Selected Paper

Synthesis of Helicenediamine Oligomers and Their Formation of Multilayer Structures in Aqueous Solvents

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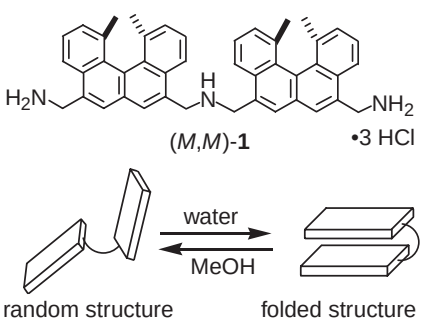
Optically active polyamine oligomers containing three to six (*P*)-5,8-bis(aminomethyl)-1,12-dimethylbenzo[*c*]-phenanthrenes were synthesized employing the two-directional chain extension method. It was critical for the effective coupling of amines and aldehydes to precipitate imine intermediates using the appropriate solvents. UV, CD, fluorescent, and NMR spectroscopic studies revealed that the above-mentioned oligomers form multilayer structures in aqueous solvents, while they form random coil structures in methanol. Such layer structures contained helicene dyads with an *anti*-conformation in which the BC-rings of helicenes were stacked on each other, and 1,12-dimethyl groups were arranged in the opposite direction. A diastereomeric trimer was also synthesized, the layer structure of which was different from that of the parent trimer. The stereochemistry of the helicene moiety influenced the layer structure.

The layer structure of arenes is a characteristic structural feature of double-stranded DNA.[1] The design and synthesis of unnatural aromatic oligomers to construct such an ordered structure have attracted much interest.[2] Several compounds with rigid layer structures have been synthesized and characterized in solution and solid state. However, it is not easy to form layer structures with flexible linear aromatic oligomers and only a few examples of such structures are known.[3–9] Iverson synthesized oligomers containing 1,4,5,8-naphthalenetetracarboxylic diimide and 1,5-dialkoxynaphthalene, and showed that they form multilayer structures in water.[3] Hydrophobic and donor–acceptor interactions are considered to play important roles in this formation. Donor–acceptor interactions have recently been used by Chen in the formation of the zipper-featured layer structures of peptides containing electron-deficient pyromellitic diimide (1,2,4,5-benzenetetracarboxylic diimide) and electron-rich 1,5-dioxynaphthalene.[4] Kagechika showed that synthetic oligomers of *N*,*N*′-dimethyl-*N*,*N*′-diphenylguanidine or *N*,*N*′-dimethyl-*N*,*N*′-diphenylurea form multilayer structures in solution and solid state.[5,6] *N*,*N*′-Dimethyl-*N*,*N*′-diphenylguanidine and urea prefer a *cis*-conformation with their two phenyl groups located in a face-to-face position; a structural motif is utilized in the formation of their layer structure. Nuckolls reported that oligomers of hexasubstituted benzene form folded columnar layer structures in dichloromethane by hydrogen bonds and π–π interactions.[7] Multilayer structures have been obtained in chloroform for oligomers containing polycyclic arenes such as fluorene or perylene.[8,9]

The above-mentioned compounds with multilayer structures can be used to construct new environments for chemical reaction and molecular recognition. Their biological activities may be interesting. For example, *N*,*N*′-dimethyl-*N*,*N*′-diphenylguanidine oligomers were found to bind double-stranded DNA at the minor groove.[5d] In addition, a study using flexible compounds can lead to the development of molecular switches that can change their structures between layer and random coil structures depending on their environment.

We previously synthesized the optically active triamine (*M*,*M*)-**1** containing two (*M*)-helicenes, and examined its structure in organic solvents and water (Scheme 1).[10] CD, UV, fluorescence, and ^{1}H NMR studies of (*M*,*M*)-**1** revealed its formation of a folded structure in water and a random coil structure in methanol. It was also observed that isomeric (*M*,*M*)-**1** and (*P*,*M*)-**1** behave differently, and that the folding structure of (*M*,*M*)-**1** is thermodynamically more stable than that of (*P*,*M*)-**1**. This is consistent with the results of our previous study of helicene derivatives that the combination of the same configuration of helicenes forms more stable aggregates.[10,11] We describe here the synthesis of higher helicenediamine oligomers, that is, the trimer (*P*,*P*,*P*)-**2** to the hexamer (*P*,*P*,*P*,*P*,*P*,*P*)-**5**, and characterized their structures in solution by NMR, UV,



Scheme 1.

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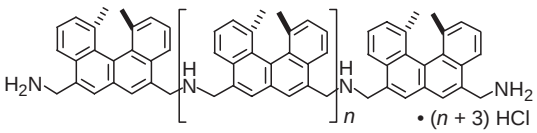


n = 1 (*P*,*P*,*P*)-**2**
n = 2 (*P*,*P*,*P*,*P*)-**3**
n = 3 (*P*,*P*,*P*,*P*,*P*)-**4**
n = 4 (*P*,*P*,*P*,*P*,*P*,*P*)-**5**

Chart 1.

CD, and fluorescent spectroscopies (Chart 1). These oligomers form multilayer structures in aqueous solvents and random coil structures in methanol. Solvophobic and π–π interactions are considered to play important roles in this system. It should also be noted that such multilayer structural formation by chiral and flexible aromatic oligomers has no precedent.

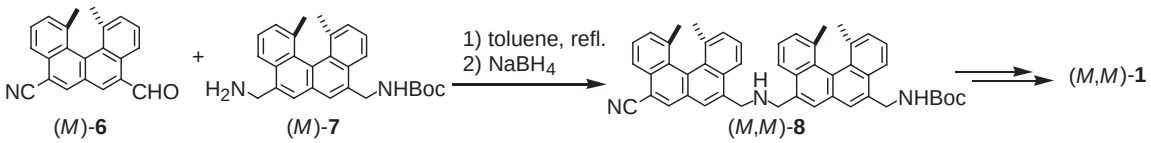
Results and Discussion

Synthesis. The synthesis of (*M*,*M*)-**1** employing the reductive coupling of the aldehyde (*M*)-**6** and the amine (*M*)-**7** has problems in its application to higher oligomers (Scheme 2): 1) The reduction of the nitrile (*M*,*M*)-**8** to form an amine at a later stage is not suitable for molecules with a relatively high molecular weight, because the functional manipulation of such molecules is considered not facile. 2) (*M*)-**6** and (*M*)-**7** are obtained from symmetrical compounds in relatively low yields.[10]

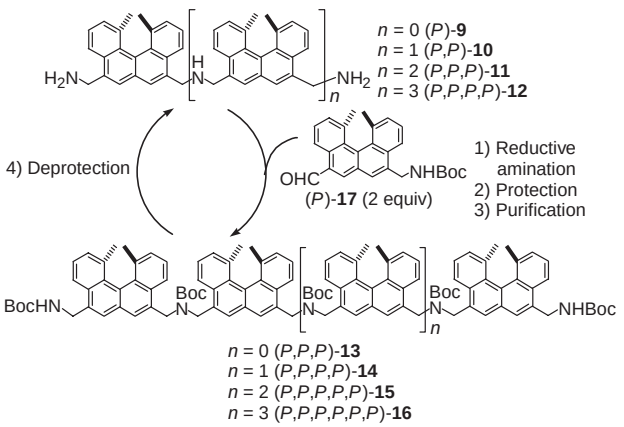
A new synthetic method was therefore developed in this study that involves the reductive amination of a diamine with 2 equivalents of the protected amino aldehyde (*P*)-**17** (Scheme 3). All of the amine moieties of the resulting oligomers were protected with *t*-butoxycarbonyl (Boc) groups for purification. Deprotection gave a polyamine that can be used for the subsequent coupling reaction to obtain higher oligomers. This method does not entail the reduction of terminal nitrile after reductive amination, which solves the above-mentioned problem 1). A series of chiral oligomers with odd numbers of helicenes were synthesized from the monomer (*P*)-**9**, and those with even numbers of helicenes were synthesized from the dimer (*P*,*P*)-**10**. An issue in this methodology is whether the efficient and selective coupling of primary amine and aldehyde proceeded in the presence of the secondary amine moiety. As will be discussed later, this issue could be resolved by the precipitation of the imine intermediate from the reaction media by selecting an appropriate solvent.

The protected amino aldehyde (*P*)-**17**, required as a building block was synthesized from the monocarboxylic acid (*P*)-**18** (Scheme 4), which was obtained from the corresponding dimethyl ester in high yield.[12] (*P*)-**18** was heated under reflux in thionyl chloride, and then treated with liquid NH_3 at $-78\,^{\circ}C$ to produce the amide (*P*)-**19** in 92% yield in two steps. Then, (*P*)-**19** was dehydrated with P_2O_5 under toluene reflux giving the nitrile (*P*)-**20** (95%), the hydrogenation of which was followed by treatment with di(*t*-butyl) dicarbonate (Boc_2O) converted to (*P*)-**21** in 84% yield in two steps. The DIBAL-H reduction of (*P*)-**21** followed by Swern oxidation gave (*P*)-**17**. This efficient synthesis of (*P*)-**17** solved the above-mentioned problem 2).

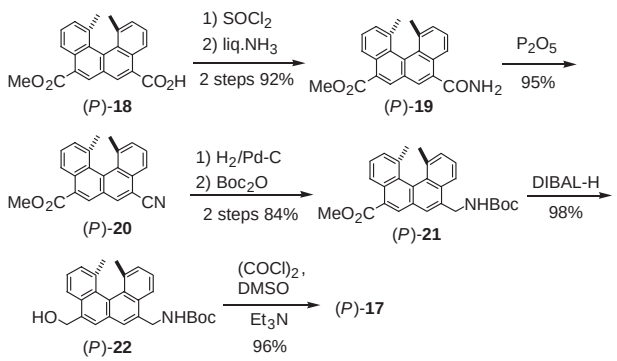
Amine oligomers with odd numbers of helicenes were synthesized starting from the diamine (*P*)-**9**[10] (Scheme 5). Treatment of (*P*)-**9** with 2 equivalents of (*P*)-**17** in MeOH at $40\,^{\circ}C$ immediately formed the diimine trimer (*P*,*P*,*P*)-**23** as a precipitate. Then, the imine was collected by filtration, washed with MeOH, and the structure was confirmed by ^1H NMR δ 9.05. The reduction of (*P*,*P*,*P*)-**23** with $NaBH_4$ in MeOH/THF provided an amine, which was successively protected by Boc_2O giving the trimer (*P*,*P*,*P*)-**13** in 88% yield from (*P*)-**9**. Then, (*P*,*P*,*P*)-**13** was treated with trifluoroacetic acid to produce the amine (*P*,*P*,*P*)-**11**, which was ready for the next coupling. In MeOH, the reductive coupling of (*P*,*P*,*P*)-**11** and (*P*)-**17** did not proceed because of the low solubility of (*P*,*P*,*P*)-**11**. When THF or DMF was used as the solvent, diimine did not precipitate and the treatment of the mixture with $NaBH_4$ followed



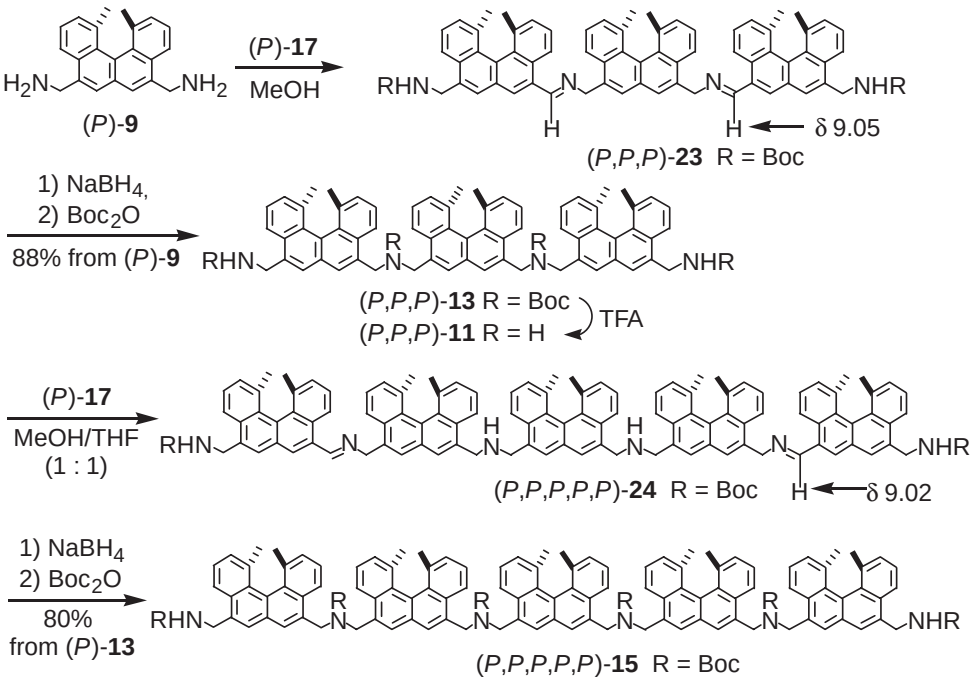
Scheme 2.



