline oligomers or polymers for molecular recognition and molecular dynamics are now in progress.

Experimental Section

Synthesis of Ethyl 2-(4-Aminophenylamino)benzoate. To a mixture of cesium carbonate (3.10 g, 9.5 mmol), palladium(II) acetate (89.8 mg, 0.40 mmol), (±)-BINAP (218 mg, 0.35 mmol), ethyl 2-bromobenzoate (454 mg, 2.0 mmol), and *p*-phenylenediamine (865 mg, 8.0 mmol) was added anhydrous toluene (40 mL). The mixture was stirred at 100 °C for 48 h under argon atmosphere. After cooling to ambient temperature, dichloromethane (30 mL) was added to the brown suspension and filtered. After evaporation of the solvent, a residue was purified by silica-gel column chromatography (from hexane to hexane/EtOAc = 4:1) to give the expected compound (62.0 mg, 0.24 mmol) as a brown-yellow solid, R_f = 0.64 (hexane/EtOAc = 5:2): yield 66%; mp 72−73 °C (uncorrected); IR (KBr) 3289, 3253, 3033, 2992, 2975, 1681, 1583, 1522, 1478, 1449 cm^{-1}; ^1H NMR (400 MHz, CD_2Cl_2, 1.0 × 10^{-2} M) δ 9.17 (s, 1H), 7.93 (dd, 1H, J = 7.8, 1.8 Hz), 7.23 (dt, 1H, J = 7.8, 1.8 Hz), 7.02 (dd, 2H, J = 6.4, 1.8 Hz), 6.89 (dd, 1H, J = 7.8, 0.9 Hz), 6.69 (dd, 2H, J = 6.4, 1.8 Hz), 6.62 (dt, 1H, J = 7.8, 0.9 Hz), 4.33 (q, 2H, J = 7.3 Hz), 3.69 (s, 2H), 1.38 (t, 3H, J = 7.3 Hz); ^{13}C NMR (100 MHz, CD_2Cl_2, 1.0 × 10^{-2} M) 168.9, 150.5, 144.5, 134.3, 131.8, 131.6, 126.7, 116.1, 116.0, 113.6, 111.2, 60.9, 14.6 ppm; HRMS (FAB) m/z: $[M]^+$ 256.1220, $C_{15}H_{16}N_2O_2$ (calcd 256.1212); Anal. Calcd for $C_{15}H_{16}N_2O_2$: C, 71.27; H, 5.98; N, 6.93. Found: C, 71.15; H, 5.91; N, 6.87.