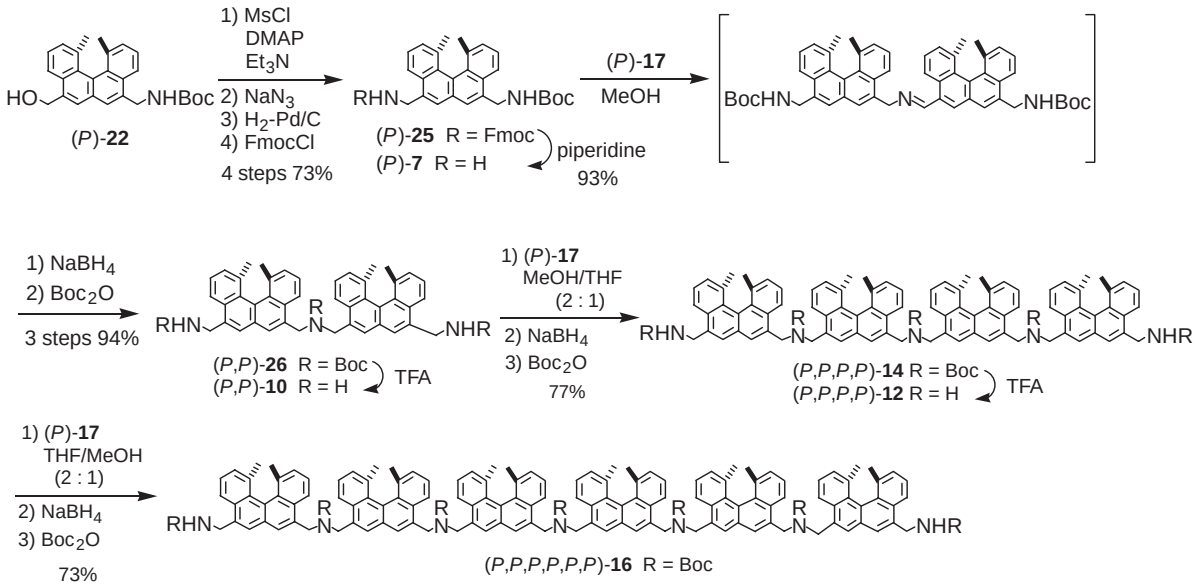
Scheme 3.



Scheme 4.



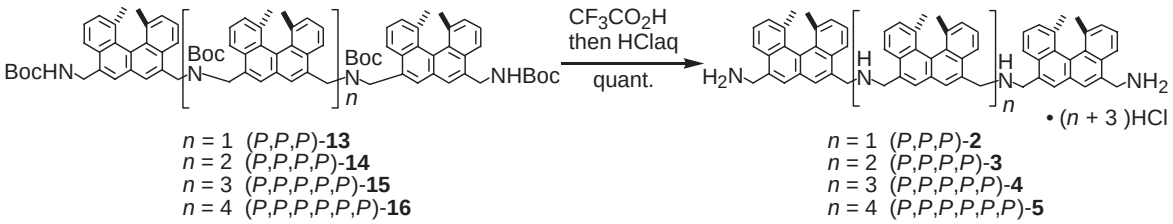
Scheme 5.



Scheme 6.

by Boc protection gave the pentamer (*P*,*P*,*P*,*P*,*P*)-**15** in moderate yield. Considerable amounts of the starting materials were recovered, indicating the inefficiency of imine formation. It was considered that the yield could be improved if the diimine (*P*,*P*,*P*,*P*,*P*)-**24** could be precipitated and removed from the solution to shift equilibrium. In a solution of MeOH/THF (1:1), (*P*,*P*,*P*,*P*,*P*)-**24** gradually precipitated, which was collected by filtration and washed with MeOH. Then, reduction followed by Boc protection gave the desired pentamer (*P*,*P*,*P*,*P*,*P*)-**15** in 80% yield from (*P*,*P*,*P*)-**13**. Presumably, the formation of iminium salts also took place at the secondary amine moiety of (*P*,*P*,*P*)-**11**. However, since such a side reaction is under equilibrium, the precipitation shifted the equilibrium to (*P*,*P*,*P*,*P*,*P*)-**24**, possessing a symmetrical structure and accordingly being less soluble.

Oligomers containing even numbers of helicenes were synthesized from the dimer (*P*,*P*)-**10**, which in turn was obtained from the protected amino alcohol (*P*)-**22** (Scheme 6). The mesylation of (*P*)-**22** followed by reaction with NaN_3 in DMF at 120 °C gave an azide, which was reduced by hydrogenation using 5% Pd–C, thereby producing a monoprotected diamine. Treatment with 9-fluorenylmethyl chloroformate (FmocCl) gave (*P*)-**25** in 73% yield from (*P*)-**22**. The removal of the Fmoc group with piperidine in DMF provided (*P*)-**7** with two distinct amino groups. This synthesis is more effective than the previous synthesis employing the nonselective monoprotection



n = 1 (*P*,*P*,*P*)-**13**
n = 2 (*P*,*P*,*P*,*P*)-**14**
n = 3 (*P*,*P*,*P*,*P*,*P*)-**15**
n = 4 (*P*,*P*,*P*,*P*,*P*,*P*)-**16**

n = 1 (*P*,*P*,*P*)-**2**
n = 2 (*P*,*P*,*P*,*P*)-**3**
n = 3 (*P*,*P*,*P*,*P*,*P*)-**4**
n = 4 (*P*,*P*,*P*,*P*,*P*,*P*)-**5**

Scheme 7.

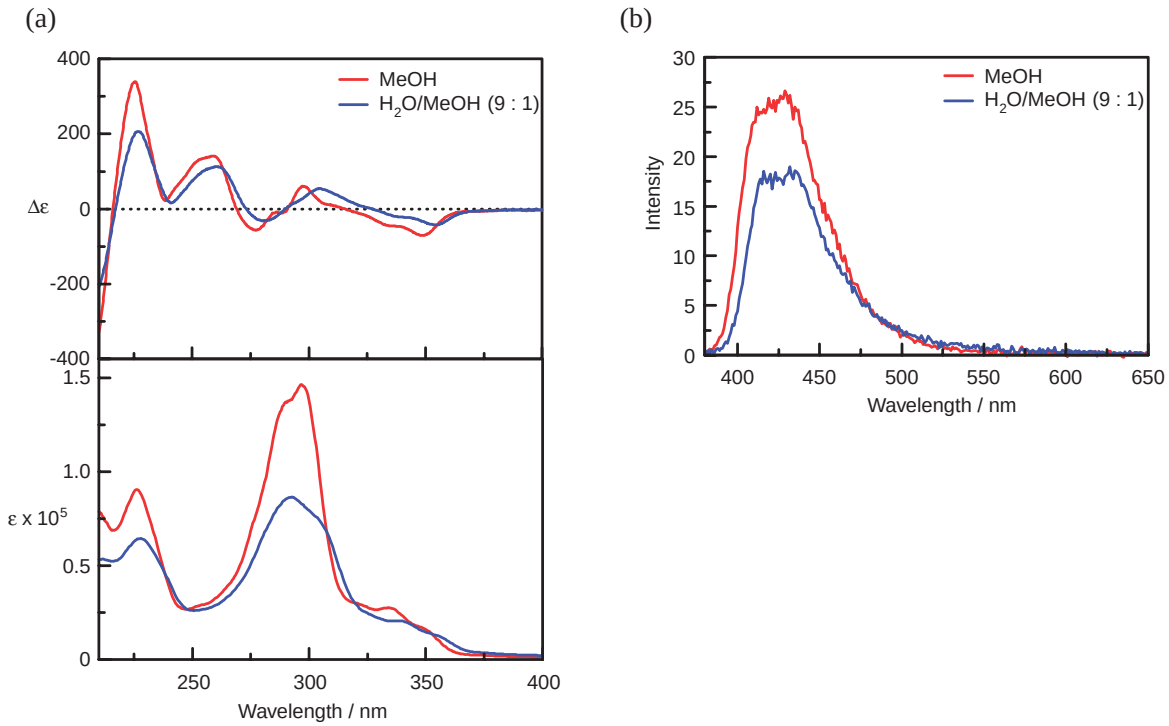


Fig. 1. (a) CD (top), UV (bottom), and (b) fluorescence spectra of (*P*,*P*,*P*)-**2** (1.0×10^{-5} M, 25 °C) in MeOH (red line) and H_2O/MeOH (9:1, blue line) with excitation at 330 nm.

of diamine (*P*)-**9**.[10] The reaction of the aldehyde (*P*)-**17** and 1.15 equivalents of (*P*)-**7** in MeOH at 40 °C for 1 h followed by concentrating the reaction mixture gave a crude imine. The imine was reduced by $NaBH_4$, and successively treated with Boc_2O giving the dimer (*P*,*P*)-**26** in 94% yield from (*P*)-**7**. The removal of the Boc groups followed by reductive coupling with (*P*)-**17** in a mixed solvent of MeOH/THF (2:1) gave a diimine tetramer as a precipitate, which was filtered, reduced, and protected to give the tetramer (*P*,*P*,*P*,*P*)-**14** in 77% yield. The subsequent deprotection and reductive coupling in MeOH/THF (1:2) gave the hexamer (*P*,*P*,*P*,*P*,*P*,*P*)-**16** in 73% yield. Use of appropriate MeOH/THF ratios for the solvent were essential for the effective precipitation of diimines.[13]

The Boc protecting groups of (*P*,*P*,*P*)-**13**, (*P*,*P*,*P*,*P*)-**14**, (*P*,*P*,*P*,*P*,*P*)-**15**, and (*P*,*P*,*P*,*P*,*P*,*P*)-**16** were removed with trifluoroacetic acid. Treatment with a small amount of 2 M hydrochloric acid gave the corresponding hydrochlorides (*P*,*P*,*P*)-**2**, (*P*,*P*,*P*,*P*)-**3**, (*P*,*P*,*P*,*P*,*P*)-**4**, and (*P*,*P*,*P*,*P*,*P*,*P*)-**5** in quantitative yields (Scheme 7).

Formation of Multilayer Structures in Aqueous Solvents. The structures of the oligomers (*P*,*P*,*P*)-**2**, (*P*,*P*,*P*,*P*)-**3**, (*P*,*P*,*P*,*P*,*P*)-**4**, and (*P*,*P*,*P*,*P*,*P*,*P*)-**5** were examined in MeOH and H_2O/MeOH by UV, CD, fluorescence, and NMR spectroscopies with the expectation that such oligomers would form multilayer structures in aqueous solvents. The UV spectrum of (*P*,*P*,*P*)-**2** measured in H_2O/MeOH (9:1) considerably differed from that measured in MeOH (Fig. 1). The absorbances at 230 and 290 nm markedly decreased in the aqueous solvent and the intensities were almost half of that in MeOH. The fluorescence spectra were also solvent-dependent and the intensity decreased when the solvent was changed from MeOH to H_2O/MeOH (9:1). Such a tendency was also observed in CD, where the extent of the Cotton effect was moderately reduced in H_2O/MeOH (9:1) compared with that in MeOH. These results suggest the formation of π-stacked conformation of aromatic moieties in the aqueous solvent.

The trimer (*P*,*P*,*P*)-**2** exhibited considerably different ^{1}H NMR spectra between D_2O/CD_3OD (4:1) and CD_3OD (Fig. 2). The aromatic protons of (*P*,*P*,*P*)-**2**, particularly the three singlet signals 6-H^I, 7-H^I, and 6-H^{II}, shifted upfield in D_2O/CD_3OD (4:1) compared with those in CD_3OD. The ROESY cross-peaks observed between δ 7.00 and 7.25 in D_2O/CD_3OD were assigned to 6-H^I/7-H^I, and the peak at δ 5.84 was assigned to 6-H^{II}. The proton numberings were defined in this study as follows: The protons H^I and H^{II} indicate those of the terminal helicene I and the next helicene II, respectively. For

example, 6-H^{II} indicates the 6-proton of helicene II. It is not always possible to assign all of the protons; for example, 6-H^{I} and 7-H^{I}, and in other exchangeable cases, the assignment is shown as 6-H^{I}/7-H^{I}. A larger upfield shift of 6-H^{II} than those of 6-H^{I} and 7-H^{I} is likely due to the shielding by two helicene rings in the triple-layer structure. The ^{1}H NMR spectra in D_2O/CD_3OD (4:1) and CD_3OD were concentration-independent between 0.1 mM and 1 mM, indicating the intramolecular nature of this phenomenon.

To investigate the layer structure of (*P*,*P*,*P*)-**2** in detail, H–H COSY and ROESY studies were performed in D_2O/CD_3OD (4:1). The proton assignments of (*P*,*P*,*P*)-**2** using H–H COSY and ROESY correlations are summarized in Fig. 3. The ROESY cross-peaks were observed between 6-H^{I}/7-H^{I} and 1-CH_3^{II}, and 6-H^{II} and 1-CH_3^{I}/12-CH_3^{I} (Fig. 3b). Such observations can be explained by the stacked structure of helicenes I and II at BC-rings with the 1,12-dimethyl groups in opposite directions. The structure was named *anti*-conformation in this study and *syn*-conformation was defined as the stacked structure in the same direction of the 1,12-dimethyl groups (Fig. 4). Therefore, it was concluded that (*P*,*P*,*P*)-**2** has a triple-layer structure stacked at the BC-ring of the helicene moiety with the *anti*-conformation in the aqueous solvent. The proposed structure of (*P*,*P*,*P*)-**2** is shown in Fig. 5.

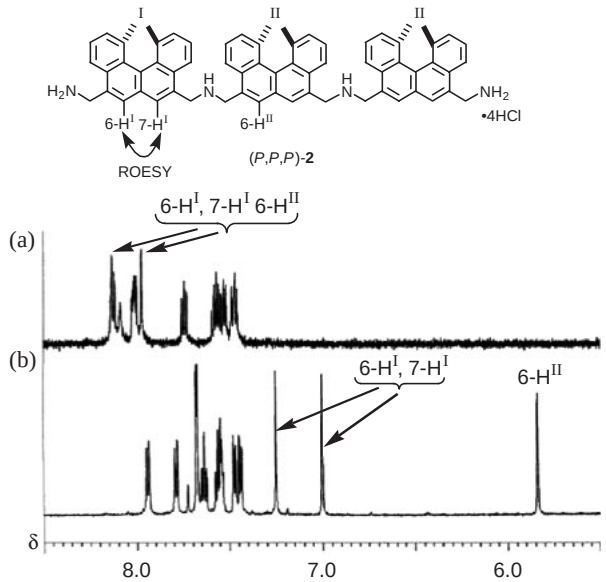


Fig. 2. ^{1}H NMR (600 MHz) spectra of (*P*,*P*,*P*)-**2** in (a) CD_3OD and (b) D_2O/CD_3OD (4:1) (25 °C, 1.0×10^{-3} M).

Next, the tetramer (*P*,*P*,*P*,*P*)-**3** was studied in MeOH and H_2O/MeOH, where similar spectral changes were observed (Fig. 6). The intensities of the UV absorption, Cotton effect, and fluorescence of (*P*,*P*,*P*,*P*)-**3** in the aqueous solvent decreased compared with those in MeOH, which indicates that (*P*,*P*,*P*,*P*)-**3** also folded by stacking at aromatic moieties in the aqueous solvent.

The aromatic protons of (*P*,*P*,*P*,*P*)-**3**, particularly the four singlet signals 6-H^{I}, 7-H^{I}, 6-H^{II}, and 7-H^{II}, shifted upfield in D_2O/CD_3OD (4:1) compared with those in CD_3OD (Fig. 7).

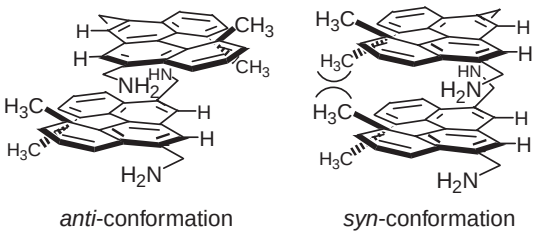


Fig. 4. Schematic representation of *anti*- and *syn*-conformations.

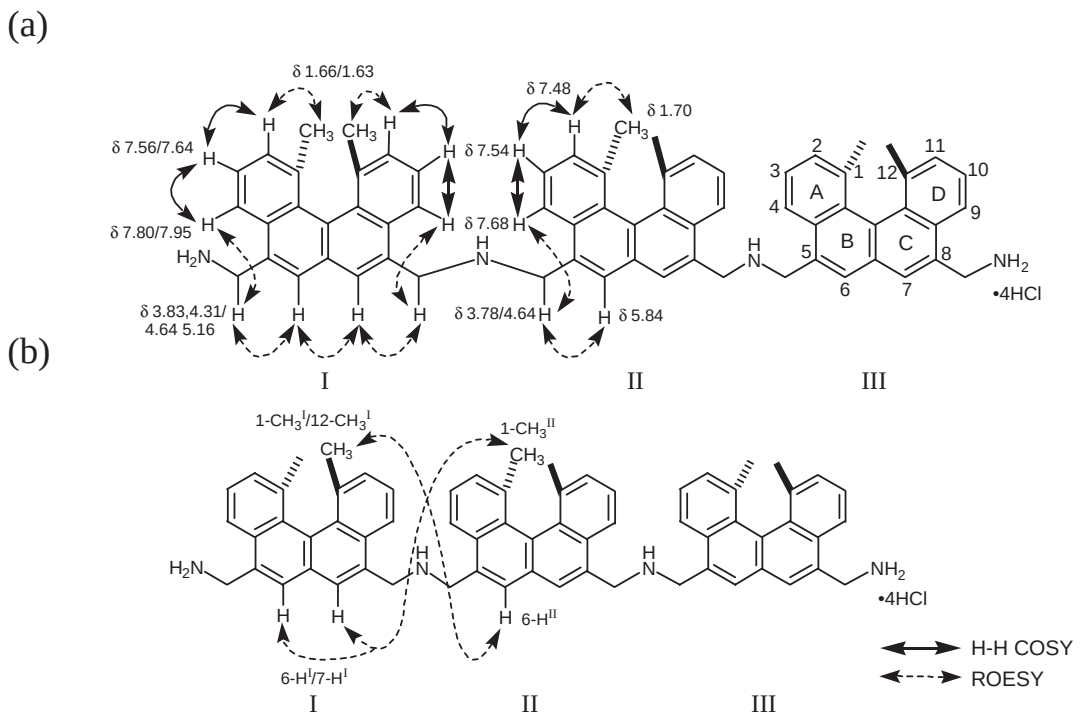


Fig. 3. (a) H–H COSY and ROESY correlations; (b) long range ROESY correlations of (*P*,*P*,*P*)-**2** in CD_3OD/D_2O (1:4).

ROESY cross-peaks were observed between the protons δ 7.43 and 7.24 in D_2O/CD_3OD, which were assigned to 6-H^I/7-H^I. Then, the protons δ 6.07 and 6.06 were assigned to 6-H^{II}/7-H^{II}, similarly to the trimer (*P*,*P*,*P*)-**2**, in which 6-H/7-H of an internal helicene exhibited a larger upfield shift. The proton assignments of (*P*,*P*,*P*,*P*)-**3** using H–H COSY and ROESY correlations are shown in Fig. 8. Two ROESY correlations between 6-H^{II}/7-H^{II} δ 6.07/6.06 and 1-CH_3^I/12-CH_3^I δ 1.61/1.58, and between 6-H^I/7-H^I δ 7.43/7.24 and 1-CH_3^{II}/12-CH_3^{II} δ 1.62/1.67 could be explained as those between neighboring helicenes I and II. An unusual ROESY correlation between 6-H^{II}/7-H^{II} δ 6.07/6.06 and 1-CH_3^{II}/12-CH_3^{II} δ 1.62/1.67 in the same helicene ring should be that between 6-H^{II}/7-H^{II} and 1-CH_3^{III}/12-CH_3^{III} (Fig. 8b). The tetramer (*P*,*P*,*P*-*P*)-**3** was found to have a four-layer structure with all *anti*-conformations.

The pentamer (*P*,*P*,*P*,*P*,*P*)-**4** also exhibited solvent dependences as shown by UV, CD, and fluorescence spectra, and its intensity was decreased by changing the solvent from MeOH to H_2O/MeOH (9:1), as was observed in the trimer (*P*,*P*,*P*)-**2** and tetramer (*P*,*P*,*P*,*P*)-**3** (Fig. 9).

The five singlet signals of (*P*,*P*,*P*,*P*,*P*)-**4**, namely, 6-H^I, 7-H^I, 6-H^{II}, 7-H^{II}, and 6-H^{III}, moved upfield in D_2O/CD_3OD (4:1) compared with those in CD_3OD; in particular, the three singlet signals 6-H^{II}, 7-H^{II}, and 6-H^{III} of internal helicenes exhibited larger upfield shifts than 6-H^I and 7-H^I (Fig. 10).

Since ROESY cross-peaks were observed between protons δ 7.25 and 7.10, they were assigned to 6-H^I/7-H^I. The protons

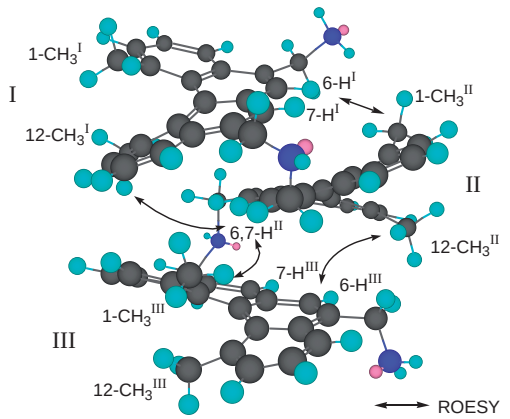
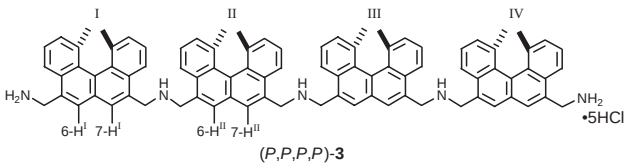


Fig. 5. Proposed structure of (*P*,*P*,*P*)-**2** in aqueous solvent.



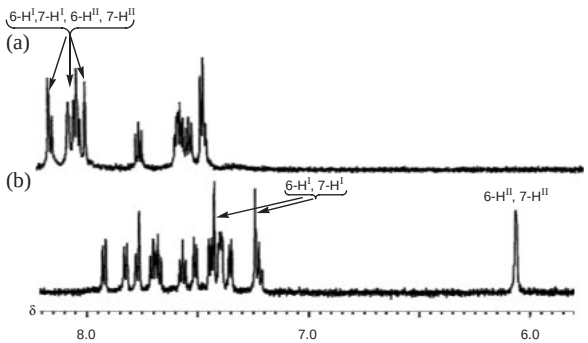
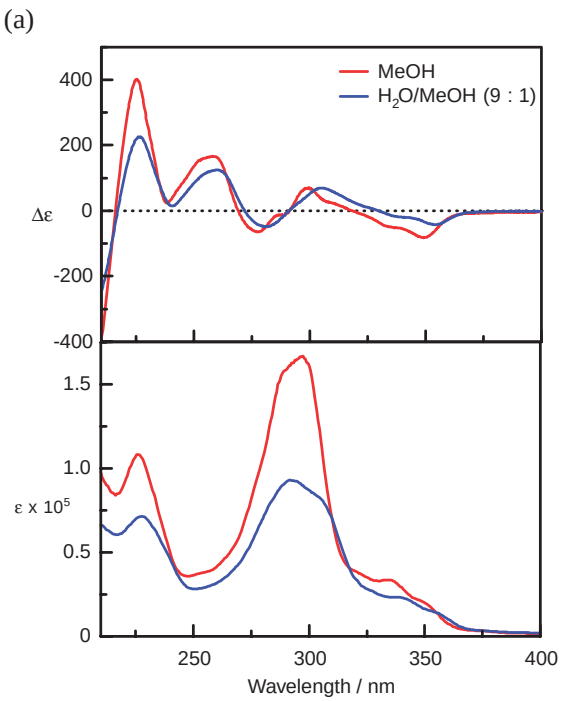


Fig. 7. ^{1}H NMR (600 MHz) spectra of (*P*,*P*,*P*,*P*)-**3** in (a) CD_3OD and (b) D_2O/CD_3OD (4:1) (25 °C, 1.0×10^{-3} M).



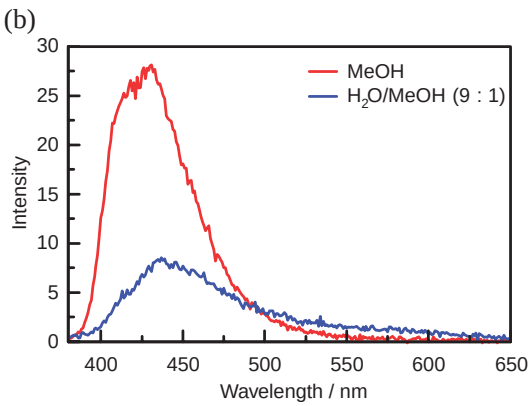


Fig. 6. (a) CD (top), UV (bottom), and (b) fluorescence spectra of (*P*,*P*,*P*,*P*)-**3** (1.0×10^{-5} M, 25 °C) in MeOH (red line) and H_2O/MeOH (9:1, blue line) with excitation at 330 nm.

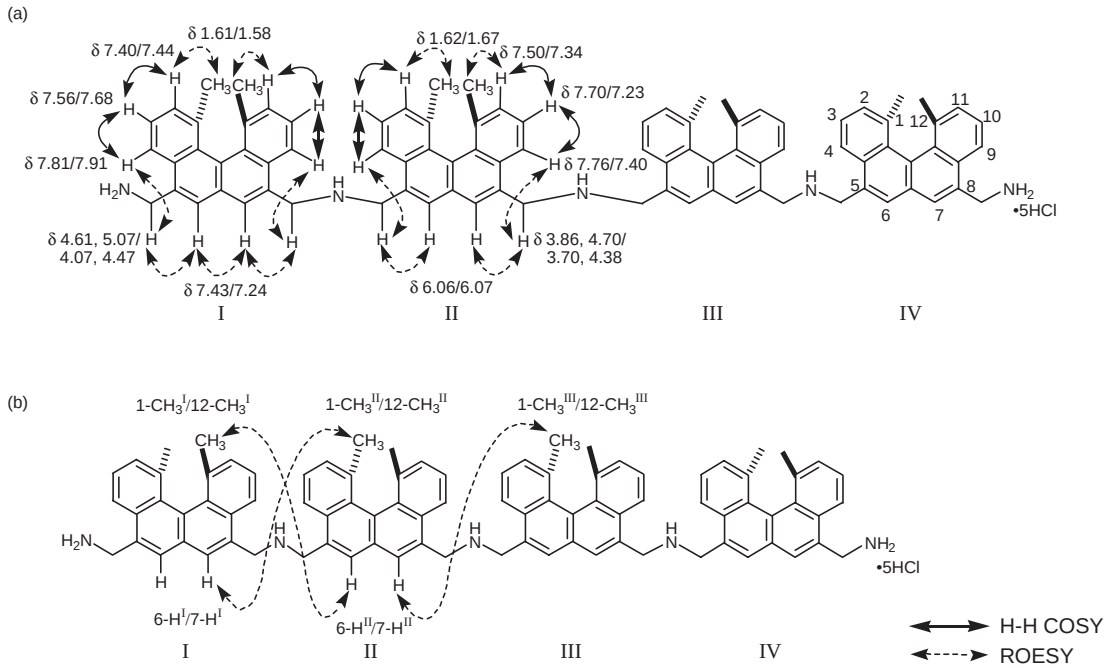


Fig. 8. (a) H–H COSY and ROESY correlations; (b) long range ROESY correlations of (*P*,*P*,*P*,*P*)-**3** in D_2O/CD_3OD (4:1).