General Procedure for Synthesis of Tetraalanyl Derivative 1. A mixture of **3** (73.0 mg 0.10 mmol) and sodium hydroxide (~180 mg) in tetrahydrofuran (10 mL) was refluxed for 27 h. After the reaction was completed, the solvent was evaporated, and the residue was dried in vacuo. Water (15 mL) was added to the residue, and the solution was acidified with 1 N HCl aqueous solution. The dark-brown precipitate was isolated by filtration, washed with water, and dried in vacuo. Anhydrous dichloromethane (40 mL) was added to a mixture of the thus-obtained dark-brown solid, 1-hydroxybenzotriazole (108 mg, 0.80 mmol), L/D-alanine methyl ester hydrochloride (112 mg, 0.8 mmol), and triethylamine (0.5 mL). The mixture was stirred at 0 °C, and a solution of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (154 mg, 0.80 mmol) in anhydrous dichloromethane (40 mL) was dropwise added to the mixture over 1 h. Then, the mixture was stirred at ambient temperature for 25 h. The resulting mixture was diluted with dichloromethane (10 mL), washed with saturated $NaHCO_3$ aqueous solution (30 mL × 2), water (30 mL) and saturated NaCl aqueous solution (30 mL). After separating and discarding the water phase, the organic phase was dried on Na_2SO_4. After evaporation of the solvent, a mixture was purified by silica-gel column chromatography (from CH_2Cl_2 to CH_2Cl_2/EtOAc = 3:1) to give **1** as a yellow solid (**1-L**: 162 mg; **1-D**: 87.6 mg), R_f = 0.25 (CH_2Cl_2/EtOAc = 3:1); **1-L**: yield 61%; mp 167−168 °C (uncorrected); IR (CH_2Cl_2, 5.0 × 10^{-3} M) 3316, 1696, 1578, 1522, 1443, 1414, 1313, 1237, 1211 cm^{-1}; ^1H NMR (400 MHz, CD_2Cl_2, 5.0 × 10^{-3} M) δ 9.26 (s, 2H), 8.02 (s, 2H), 7.53 (s, 2H), 7.50 (d, 2H, J = 7.9 Hz), 7.27 (t, 2H, J = 7.9 Hz), 7.19 (d, 2H, 7.9 Hz), 7.15 (d, 4H, J = 6.7 Hz), 7.06 (d, 4H, J = 6.7 Hz), 7.00 (d, 2H, J = 7.3 Hz), 6.74 (t, 2H, J = 7.9 Hz), 6.69 (d, 2H, J = 6.9 Hz), 4.71 (quint, 2H, J = 7.3 Hz), 4.64 (quint, 2H, J = 7.3 Hz), 3.77 (s, 6H), 3.72 (s, 6H), 1.50 (d, 6H, J = 7.3 Hz), 1.42 (d, 6H, J = 7.3 Hz); ^{13}C NMR (100 MHz, CD_2Cl_2, 5.0 × 10^{-3} M) 173.9, 173.4, 169.3, 167.6, 147.3, 139.0, 137.3, 136.0, 132.9, 128.2, 125.0, 123.9, 120.7, 118.4, 117.5, 116.8, 115.0, 52.9, 52.8, 48.9, 48.8, 18.6, 18.4 ppm; HRMS (FAB) m/z: $[M]^+$ 958.3864, $C_{50}H_{54}N_8O_{12}$ (calcd 958.3861) Anal. Calcd for $C_{50}H_{54}N_8O_{12}$: C, 62.62; H, 5.68; N, 11.68. Found: C, 62.48; H, 5.41; N, 11.54: **1-D**: yield 33%; mp 167−168 °C (uncorrected); IR (CH_2Cl_2, 5.0 × 10^{-3} M) 3316, 1696, 1578, 1522, 1443, 1414, 1313, 1237, 1211 cm^{-1}; ^1H NMR (400 MHz, CD_2Cl_2, 5.0 × 10^{-3} M) δ 9.26 (s, 2H), 8.02 (s, 2H), 7.53 (s, 2H),

7.50 (d, 2H, J = 7.9 Hz), 7.27 (t, 2H, J = 7.9 Hz), 7.19 (d, 2H, 7.9 Hz), 7.15 (d, 4H, J = 6.7 Hz), 7.06 (d, 4H, J = 6.7 Hz), 7.00 (d, 2H, J = 7.3 Hz), 6.74 (t, 2H, J = 7.9 Hz), 6.69 (d, 2H, J = 6.9 Hz), 4.71 (quint, 2H, J = 7.3 Hz), 4.64 (quint, 2H, J = 7.3 Hz), 3.77 (s, 6H), 3.72 (s, 6H), 1.50 (d, 6H, J = 7.3 Hz), 1.42 (d, 6H, J = 7.3 Hz); ^{13}C NMR (100 MHz, CD_2Cl_2, 5.0×10^{-3} M) 173.9, 173.4, 169.3, 167.6, 147.3, 139.0, 137.3, 136.0, 132.9, 128.2, 125.0, 123.9, 120.7, 118.4, 117.5, 116.8, 115.0, 52.9, 52.8, 48.9, 48.8, 18.6, 18.4 ppm; HRMS (FAB) m/z: $[M]^+$ 958.3858, $C_{50}H_{54}N_8O_{12}$ (calcd 958.3861).