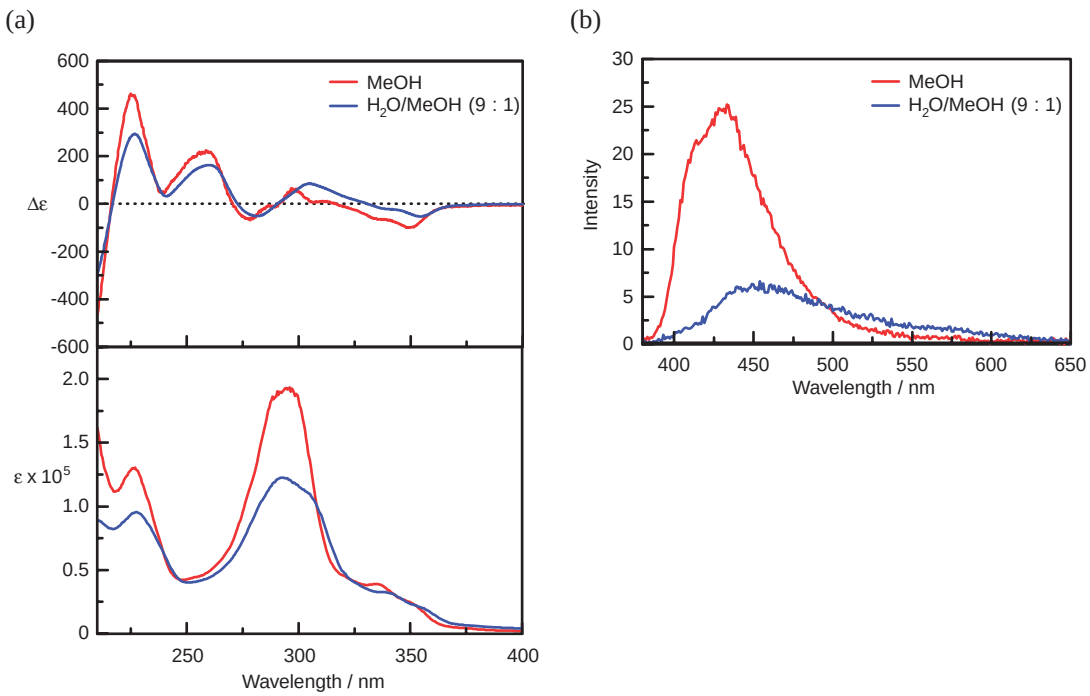


Fig. 9. (a) CD (top), UV (bottom), and (b) fluorescence spectra of (*P*,*P*,*P*,*P*,*P*)-**4** (1.0×10^{-5} M, 25 °C) in MeOH (red line) and H_2O/MeOH (9:1, blue line) with excitation at 330 nm.

$6\text{-H}^{II}/7\text{-H}^{II}$ were assigned to δ 6.15/6.13, similarly to those in the trimer (*P*,*P*,*P*)-**2** and the tetramer (*P*,*P*,*P*,*P*)-**3**; therefore, 6-H^{III} was assigned to δ 5.92. Using H–H COSY and ROESY, all of the aromatic protons correlated (Fig. 11). These assignments were again consistent with the largest upfield shift of 6-H^{III} and the larger upfield shift of $6\text{-H}^{II}/7\text{-H}^{II}$, which occurred between two helicenes. ROESY cross-peaks observed between $6\text{-H}^{I}/7\text{-H}^{I}$ and $1\text{-CH}_3{}^{II}/12\text{-CH}_3{}^{II}$, $6\text{-H}^{II}/7\text{-H}^{II}$ and $1\text{-CH}_3{}^{I}/12\text{-CH}_3{}^{I}$, $6\text{-H}^{II}/7\text{-H}^{II}$ and $1\text{-CH}_3{}^{III}$, and 6-H^{III} and $1\text{-CH}_3{}^{II}/12\text{-CH}_3{}^{II}$ indicated the formation of all *anti*-conformations of (*P*,*P*,*P*,*P*,*P*)-**4**. The pentamer (*P*,*P*,*P*,*P*,*P*)-**4** was therefore concluded to possess a five-layer structure stacked at the BC-ring of the helicene moiety with all *anti*-conformations (Fig. 12).

The UV, CD, and fluorescence spectra of the hexamer (*P*,*P*,*P*,*P*,*P*,*P*)-**5** exhibited solvent dependences between MeOH and H_2O/MeOH (9:1), and their intensities decreased in the aqueous solvent (Fig. 13). The aromatic ^{1}H NMR peaks of (*P*,*P*,*P*,-

P,*P*,*P*)-**5** shifted upfield in D_2O/CD_3OD (2:1) compared with those in CD_3OD (Fig. 14). Precise assignments, however, could not be made because of the severe overlap of the peaks. Although the spectral behaviors of (*P*,*P*,*P*,*P*,*P*,*P*)-**5** were slightly different from the lower homologues, (*P*,*P*,*P*,*P*,*P*,*P*)-**5** was speculated to possess a six-layer structure in the aqueous solvent.

It was noticed that the UV and CD spectra of (*P*,*P*,*P*)-**2**, (*P*,*P*,*P*,*P*)-**3**, and (*P*,*P*,*P*,*P*,*P*)-**4** in both MeOH and H_2O/MeOH (9:1) at 10 μM showed additivity in ε and $\Delta\varepsilon$. The CD spectra of (*P*,*P*,*P*,*P*,*P*,*P*)-**5**, however, was slightly weaken at 227 and 260 nm compared to those of (*P*,*P*,*P*,*P*,*P*)-**4**, and did not fit with the rule. It may be interesting to compare the structure with the higher homologues.

Effect of Helicene Chirality. The stereochemistry of a helicene moiety plays an important role in the stability of the folded structures of the dimer (*M*,*M*)-**1** and (*P*,*M*)-**1**.[10] It was therefore considered interesting to compare (*P*,*P*,*P*)-**2** with diastereomeric (*P*,*M*,*P*)-**2**. (*P*,*M*,*P*)-**2** was synthesized from the aldehyde (*P*)-**17** and the diamine (*M*)-**9** in 64% yield in 4 steps (Scheme 8).

Although the intensities of the UV, CD, and fluorescence spectra of the trimer (*P*,*M*,*P*)-**2** were weaker than those of (*P*,*P*,*P*)-**2**, the spectra of the trimer (*P*,*M*,*P*)-**2** in MeOH and H_2O/MeOH (9:1) were similar to those of (*P*,*P*,*P*)-**2**. It is likely that the trimer (*P*,*M*,*P*)-**2** also formed a triple-layer structure in the aqueous solvent (Fig. 15).

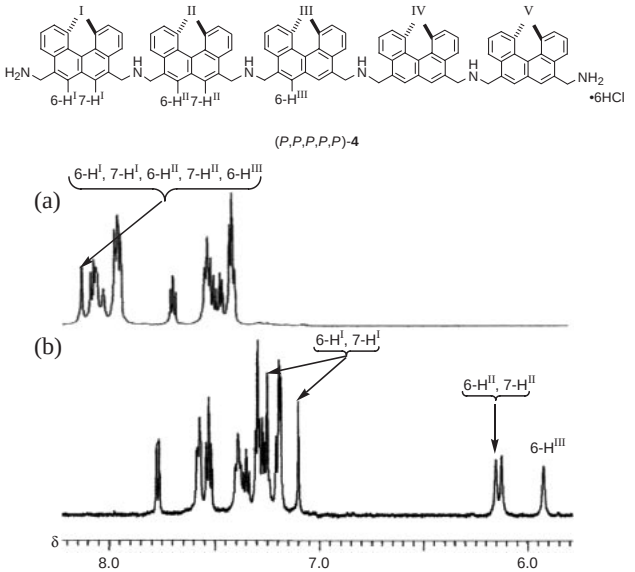


Fig. 10. ^{1}H NMR spectra (600 MHz) of (*P*,*P*,*P*,*P*,*P*)-**4** in (a) CD_3OD and (b) D_2O/CD_3OD (4:1) (25 °C, 1.0×10^{-3} M).

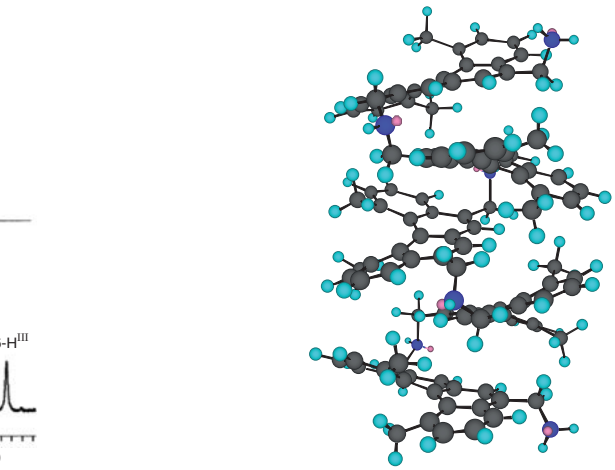


Fig. 12. Proposed layer structure of (*P*,*P*,*P*,*P*,*P*)-**4** in aqueous solvent.

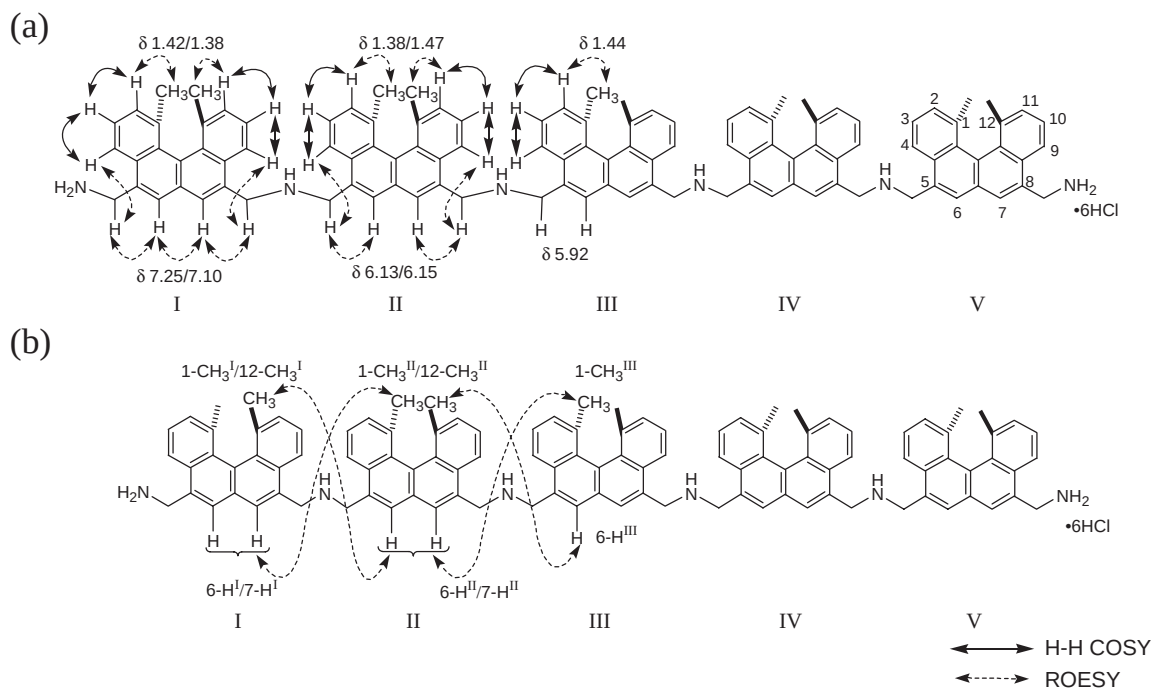


Fig. 11. (a) H–H COSY and ROESY correlations; (b) long range ROESY correlations of (*P*,*P*,*P*,*P*,*P*)-**4** in D_2O/CD_3OD (4:1).

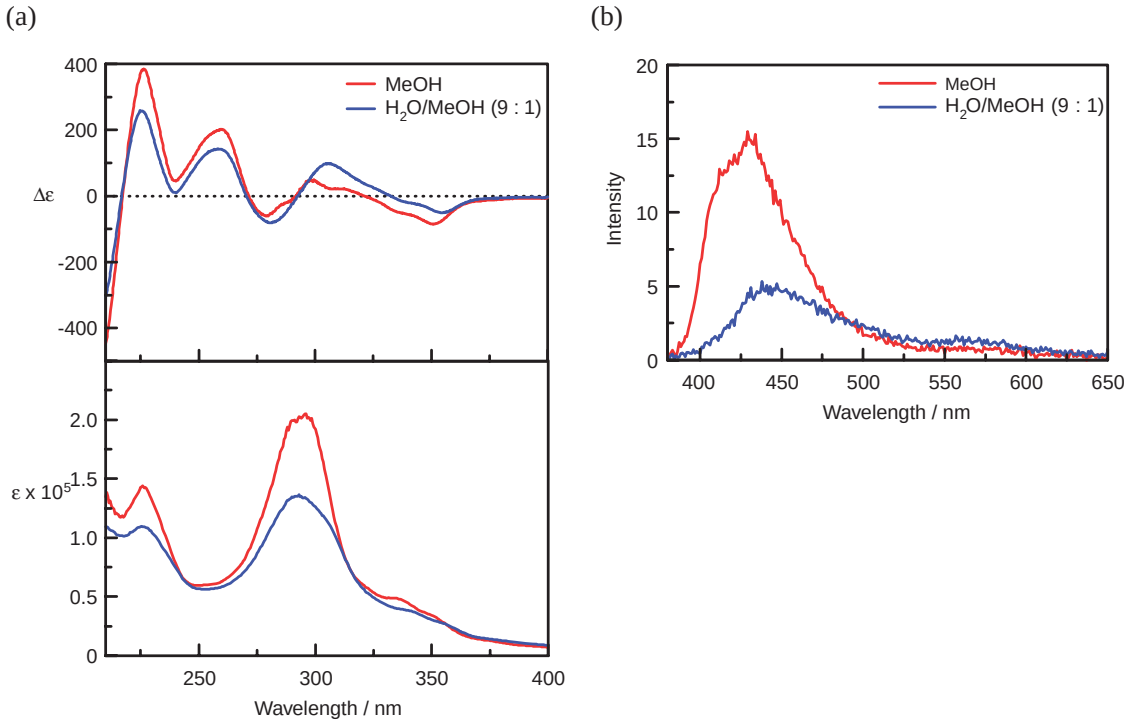


Fig. 13. (a) CD (top), UV (bottom), and (b) fluorescence spectra of (*P*,*P*,*P*,*P*,*P*)-**5** (1.0×10^{-5} M, 25 °C) in MeOH (red line) and H_2O/MeOH (9:1, blue line) with excitation at 330 nm.

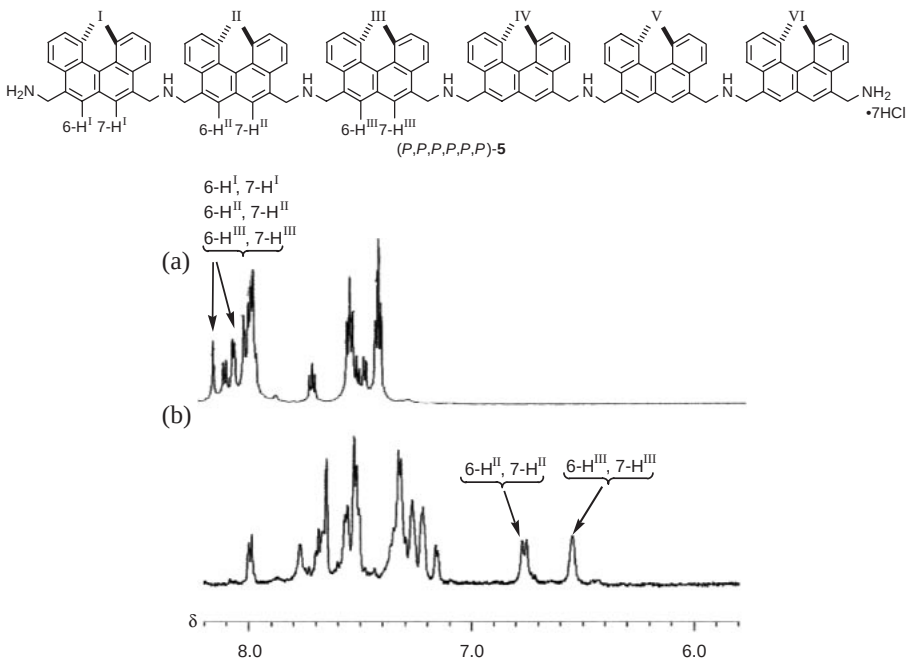
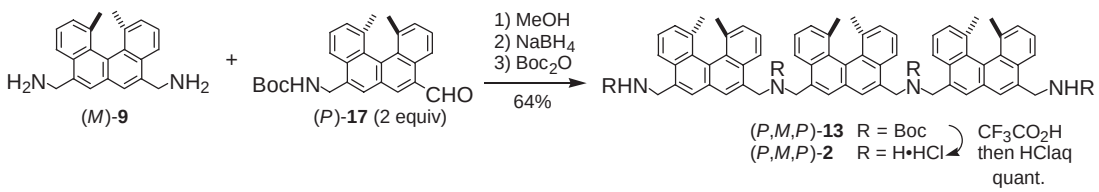


Fig. 14. ^{1}H NMR (600 MHz) spectra of (*P*,*P*,*P*,*P*,*P*)-**5** in (a) CD_3OD and (b) D_2O/CD_3OD (2:1) (5.0×10^{-4} M, 25 °C).



Scheme 8.

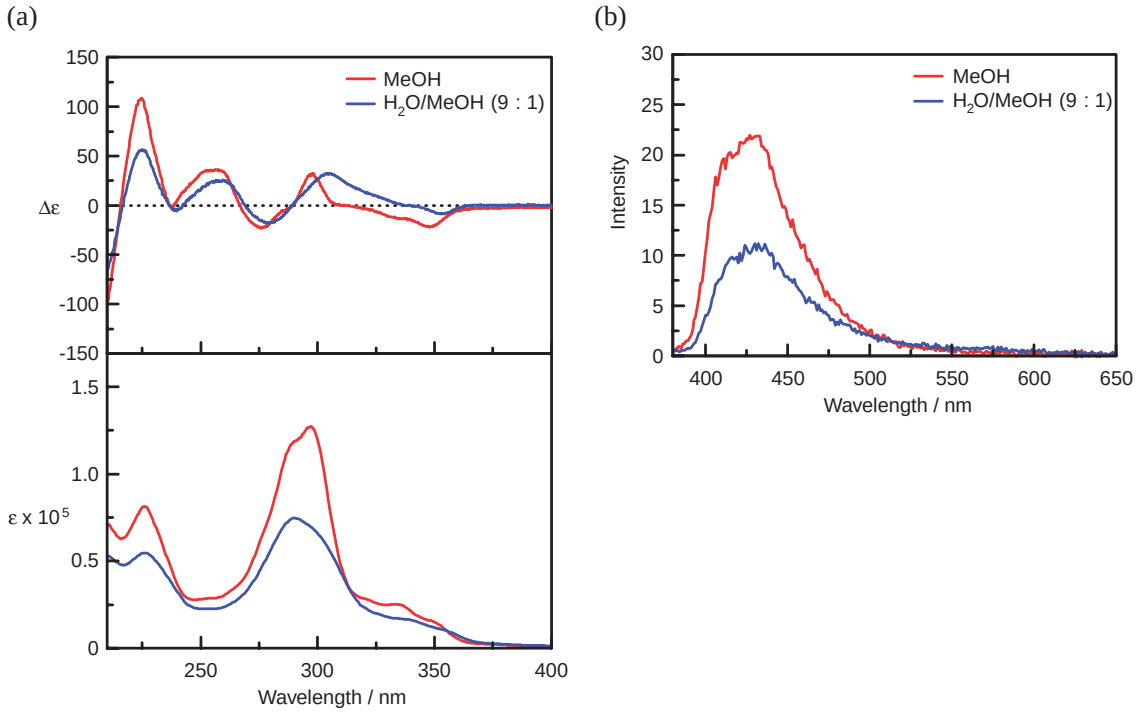


Fig. 15. (a) CD (top), UV (bottom), and (b) fluorescence spectra of (*P*,*M*,*P*)-**2** (1.0×10^{-5} M, 25 °C) in MeOH (red line) and H_2O/MeOH (9:1, blue line) with excitation at 330 nm.

The ^{1}H NMR spectra of the aromatic protons of (*P*,*M*,*P*)-**2** moved upfield in D_2O/CD_3OD (4:1) compared with those in CD_3OD (Fig. 16), and the singlet signal 6-H^{II} moved 1.5 ppm upfield. The ROESY cross-peaks observed between δ 7.55 and 7.80 were assigned to 6-H^I/7-H^I, and the peak at δ 6.64 was assigned to 6-H^{II}. The methyl groups of (*P*,*M*,*P*)-**2** shifted 0.5–1.0 ppm upfield, which was not observed in (*P*,*P*,*P*)-**2**. The proton assignments of (*P*,*M*,*P*)-**2** using H–H COSY and ROESY correlations are shown in Fig. 17; the methyl groups were assigned to 1-CH_3^I/12-CH_3^I δ 1.40/0.98 and 1-CH_3^{II} δ 0.92. Since both of the protons, 1-CH_3^I and 12-CH_3^I, exhibited a ROESY correlation with 6-H^{II}, helicenes I and II were considered to possess an *anti*-conformation similar to that of (*P*,*P*,*P*)-**2** (Fig. 17b). Notably, a ROESY correlation was observed between 6-H^I/7-H^I and 1-CH_3^I/12-CH_3^I, which should be the correlation between 6-H^I/7-H^I and 1-CH_3^{III}/12-CH_3^{III}.

The differences in the spectra of (*P*,*M*,*P*)-**2** from (*P*,*P*,*P*)-**2** that are notable: 1) The methyl groups of (*P*,*M*,*P*)-**2** shifted upfield compared with those of (*P*,*P*,*P*)-**2**. 2) A ROESY correlation was observed between 6-H^I/7-H^I and 1-CH_3^{III}/12-CH_3^{III} in (*P*,*M*,*P*)-**2**. These results may reasonably be explained as follows: Helicenes I and II of (*P*,*M*,*P*)-**2** formed the *anti*-conformation, while helicenes II and III formed the *syn*-conformation. The proposed structure of (*P*,*M*,*P*)-**2** is shown in Fig. 18. It is interesting that the chirality at the helicene moiety considerably affects the multilayer structures.

Conclusion

A series of optically active polyamine oligomers containing three to six (*P*)-helicenes were synthesized by reductive amination, where the precipitation of imine intermediates was essential in obtaining oligomers in high yields. UV, CD, fluores-

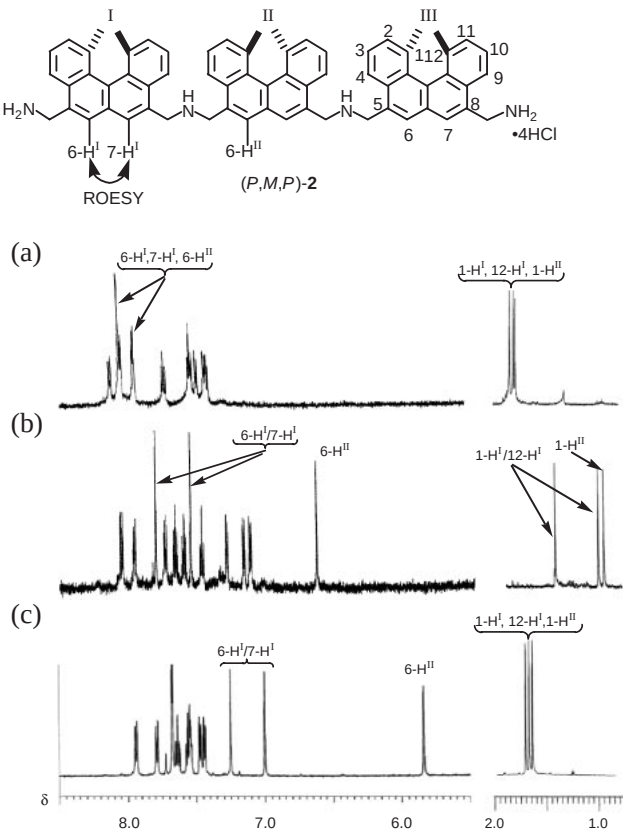


Fig. 16. ^{1}H NMR (600 MHz) spectra of (*P*,*M*,*P*)-**2** in (a) CD_3OD and (b) D_2O/CD_3OD (4:1). (c) ^{1}H NMR (600 MHz) spectra of (*P*,*P*,*P*)-**2** in D_2O/CD_3OD (4:1) (25 °C, 1.0×10^{-3} M).

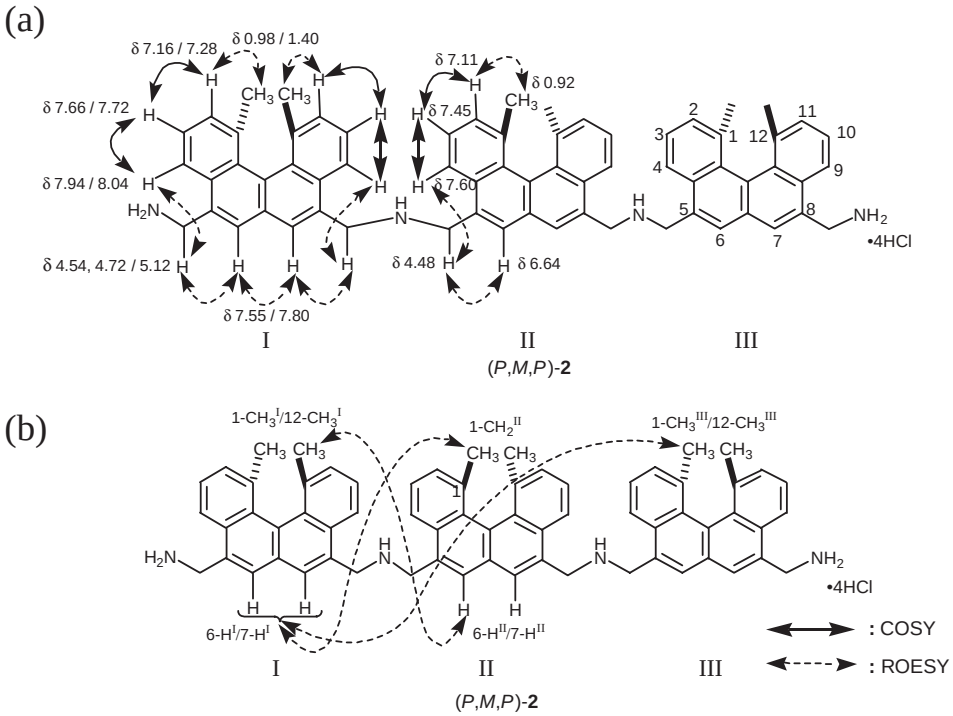


Fig. 17. (a) H–H COSY and ROESY correlations; (b) long range ROESY correlations of (*P*,*M*,*P*)-**2** in D_2O/CD_3OD (4:1).

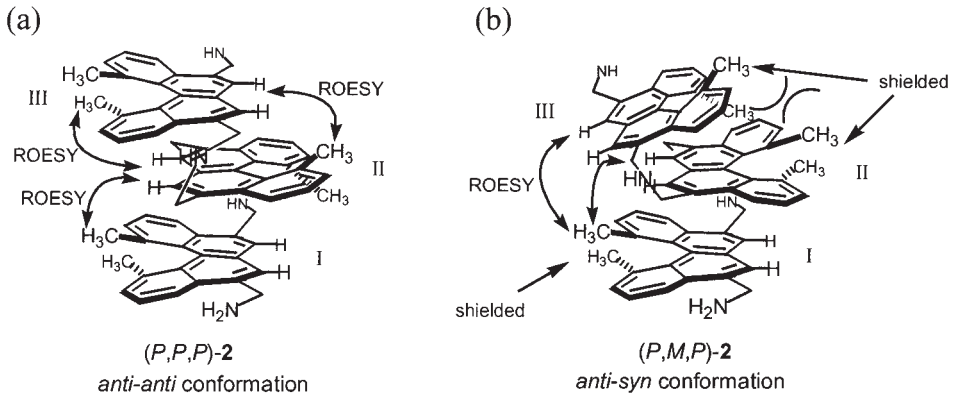


Fig. 18. Schematic representation of layer structures for (a) (*P*,*P*,*P*)-**2** and (b) (*P*,*M*,*P*)-**2**.

cence, and NMR spectroscopic studies revealed that the oligomers form multilayer structures in aqueous solvents, whereas they form random coil structures in methanol. It was shown that dyads containing the same (*P*)-configuration possess the *anti*-conformation in their layer structure. In contrast, a dyad of (*P*)- and (*M*)-helicenes was suggested to form the *syn*-conformation. It was also shown that a regulated aromatic multilayer structure can be constructed by solvophobic interactions and π–π interactions of the helicene moiety, in which chirality plays an important role.