General Procedure for Synthesis of Dialanyl Derivative 2. A mixture of **4** (58.6 mg, 0.10 mmol) and sodium hydroxide (~100 mg) in tetrahydrofuran (10 mL) was refluxed for 20 h. After the reaction was completed, the solvent was evaporated, and the residue was dried in vacuo. Water (15 mL) was added to the residue, and the solution was acidified with 1 N HCl aqueous solution. The dark-brown precipitate was isolated by filtration, washed with water, and dried in vacuo. Anhydrous dichloromethane (40 mL) was added to a mixture of the thus-obtained black solid, 1-hydroxybenzotriazole (27.0 mg, 0.20 mmol), L/D-alanine methyl ester hydrochloride (27.9 mg, 0.20 mmol), and triethylamine (0.5 mL). The mixture was stirred at 0 °C, and a solution of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (38.3 mg, 0.20 mmol) in anhydrous dichloromethane (40 mL) was dropwise added to the mixture over 1 h. Then, the mixture was stirred at ambient temperature for 45 h. The resulting mixture was diluted with dichloromethane (10 mL), washed with saturated $NaHCO_3$ aqueous solution (30 mL × 2), water (30 mL), and saturated NaCl aqueous solution (30 mL). After separating and discarding the water phase, the organic phase was dried on Na_2SO_4. After evaporation of the solvent, a mixture was purified by silica-gel column chromatography (from CH_2Cl_2 to CH_2Cl_2/MeOH = 10:1) to give **2** as a yellow solid (**2-L**: 29.2 mg; **2-D**: 18.9 mg), R_f = 0.63 (CH_2Cl_2/MeOH = 10:1); **2-L**: yield 42%; mp 178−180 °C (uncorrected); IR (CH_2Cl_2, 5.0×10^{-3} M) 3424, 3342, 2848, 1738, 1651, 1594, 1508, 1211, 1162, 1063 cm^{-1}; ^{1}H NMR (400 MHz, CD_2Cl_2, 5.0×10^{-3} M) δ 7.94 (s, 2H), 7.48 (s, 2H), 7.22 (t, 4H, J = 7.3 Hz), 7.08 (d, 4H, J = 9.2 Hz), 7.03 (d, 4H, J = 9.2 Hz), 6.99 (d, 4H, J = 7.3 Hz), 6.85 (t, 4H, J = 7.3 Hz), 5.70 (s, 2H), 4.64 (quint, 2H, J = 7.3 Hz), 3.71 (s, 6H), 1.41 (d, 6H, J = 7.3 Hz); ^{13}C NMR (100 MHz, CD_2Cl_2, 5.0×10^{-3} M) 173.6, 167.6, 144.8, 137.9, 137.7, 137.6, 129.7, 124.7, 121.2, 121.0, 120.3, 118.2, 116.6, 52.9, 48.9, 18.4 ppm; HRMS (FAB) m/z: $[M]^+$ 700.2998, $C_{40}H_{40}N_6O_6$ (calcd 700.3009); **2-D**: yield 27%; mp 178−180 °C (uncorrected); IR (CH_2Cl_2, 5.0×10^{-3} M) 3424, 3342, 2848, 1738, 1651, 1594, 1508, 1211, 1162, 1063 cm^{-1}; ^{1}H NMR (400 MHz, CD_2Cl_2, 5.0×10^{-3} M) δ 7.94 (s, 2H), 7.48 (s, 2H), 7.22 (t, 4H, J = 7.3 Hz), 7.08 (d, 4H, J = 9.2 Hz), 7.03 (d, 4H, J = 9.2 Hz), 6.99 (d, 4H, J = 7.3 Hz), 6.85 (t, 4H, J = 7.3 Hz), 5.70 (s, 2H), 4.64 (quint, 2H, J = 7.3 Hz), 3.71 (s, 6H), 1.41 (d, 6H, J = 7.3 Hz); ^{13}C NMR (100 MHz, CD_2Cl_2, 5.0×10^{-3} M) 173.6, 167.6, 144.8, 137.9, 137.7, 137.6, 129.7, 124.7, 121.2, 121.0, 120.3, 118.2, 116.6, 52.9, 48.9, 18.4 ppm; HRMS (FAB) m/z: $[M]^+$ 700.3022, $C_{40}H_{40}N_6O_6$ (calcd 700.3009).

Synthesis of 3. A solution of *p*-toluenesulfonate monohydrate (28.5 mg, 0.15 mmol) in ethanol (15 mL) was added to a mixture of diethyl 2,5-dioxocyclohexane-1,4-dicarboxylate (51.3 mg, 0.20 mmol) and ethyl 2-(4-aminophenylamino)benzoate (154 mg, 0.60 mmol). The mixture was stirred at reflux for 12 h under argon atmosphere. Once cooling to ambient temperature, the mixture was stirred at reflux for 32 h under oxygen atmosphere. After cooling to ambient temperature, the precipitate was isolated by filtration, washed with ethanol, and dried in vacuo. Aniline tetramer **3** (157 mg) was obtained as a red crystal by recrystallization from dichloromethane: yield 98%; mp 195−197 °C (uncorrected); IR (CH_2Cl_2, 5.0×10^{-3} M) 3412, 3337, 3268, 3181, 3161, 1684, 1581, 1515, 1382, 1370, 1314 cm^{-1}; ^{1}H NMR (400 MHz, CD_2Cl_2, 5.0×10^{-3} M) δ 9.38 (s, 2H), 7.99 (s, 2H), 7.97 (d, 2H, J = 8.0 Hz), 7.30 (t, 2H, J = 8.0 Hz), 7.23−7.19 (m, 10H), 7.13 (d, 2H, J = 8.0 Hz), 6.70 (t, 2H, J = 8.0 Hz), 4.35 (q, 4H, J = 7.3 Hz), 4.33 (q, 4H, J = 7.3 Hz), 1.40 (t, 6H, J = 7.3 Hz), 1.34 (t, 6H, J = 7.3 Hz); ^{13}C NMR (100 MHz, CD_2Cl_2, 5.0×10^{-3} M) 167.7, 166.7, 148.1, 133.2, 130.8, 123.9, 123.8, 120.9, 120.3, 118.3, 117.4, 115.8, 115.7, 112.8, 110.9, 60.5, 59.9, 13.4, 13.2 ppm; HRMS (FAB) m/z: $[M]^+$ 730.2989, $C_{42}H_{42}N_4O_8$ (calcd 730.3003).

Synthesis of 4. A mixture of diethyl 2,5-dioxocyclohexane-1,4-dicarboxylate (256 mg, 1.0 mmol) and *p*-aminodiphenylamine (369 mg, 2.0 mmol) in acetic acid (15 mL) was stirred at 100 °C for 18 h. After cooling to ambient temperature, the precipitate was isolated by filtration, washed with ethanol, and dried in vacuo. Chloroform (15 mL) was added to the pink solid, which was refluxed for 10 h under oxygen atmosphere. After evaporation of the solvent, **4** (498 mg) was obtained as a red crystal by recrystallization from toluene: yield 85%; mp 211−213 °C (uncorrected); IR (CH_2Cl_2, 5.0×10^{-3} M) 3416, 3361, 2926, 1686, 1599, 1513, 1103, 1020 cm^{-1}; ^{1}H NMR (400 MHz, CD_2Cl_2, 5.0×10^{-3} M) δ 8.63 (s, 2H), 7.89 (s, 2H), 7.24 (t, 4H, J = 7.8 Hz), 7.14 (d, 4H, J = 8.7 Hz), 7.10 (d, 4H, J = 8.7 Hz), 7.01 (d, 2H, J = 7.8 Hz), 6.86 (t, 2H, J = 7.8 Hz), 5.73 (s, 2H), 4.31 (q, 4H, J = 7.3 Hz), 1.33 (t, 6H, J = 7.3 Hz); ^{13}C NMR (100 MHz, CD_2Cl_2, 5.0×10^{-3} M) 167.9, 144.8, 138.9, 138.2, 136.7, 129.7, 122.4, 120.8, 120.4, 119.0, 118.1, 116.7, 61.6, 14.4 ppm; HRMS (FAB) m/z: $[M]^+$ 586.2582, $C_{36}H_{34}N_4O_4$ (calcd 586.2580).

Acknowledgment. One of the authors, S.D.O., expresses special thanks for the Global COE (center of excellence) Program "Global Education and Research Center for Bio-Environmental Chemistry" of Osaka University. Thanks are due to the Analytical Center, Graduate School of Engineering, Osaka University, for the use of the NMR and MS instruments.

Supporting Information Available: Experimental details, spectroscopic data, and X-ray crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.