Experimental

(*P*)-5-Carbamoyl-8-methoxycarbonyl-1,12-dimethylbenzo[*c*]-phenanthrene, (*P*)-19. Under an argon atmosphere, a mixture of (*P*)-**18**[12] (956 mg, 2.67 mmol) and thionyl chloride (10 mL) was heated under reflux for 2 h. Then, excess thionyl chloride was removed under reduced pressure, and the residue was azeotropically dried by evaporation with toluene (10 mL) twice. The crude acid chloride was dissolved in toluene (20 mL) and was added to a mixture of toluene (10 mL) and liquid NH_3 at $-78\,^{\circ}C$. The reaction mixture was warmed to room temperature and stirred for 2 h. Then, the reaction was quenched by adding water. Organic materials were extracted with ethyl acetate three times, and the combined organic layer was washed with water and brine, and then dried over anhydrous potassium carbonate. The solvent was evaporated under reduced pressure. Purification by flash silica-gel column chromatography (ethyl acetate/hexane = 2:1) gave (*P*)-**19** (878 mg, 2.46 mmol, 92%). mp 220–222 °C. (toluene). $[\alpha]^{30}_{D}$ −245 (*c* 1.0, $CHCl_3$). Anal. Calcd for $C_{23}H_{19}NO_3$: C, 77.29; H, 5.36; N, 3.92%. Found: C, 77.29; H, 5.45; N, 3.95%. LRMS (EI) *m*/*z* 357 (M^+, 100%), 326 ($M^+ - OMe$, 10%). HRMS (EI) Calcd for $C_{23}H_{19}NO_3$: 357.1365. Found: 357.1355. IR (KBr) 3385, 3287, 3179, 1708, 1672 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ 1.90 (6H, s), 4.07 (3H, s), 6.20 (2H, br), 7.43–7.46 (2H, m), 7.64–7.69 (2H, m), 8.04 (1H, s), 8.40 (1H, d, J = 8.2 Hz), 8.46 (1H, s), 8.82 (1H, d, J =

8.4 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 23.5, 23.7, 52.6, 122.9, 123.1, 124.7, 127.0, 127.6, 127.7, 129.0, 129.4, 129.5, 129.8, 130.0, 130.2, 131.2, 131.3, 132.9, 136.7, 137.1, 167.7, 171.1.

(*P*)-8-Methoxycarbonyl-1,12-dimethylbenzo[*c*]phenanthrene-5-carbonitrile, (*P*)-20. Under an argon atmosphere, a mixture of (*P*)-**19** (700 mg, 1.96 mmol) and diphosphorus pentaoxide (1.68 g, 11.8 mmol) in toluene (35 mL) was heated under reflux for 2 h. The reaction was quenched by adding ice water, and the mixture was stirred for 1 day at room temperature. Then, the organic layer was separated, and the aqueous layer was extracted with toluene three times. The combined organic layer was washed with water and brine, and then dried over anhydrous magnesium sulfate. The solvent was evaporated under reduced pressure. Purification by flash silica-gel column chromatography (toluene) gave (*P*)-**20** (632 mg, 1.86 mmol, 95%). mp 206–208 °C (toluene). $[\alpha]^{22}_{D}$ −188 (*c* 1.0, $CHCl_3$). Anal. Calcd for $C_{23}H_{17}NO_2$: C, 81.40; H, 5.05; N, 4.13%. Found: C, 81.57; H, 5.22; N, 4.15%. LRMS (EI) *m*/*z* 339 (M^+, 100%), 308 ($M^+ - OMe$, 10%). HRMS (EI) Calcd for $C_{23}H_{17}NO_2$: 339.1259. Found: 339.1248. IR (KBr) 2228, 1713 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.88 (3H, s), 1.92 (3H, s), 4.09 (3H, s), 7.47 (1H, d, J = 7.2 Hz), 7.54 (1H, d, J = 6.8 Hz), 7.71 (1H, t, J = 7.2 Hz), 7.77 (1H, dd, J = 6.8, 8.4 Hz), 8.30 (1H, s), 8.31 (1H, d, J = 7.2 Hz), 8.46 (1H, s), 8.83 (1H, d, J = 8.4 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 23.5, 23.9, 53.0, 110.1, 118.1, 123.1, 123.5, 127.9, 128.7, 128.8, 129.1, 129.7, 130.6 (2 peaks), 131.0 (2 peaks), 131.2, 131.3, 131.5, 133.2, 137.2, 137.9, 167.5.

(*P*)-5-*t*-Butoxycarbonylaminomethyl-8-methoxycarbonyl-1,12-dimethylbenzo[*c*]phenanthrene, (*P*)-21. Under a hydrogen atmosphere, a mixture of (*P*)-**20** (455 mg, 1.34 mmol), 5% palladium on carbon (455 mg), ethyl acetate (50 mL), methanol (50 mL), and 2 M hydrochloric acid (5 mL) was vigorously stirred for 24 h at 40 °C. Insoluble materials were removed by filtration, and the solution was concentrated under reduced pressure. To the resulting amorphous solid was added dichloromethane (15 mL), 10% aqueous sodium hydroxide (15 mL), and di(*t*-butyl) dicarbonate (1.5 g, 6.70 mmol) at 0 °C, and the mixture was stirred for 10 min at that temperature. Organic materials were extracted with dichloromethane three times. The combined organic layer was washed with water and brine, and then dried over anhydrous potassium carbonate. The solvent was evaporated under reduced pressure. Purification by flash silica-gel column chromatography (hexane/ethyl acetate = 4:1) gave (*P*)-**21** (497 mg, 1.12 mmol, 84%). mp 165–168 °C (toluene). $[\alpha]^{28}_{D}$ −73.6 (*c* 1.0, $CHCl_3$). Anal. Calcd for $C_{28}H_{29}NO_4$: C, 75.82; H, 6.59; N, 3.16%. Found: C, 75.54; H, 6.56; N, 3.16%. LRMS (EI) *m*/*z* 443 (M^+, 50%), 412 ($M^+ - OMe$, 5%), 386 ($M^+ - t$-Bu, 80%). HRMS (EI) Calcd for $C_{28}H_{29}NO_4$: 443.2097. Found: 443.2108. IR (KBr) 3600–3000 (br), 1718, 1697, 1247 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.50 (9H, s), 1.87 (3H, s), 1.90 (3H, s), 4.04 (3H, s), 4.86 (1H, dd, J = 9.6, 5.6 Hz), 4.94 (1H, dd, J = 9.6, 5.6 Hz), 5.05 (1H, br), 7.40 (1H, d, J = 8.0 Hz), 7.42 (1H, d, J = 8.4 Hz), 7.61 (1H, t, J = 8.0 Hz), 7.64 (1H, t, J = 8.4 Hz), 7.71 (1H, s), 8.05 (1H, d, J = 8.0 Hz), 8.42 (1H, s), 8.82 (1H, d, J = 8.4 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 23.7, 23.8, 28.8, 43.0, 52.6, 79.9, 120.8, 123.1, 124.8, 126.5, 127.0, 127.2, 128.4, 128.7, 129.8 (2 peaks), 130.2, 131.5, 131.6, 134.0, 136.3, 137.5, 155.8, 168.0.

(*P*)-5-*t*-Butoxycarbonylaminomethyl-8-hydroxymethyl-1,12-dimethylbenzo[*c*]phenanthrene, (*P*)-22. Under an argon atmosphere, to a solution of (*P*)-**21** (517 mg, 1.17 mmol) in dichloromethane (10 mL) was added 1.0 M diisobutylaluminium hydride in hexane (3.51 mL, 3.51 mmol) at −78 °C, and the mixture was stirred for 30 min at that temperature. The reaction was quenched by adding aqueous potassium sodium (+)-tartrate. The organic materials were extracted with dichloromethane three times. The combined organic layer was washed with water and brine, and then dried over anhydrous potassium carbonate. The solvent was evaporated under reduced pressure. Purification by flash silica-gel column chromatography (hexane/ethyl acetate = 2:1) gave (*P*)-**22** (477 mg, 1.15 mmol, 98%). Amorphous solid. $[\alpha]^{27}_{D}$ +123 (*c* 1.0, $CHCl_3$). LRMS (EI) *m*/*z* 415 (M^+, 60%), 358 ($M^+ - t$-Bu, 80%). HRMS (EI) Calcd for $C_{27}H_{29}NO_3$: 415.2147. Found: 415.2158. IR (KBr) 3710–3100 (br), 1690 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.48 (9H, s), 1.89 (3H, s), 1.90 (3H, s), 2.44 (1H, br), 4.79 (1H, dd, J = 9.2, 5.6 Hz), 4.93 (1H, dd, J = 9.2, 5.6 Hz), 5.00 (1H, br), 5.20 (1H, d, J = 12.8 Hz), 5.28 (1H, d, J = 12.8 Hz), 7.37 (2H, d, J = 7.6 Hz), 7.53–7.58 (2H, m), 7.62 (1H, s), 7.74 (1H, s), 8.00 (1H, d, J = 7.6 Hz), 8.06 (1H, d, J = 8.0 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 23.5, 28.5, 42.9, 63.5, 77.2, 79.7, 120.5, 120.6, 124.0, 125.0, 125.3, 125.8, 125.9, 128.1 (2 peaks), 130.1, 130.3, 131.2, 131.5, 131.6, 132.9, 135.4, 136.6, 136.7, 155.6.

(*P*)-8-*t*-Butoxycarbonylaminomethyl-1,12-dimethylbenzo[*c*]-phenanthrene-5-carbaldehyde, (*P*)-17. Under an argon atmosphere, to a solution of oxalyl chloride (1.0 mL, 11.5 mmol) in dichloromethane (5.0 mL) was added dimethyl sulfoxide (0.82 mL, 11.5 mmol) in dichloromethane (5.0 mL) at −78 °C. After being stirred for 30 min at that temperature, (*P*)-**22** (477 mg, 1.15 mmol) in dichloromethane (12 mL) was added at −78 °C, and the mixture was stirred for 30 min at that temperature. Then, triethylamine (4.8 mL, 34.5 mmol) was added at −78 °C, and stirring was continued for 2 h at that temperature. The reaction was quenched by adding saturated aqueous ammonium chloride. Organic materials were extracted with ethyl acetate three times. The combined organic layer was washed with water and brine, and then dried over anhydrous potassium carbonate. The solvent was evaporated under reduced pressure. Purification by flash silica-gel column chromatography (hexane/ethyl acetate = 2:1) gave (*P*)-**17** (456 mg, 1.10 mmol, 96%). mp 88–91 °C (chloroform–hexane). $[\alpha]^{28}_{D}$ −103 (*c* 1.0, $CHCl_3$). Anal. Calcd for $C_{27}H_{27}NO_3$: C, 78.42; H, 6.58; N, 3.39%. Found: C, 78.31; H, 6.75; N, 3.29%. LRMS (EI) *m*/*z* 413 (M^+, 50%), 357 ($M^+ + H - t$-Bu, 100%). HRMS (EI) Calcd for $C_{27}H_{27}NO_3$: 413.1991 Found: 413.1980. IR (KBr) 3700–3200, 2722, 1685 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.51 (9H, s), 1.90 (3H, s), 1.91 (3H, s), 4.87–5.10 (3H, m), 7.46 (2H, d, J = 8.4 Hz), 7.68 (2H, t, J = 8.4 Hz), 7.80 (1H, s), 8.08 (1H, d, J = 8.4 Hz), 8.22 (1H, s), 9.23 (1H, d, J = 8.4 Hz), 10.43 (1H, s). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 23.8, 23.9, 28.9, 43.1, 80.1, 121.0, 122.4, 124.7, 127.9, 128.0, 128.8, 129.1, 129.5, 130.1, 130.4, 130.9, 131.6, 131.7, 132.2, 134.4, 136.5, 137.8, 137.9, 155.9, 193.0.

(*P*)-5-*t*-Butoxycarbonylaminomethyl-8-(9-fluorenylmethoxycarbonyl)aminomethyl-1,12-dimethylbenzo[*c*]phenanthrene, (*P*)-25. Under an argon atmosphere, to a solution of (*P*)-**22** (300 mg, 0.723 mmol) in dichloromethane (5.0 mL) was added triethylamine (0.75 mL), 4-(dimethylamino)pyridine (0.88 mg, 7.3 μmol), and methanesulfonyl chloride (125 mg, 1.08 mmol) at 0 °C, and the mixture was warmed to room temperature. After being stirred for 1 h, the reaction was quenched by adding saturated aqueous sodium hydrogencarbonate. The organic materials were extracted with ethyl acetate three times. The combined organic layer was washed with water and brine, and then dried over anhydrous potassium carbonate. The solvent was evaporated under reduced pressure giving the mesylate. To a solution of the mesylate in *N*,*N*-dimethylformamide (4.0 mL) was added sodium azide (234 mg, 3.62 mmol) at 120 °C, and the mixture was stirred for 2 h. Then, the reaction was quenched by adding water. The organic materials

were extracted with toluene three times. The combined organic layer was washed with water and brine, and then dried over anhydrous potassium carbonate. The solvent was evaporated under reduced pressure giving the azide, which was used for the next reaction without further purification.

Under a hydrogen atmosphere, a mixture of the azide, methanol (9.0 mL), and 5% palladium on carbon (100 mg) was vigorously stirred for 1 h. Insoluble materials were removed by filtration, and the solution was concentrated under reduced pressure. The crude amine was dissolved in dichloromethane (4.0 mL) and 10% aqueous sodium hydrogencarbonate (4.0 mL) to which was added 9-fluorenylmethyl chloroformate (281 mg, 1.08 mmol) at 0 °C. After being stirred for 10 min at that temperature, the organic materials were extracted with ethyl acetate three times. The combined organic layer was washed with water and brine, and dried over anhydrous potassium carbonate. The solvent was evaporated under reduced pressure. Purification by flash silica-gel column chromatography (hexane/ethyl acetate = 2:1) gave (*P*)-**25** (334 mg, 0.525 mmol, 73%). mp 196–198 °C (toluene). $[\alpha]^{28}_{D}$ +53.0 (*c* 1.0, $CHCl_3$). Anal. Calcd for $C_{42}H_{40}N_2O_4$: C, 79.22; H, 6.33; N, 4.40%. Found: C, 79.46; H, 6.38; N, 4.36%. LRMS (FAB) *m*/*z* 636.3 (M^+, 20%). HRMS (FAB) Calcd for $C_{42}H_{40}N_2O_4$: 636.2988. Found: 636.2987. IR (KBr) 3411, 3321, 1697 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ 1.49 (9H, s), 1.91 (6H, s), 4.20 (1H, t, J = 6.8 Hz), 4.46–4.50 (2H, m), 4.84–5.07 (4H, m), 5.22 (1H, br), 7.27 (1H, t, J = 7.6 Hz), 7.36–7.41 (6H, m), 7.58–7.62 (4H, m), 7.68 (2H, s), 7.75 (2H, d, J = 7.6 Hz), 8.04 (2H, d, J = 8.0 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 23.6, 28.5, 42.9, 43.3, 47.3, 66.8, 77.2, 79.7, 119.8, 120.4, 120.5, 124.8, 124.9, 125.0, 125.4, 126.0, 126.1, 126.9, 127.5, 128.2 (2 peaks), 130.2, 130.3, 131.1, 131.5, 131.6, 132.5, 133.1, 136.7, 136.8, 141.1, 143.7, 155.5, 156.1.

(*P*)-5-Aminomethyl-8-*t*-butoxycarbonylaminomethyl-1,12-dimethylbenzo[*c*]phenanthrene, (*P*)-7. To a solution of (*P*)-**25** (122 mg, 0.192 mmol) in *N*,*N*-dimethylformamide (4.0 mL) was added piperidine (1.0 mL). After being stirred for 2 h at room temperature, the reaction was quenched by adding water, and the organic materials were extracted with toluene three times. The combined organic layer was washed with water and brine, and then dried over anhydrous potassium carbonate. The solvent was evaporated under reduced pressure. Purification by silica-gel column chromatography (chloroform/methanol = 10:1) gave (*P*)-**7** (76 mg, 0.178 mmol, 93%). The spectra data were identical with the reported values.[10]

(*P*,*P*)-Boc Protected Dimer, (*P*,*P*)-26. Under an argon atmosphere, a mixture of (*P*)-**7** (52.4 mg, 0.127 mmol) and (*P*)-**17** (44.4 mg, 0.108 mol) in methanol (3.6 mL) was stirred for 1 h at 40 °C. The reaction mixture was concentrated under reduced pressure, and the residue was dissolved in methanol (3.0 mL) and tetrahydrofuran (3.0 mL). To the solution was added sodium tetrahydroborate (300 mg, 8.00 mmol) at 0 °C, and the mixture was stirred for 30 min at that temperature. The reaction was quenched by adding saturated aqueous ammonium chloride. The organic materials were extracted with ethyl acetate three times. The combined organic layer was washed with water and brine, dried over anhydrous potassium carbonate, and then concentrated under reduced pressure. The resulting amine was dissolved in dichloromethane (2.5 mL) to which di(*t*-butyl) dicarbonate (350 mg, 1.6 mmol) and 10% aqueous sodium hydroxide (2.5 mL) were added successively. After being stirred for 2 h at room temperature, the organic materials were extracted with ethyl acetate three times. The combined organic layer was washed with water and brine, and then dried over anhydrous potassium carbonate. The solvent was evaporated under reduced pressure. Purification by flash silica-gel column chromatography (hexane/ethyl acetate = 2:1) gave (*P*,*P*)-**26** (93.0 mg, 0.102 mmol, 94%). The spectra data were identical with the reported values.[10]

(*P*,*P*,*P*)-Boc Protected Trimer, (*P*,*P*,*P*)-13. Under an argon atmosphere, a mixture of (*P*)-**9**[10] (45.6 mg, 0.145 mmol) and (*P*)-**17** (120 mg, 0.290 mol) in methanol (4.0 mL) was stirred for 1 h at 40 °C. The precipitated diimine was collected by filtration and then washed with methanol. Then, the solid was dissolved in methanol (4.0 mL) and tetrahydrofuran (4.0 mL). To the solution was added sodium tetrahydroborate (215 mg, 5.8 mmol) at 0 °C and the mixture was stirred for 30 min at that temperature. The reaction was quenched by adding saturated aqueous ammonium chloride. The organic materials were extracted with ethyl acetate three times. The combined organic layer was washed with water and brine, and then dried over anhydrous potassium carbonate. The solvent was evaporated under reduced pressure, giving crude diamine. The diamine was dissolved in dichloromethane (4.0 mL) to which were added di(*t*-butyl) dicarbonate (1.6 g, 55 mmol) and 10% aqueous sodium hydroxide (4.0 mL). After being stirred for 2 h at room temperature, the organic materials were extracted with ethyl acetate three times. The combined organic layer was washed with water and brine, and then dried over anhydrous potassium carbonate. The solvent was evaporated under reduced pressure. Purification by flash silica-gel column chromatography (hexane/ethyl acetate = 2:1) gave (*P*,*P*,*P*)-**13** (166 mg, 0.127 mmol, 88%). mp 201–204 °C (methanol). $[\alpha]^{27}_{D}$ +38.2 (*c* 1.0, $CHCl_3$). Anal. Calcd for $C_{86}H_{92}N_4O_8 \cdot 1/2H_2O$: C, 78.33; H, 7.11; N, 4.25%. Found: C, 78.29; H, 7.24; N, 4.17%. LRMS (FAB) *m*/*z* 1309 ($M^+ + H$, 1%). IR (KBr) 3600–3200 (br), 1693 cm^{-1}. ^1H NMR (DMSO-d_6, 400 MHz, 100 °C) δ 1.42 (36H, s), 1.50 (6H, s), 1.55 (6H, s), 1.76 (6H, s), 4.59–4.72 (4H, m), 4.97 (4H, d, J = 16.4 Hz), 5.11 (2H, d, J = 15.6 Hz), 5.18 (2H, d, J = 15.6 Hz), 6.94 (2H, br), 7.24–7.33 (8H, m), 7.44–7.55 (10H, m), 8.02–8.07 (6H, m). ^{13}C NMR (DMSO-d_6, 100 MHz, 100 °C) δ 22.1, 22.2, 22.4, 27.8, 28.0, 41.6, 47.7, 77.6, 78.7, 79.2, 119.8, 119.9, 120.1, 123.3, 123.4, 125.0 (2 peaks), 125.1, 127.1, 127.2, 129.7, 130.1, 130.4, 130.5 (2 peaks), 131.8, 131.9, 133.8, 135.4, 154.7, 155.1.

(*P*,*M*,*P*)-Boc Protected Trimer, (*P*,*M*,*P*)-13. Boc protected (*P*,*M*,*P*)-**13** (45.5 mg, 0.0348 mmol, 64%) was prepared from aldehyde (*P*)-**17** (44.7 mg, 0.108 mmol) and diamine (*M*)-**9** (17.0 mg, 0.0540 mmol), as was (*P*,*P*,*P*)-**13**. mp 202–205 °C (methanol). $[\alpha]^{29}_{D}$ +16.2 (*c* 1.0, $CHCl_3$). Anal. Calcd for $C_{86}H_{92}N_4O_8 \cdot 1/2H_2O$: C, 78.33; H, 7.11; N, 4.25%. Found: C, 78.38; H, 7.12; N, 4.18%. LRMS (FAB) *m*/*z* 1309 ($M^+ + H$, 2%). IR (KBr) 3600–3200, 1693 cm^{-1}. ^1H NMR (DMSO-d_6, 400 MHz, 100 °C) δ 1.42 (6H, s), 1.44 (9H, s), 1.45 (27H, s), 1.63 (6H, s), 1.72 (6H, s), 4.61–4.70 (4H, m), 5.00–5.17 (8H, m), 6.95 (2H, br), 7.26–7.31 (6H, m), 7.42–7.52 (12H, m), 8.01–8.12 (6H, m). ^{13}C NMR (DMSO-d_6, 100 MHz, 100 °C) δ 22.0, 22.3, 27.9, 28.0, 41.7, 47.7, 77.6, 78.7, 79.2, 119.8 (2 peaks), 119.9, 120.1, 123.3, 123.4, 123.7, 125.0, 125.1, 127.1, 127.3 (2 peaks), 129.6, 129.7 (2 peaks), 129.6, 129.7 (2 peaks), 130.3, 130.4, 130.5, 131.8, 131.9, 133.8, 135.4, 154.8, 155.2.

(*P*,*P*,*P*)-Trimer Tetrahydrochloride, (*P*,*P*,*P*)-2. To a solution of (*P*,*P*,*P*)-**13** (166 mg, 0.127 mmol) in dichloromethane (4.0 mL) was added trifluoroacetic acid (4.0 mL) at 0 °C. After being stirred for 2 h at that temperature, the reaction mixture was concentrated under reduced pressure. The resulting amorphous solid was dissolved in dichloromethane to which was added 10% aqueous sodium hydroxide. The organic layer was separated,

and the aqueous layer was extracted with dichloromethane three times. The combined organic layer was washed with water and brine, and then dried over anhydrous potassium carbonate. The solvent was evaporated under reduced pressure. To the resulting solid were added methanol and a small amount of 2 M hydrochloric acid, and then the solution was concentrated under reduced pressure. Washing the resulting solid with chloroform and ether gave pure (*P*,*P*,*P*)-**2** (133 mg, 0.127 mmol, quant.). mp 140 °C dec. (ethanol–hexane). $[\alpha]^{28}_{D}$ +3.2 (*c* 0.5, methanol). LRMS (FAB) *m*/*z* 910 ($M^+ + H - 4HCl$, 1%). HRMS (FAB) Calcd for $C_{66}H_{60}N_4 + H$: 909.4896. Found: 909.4901. IR (KBr) 3700–2700 (br) cm^{-1}. ^1H NMR (CD_3OD, 600 MHz, 1.0 mM) δ 1.84 (12H, s), 1.85 (6H, s), 4.57–4.93 (12H, m), 7.42 (2H, d, $J = 7.9$ Hz), 7.44 (2H, d, $J = 7.9$ Hz), 7.50–7.55 (8H, m), 7.73 (2H, t, $J = 7.9$ Hz), 7.92 (2H, s), 7.95 (2H, s), 8.02 (2H, d, $J = 8.3$ Hz), 8.04 (2H, s), 8.11 (2H, d, $J = 7.9$ Hz). ^1H NMR ($D_2O/CD_3OD = 4:1$, 600 MHz, 1.0 mM) δ 1.63 (6H, s), 1.66 (6H, s), 1.70 (6H, s), 3.78 (2H, d, $J = 14.0$ Hz), 3.83 (2H, d, $J = 14.0$ Hz), 4.31 (2H, d, $J = 14.0$ Hz), 4.64 (4H, d, $J = 14.0$ Hz), 5.16 (2H, d, $J = 14.0$ Hz), 5.84 (2H, s), 7.00 (2H, s), 7.25 (2H, s), 7.45 (2H, d, $J = 7.2$ Hz), 7.48 (2H, d, $J = 7.2$ Hz), 7.54 (2H, t, $J = 4.1$ Hz), 7.56 (2H, t, $J = 7.2$ Hz), 7.64 (2H, t, $J = 7.2$ Hz), 7.68 (2H, d, $J = 7.2$ Hz), 7.69 (2H, d, $J = 4.1$ Hz), 7.80 (2H, d, $J = 7.2$ Hz), 7.95 (2H, d, $J = 7.2$ Hz). ^{13}C NMR (CD_3OD, 150 MHz) δ 23.5, 23.6 (2 peaks), 41.6, 48.8, 49.2, 121.4 (3 peaks), 127.8, 128.4, 128.6, 128.7, 129.9, 130.0, 130.1, 130.3, 130.4, 131.5, 131.7, 131.8, 131.9 (2 peaks), 132.6, 138.5 (2 peaks), 138.6.

(*P*,*M*,*P*)-Trimer Tetrahydrochloride, (*P*,*M*,*P*)-2. (*P*,*M*,*P*)-**2** (36.7 mg, 0.0348 mmol, quant.) was prepared from (*P*,*M*,*P*)-**13** (45.5 mg, 0.0348 mmol) as was (*P*,*P*,*P*)-**2**. mp 150 °C dec. (ethanol–hexane). $[\alpha]^{28}_{D}$ +13.2 (*c* 0.5, methanol). LRMS (FAB) *m*/*z* 910 ($M^+ + H - 4HCl$, 1%). HRMS (FAB) Calcd for $C_{66}H_{65}N_4$: 909.4896. Found: 909.4863. IR (KBr) 3690–3160 cm^{-1}. ^1H NMR (CD_3OD, 600 MHz, 1.0 mM) δ 1.77 (6H, s), 1.79 (6H, s), 1.83 (6H, s), 4.63–4.70 (6H, m), 7.39 (2H, d, $J = 6.8$ Hz), 7.41 (2H, d, $J = 7.9$ Hz), 7.47 (2H, d, $J = 7.2$ Hz), 7.52 (4H, t, $J = 6.8$ Hz), 7.72 (2H, t, $J = 7.2$ Hz), 7.93 (2H, s), 7.94 (2H, s), 8.03 (4H, d, $J = 6.8$ Hz), 8.04 (2H, s), 8.10 (2H, d, $J = 7.2$ Hz). ^1H NMR ($D_2O/CD_3OD = 4:1$, 600 MHz, 1.0 mM) δ 0.92 (6H, s), 0.98 (6H, s), 1.40 (6H, s), 4.48 (2H, d, $J = 14.1$ Hz), 4.54 (4H, d, $J = 14.1$ Hz), 4.72 (4H, d, $J = 14.1$ Hz), 5.12 (2H, d, $J = 14.1$ Hz), 6.64 (2H, s), 7.11 (2H, d, $J = 7.6$ Hz), 7.16 (2H, d, $J = 7.6$ Hz), 7.28 (2H, d, $J = 7.2$ Hz), 7.45 (2H, t, $J = 7.6$ Hz), 7.55 (2H, s), 7.60 (2H, t, $J = 7.2$ Hz), 7.66 (2H, t, $J = 7.2$ Hz), 7.72 (2H, d, $J = 7.2$ Hz), 7.80 (2H, s), 7.94 (2H, d, $J = 7.6$ Hz), 8.04 (2H, d, $J = 7.6$ Hz). ^{13}C NMR (CD_3OD, 150 MHz) δ 23.5 (2 peaks), 23.6, 41.6, 49.4, 49.5, 127.9, 128.4 (3 peaks), 128.5 (3 peaks), 130.1 (2 peaks), 130.3 (2 peaks), 130.4, 131.5, 131.8, 131.9, 132.5, 132.6 (2 peaks), 138.5 (3 peaks).

(*P*,*P*,*P*,*P*)-Boc Protected Tetramer, (*P*,*P*,*P*,*P*)-14. To a solution of (*P*,*P*)-**26** (115 mg, 0.126 mmol) in dichloromethane (4.0 mL) was added trifluoroacetic acid (4.0 mL) at 0 °C. After being stirred for 2 h at that temperature, the mixture was concentrated under reduced pressure. The resulting amorphous solid was dissolved in dichloromethane to which was added 10% sodium hydroxide. The organic layer was separated, and the aqueous layer was extracted with dichloromethane three times. The combined organic layer was washed with water and brine, and then dried over anhydrous potassium carbonate. The solvent was evaporated under reduced pressure, giving (*P*,*P*)-**10**, which was dried in vacuo at 40 °C for 2 days, and used for the next reaction without further purification (77.0 mg, 0.126 mmol).

Under an argon atmosphere, a solution of the dimer (77.0 mg, 0.126 mmol) and aldehyde (*P*)-**17** (104 mg, 0.252 mmol) in tetrahydrofuran (1.4 mL) and methanol (2.8 mL) was heated at 40 °C for 12 h. The precipitated diimine was collected by filtration and washed with methanol. The solid was dissolved in methanol (7.0 mL) and tetrahydrofuran (7.0 mL). To the solution was added sodium tetrahydroborate (327 mg, 8.76 mmol) at 0 °C, and the mixture was stirred for 30 min at that temperature. The reaction was quenched by adding saturated aqueous ammonium chloride. The organic materials were extracted with ethyl acetate three times. The combined organic layer was washed with water and brine, and then dried over anhydrous potassium carbonate. The solvent was evaporated under reduced pressure. The resulting solid was dissolved in dichloromethane (8.0 mL), to which were added di(*t*-butyl) dicarbonate (3.8 g, 13.3 mmol) and 10% aqueous sodium hydroxide (8.0 mL). After being stirred for 2 h at room temperature, the organic materials were extracted with ethyl acetate three times. The combined organic layer was washed with water and brine, and then dried over anhydrous potassium carbonate. The solvent was evaporated under reduced pressure. Purification by flash silica-gel column chromatography (hexane/ethyl acetate = 2:1) gave (*P*,*P*,*P*,*P*)-**14** (165 mg, 0.0967 mmol, 77%). mp 219–221 °C (methanol). $[\alpha]^{28}_{D}$ +10.4 (*c* 0.5, $CHCl_3$). Anal. Calcd for $C_{113}H_{119}N_5O_{10}\cdot H_2O$: C, 78.67; H, 7.07; N, 4.06%. Found: C, 78.76; H, 7.03; N, 4.03%. MALDI-TOF MS Calcd. for $^{13}C^{12}C_{112}H_{119}N_5O_{10}$: 1706.9. Found: 1729.8 ($M^+ + Na$). LRMS (FAB) *m*/*z* 1707 (M^+, 0.3%). IR (KBr) 3615–3131, 1693 cm^{-1}. ^1H NMR (DMSO-d_6, 400 MHz, 100 °C) δ 1.26 (12H, s), 1.41 (45H, s), 1.53 (6H, s), 1.76 (6H, s), 4.62–4.67 (4H, m), 4.84 (4H, d, $J = 16.4$ Hz), 4.95 (4H, d, $J = 15.6$ Hz), 5.01–5.20 (4H, m), 6.94 (2H, br), 7.17–7.33 (10H, m), 7.42–7.57 (12H, m), 8.00–8.06 (8H, m), 8.20 (2H, s). ^{13}C NMR (DMSO-d_6, 150 MHz, 60 °C) δ 22.3, 22.4, 22.5, 22.8, 28.0, 28.2, 40.2, 47.9, 48.0, 77.9, 79.1, 79.5, 120.6, 123.5, 123.7, 125.6 (2 peaks) 125.7, 127.6, 127.7 (2 peaks) 130.0, 130.1, 130.4, 130.7, 130.8, 130.9 (2 peaks), 132.2, 132.3 (2 peaks), 132.4, 134.4, 135.8, 155.1 (2 peaks).

(*P*,*P*,*P*,*P*)-Tetramer Pentahydrochloride, (*P*,*P*,*P*,*P*)-3. (*P*,*P*,*P*,*P*)-**3** (134 mg, 0.0967 mmol, quant.) was prepared from (*P*,*P*,*P*,*P*)-**14** (165 mg, 0.0967 mmol), as was (*P*,*P*,*P*)-**2**. mp 164 °C dec. (ethanol–hexane). $[\alpha]^{28}_{D}$ +8.40 (*c* 1.0, methanol). ESI-MS Calcd for $C_{88}H_{80}N_5$ [$M^+ + H - 5HCl$]: 1206.6. Found: 1206.7. IR (KBr) 3700–2500 cm^{-1}. ^1H NMR (CD_3OD, 600 MHz, 1.0 mM) δ 1.82–1.85 (24H, s), 4.65–4.93 (2H, d, $J = 16.4$ Hz), 5.02–5.10 (8H, m), 7.45–7.47 (4H, m), 7.51–7.59 (10H, m), 7.75 (2H, t, $J = 8.2$ Hz), 7.97 (2H, s), 7.99–8.02 (6H, m), 8.05 (4H, s), 8.12 (2H, d, $J = 8.9$ Hz), 8.13 (2H, s). ^1H NMR ($D_2O/CD_3OD = 4:1$, 600 MHz, 1.0 mM) δ 1.58 (6H, s), 1.61 (6H, s), 1.62 (6H, s), 1.67 (6H, s), 3.70 (2H, d, $J = 13.7$ Hz), 3.86 (2H, d, $J = 14.0$ Hz), 4.07 (2H, d, $J = 14.0$ Hz), 4.38 (2H, d, $J = 13.7$ Hz), 4.47 (2H, d, $J = 14.0$ Hz), 4.61 (2H, d, $J = 14.8$ Hz), 4.70 (2H, d, $J = 14.0$ Hz), 5.07 (2H, d, $J = 14.8$ Hz), 6.06 (2H, s), 6.07 (2H, s), 7.23 (2H, t, $J = 6.9$ Hz), 7.24 (2H, s), 7.34 (2H, d, $J = 6.9$ Hz), 7.39–7.41 (4H, d, $J = 6.0$ Hz), 7.43 (2H, s), 7.44 (2H, d, $J = 7.9$ Hz), 7.50 (2H, t, $J = 8.9$ Hz), 7.56 (2H, t, $J = 8.6$ Hz), 7.68 (2H, t, $J = 7.9$ Hz), 7.70 (2H, t, $J = 8.9$ Hz), 7.76 (2H, d, $J = 8.9$ Hz), 7.81 (2H, d, $J = 8.6$ Hz), 7.91 (2H, d, $J = 7.9$ Hz). ^{13}C NMR (CD_3OD, 150 MHz) δ 23.5, 23.6, 23.7, 41.5, 48.8, 48.9, 49.6, 121.4 (2 peaks), 121.5, 127.9, 128.4, 128.7, 129.9 (2 peaks), 130.0, 130.3, 130.4, 131.5, 131.7, 131.8 (2 peaks), 131.9, 132.6 (2 peaks), 138.5 (2 peaks).

(*P*,*P*,*P*,*P*,*P*)-Boc Protected Pentamer, (*P*,*P*,*P*,*P*,*P*)-15. (*P*,*P*,*P*,*P*,*P*)-**15** (36.8 mg, 0.0175 mmol, 80%) was prepared from (*P*,*P*,-

P)-**13** (28.8 mg, 0.0220 mmol) and (*P*)-**17** (18.0 mg, 0.0440 mmol) as was (*P*,*P*,*P*,*P*)-**14**, except that tetrahydrofuran (0.5 mL) and methanol (0.5 mL) were used for the solvent in the coupling reaction. mp 228–231 °C (methanol). $[\alpha]^{30}_{D}$ +56.6 (*c* 0.12, $CHCl_3$). Anal. Calcd for $C_{140}H_{146}N_6O_{12}$: C, 79.89; H, 6.99; N, 3.99%. Found: C, 79.85; H, 6.90; N, 3.98%. MALDI-TOF MS Calcd for $^{13}C^{12}C_{139}H_{146}N_6O_{12}$: 2104.1. Found: 2127.1 (M^+ + Na). IR (KBr) 3716–3110, 1692 cm^{-1}. ^{1}H NMR (DMSO-d_6, 400 MHz, 100 °C) δ 1.26 (18H, s), 1.40 (6H, s), 1.42 (18H, s), 1.44 (18H, s), 1.49 (6H, s), 1.57 (6H, s), 1.77 (6H, s), 1.89 (6H, s), 4.63–4.78 (6H, m), 5.02–5.12 (4H, m), 5.22–5.44 (10H, m), 6.80 (1H, br), 6.87 (1H, br), 7.19–7.66 (26H, m), 7.75–7.92 (8H, m), 8.06–8.19 (6H, m). ^{13}C NMR (DMSO-d_6, 100 MHz, 100 °C) δ 21.9, 22.0, 22.1, 22.3, 22.4, 27.8, 28.0, 41.6, 47.6, 50.4, 77.5, 79.2, 119.7, 119.8, 120.0, 120.8, 123.3, 123.6, 124.9, 125.0, 127.1, 129.6, 130.0, 130.3, 130.4, 130.5, 130.6, 131.7, 131.8, 131.9, 133.8, 135.3, 154.6 (2 peaks).

(*P*,*P*,*P*,*P*,*P*)-Pentamer Hexahydrochloride, (*P*,*P*,*P*,*P*,*P*)-4. (*P*,*P*,*P*,*P*,*P*)-**4** (28.0 mg, 0.0161 mmol, quant.) was prepared from (*P*,*P*,*P*,*P*,*P*)-**15** (33.9 mg, 0.0161 mmol), as was (*P*,*P*,*P*)-**2**. mp 170 °C dec. (ethanol–hexane). $[\alpha]^{27}_{D}$ −8.00 (*c* 0.1, methanol). ESI-MS Calcd for $^{13}C^{12}C_{109}H_{99}N_6$ [M^+ + H − 6HCl]: 1504.8. Found: 1504.9. IR (KBr) 3700–2700 (br) cm^{-1}. ^{1}H NMR (CD_3OD, 600 MHz, 1.0 mM) δ 1.75–1.77 (30H, m), 4.58 (2H, d, J = 14.1 Hz), 5.03–5.09 (8H, m), 7.38–7.52 (18H, m), 7.68 (2H, t, J = 7.2 Hz), 7.92–7.95 (12H, m), 8.00–8.06 (6H, m), 8.10 (2H, s). ^{1}H NMR (D_2O/CD_3OD = 4:1, 600 MHz, 1.0 mM) δ 1.38 (12H, s), 1.42 (6H, s), 1.46 (6H, s), 1.47 (6H, s), 3.55 (2H, d, J = 13.7 Hz), 3.74 (2H, d, J = 14.8 Hz), 3.78 (2H, d, J = 14.1 Hz), 3.95 (2H, d, J = 14.2 Hz), 4.30 (2H, d, J = 14.2 Hz), 4.33 (2H, d, J = 13.7 Hz), 4.40 (2H, d, J = 14.1 Hz), 4.48 (2H, d, J = 14.3 Hz), 4.54 (2H, d, J = 14.8 Hz), 4.88 (2H, d, J = 14.3 Hz), 5.92 (2H, s), 6.13 (2H, s), 6.15 (2H, s), 7.10 (2H, s), 7.21–7.19 (4H, m), 7.25–7.31 (12H, m), 7.36 (2H, t, J = 7.9 Hz), 7.40 (4H, m), 7.51–7.54 (4H, m), 7.57–7.58 (4H, m), 7.78 (2H, d, J = 8.5 Hz). ^{13}C NMR (CD_3OD, 150 MHz) δ 23.5, 23.7, 41.5, 48.9, 49.1, 49.2, 49.4, 121.4 (3 peaks), 127.9 (2 peaks), 128.2 (2 peaks), 128.3 (2 peaks), 128.4, 128.5, 128.7, 130.0 (3 peaks), 130.1, 130.3, 130.4, 131.5, 131.7 (3 peaks), 131.8, 131.9, 132.6 (3 peaks), 138.5 (2 peaks), 138.6.

(*P*,*P*,*P*,*P*,*P*,*P*)-Boc Protected Hexamer, (*P*,*P*,*P*,*P*,*P*,*P*)-16. (*P*,*P*,*P*,*P*,*P*,*P*)-**16** (25.5 mg, 0.0121 mmol, 73%) was prepared from (*P*,*P*,*P*,*P*)-**14** (28 mg, 0.0166 mmol) and (*P*)-**17** (13.7 mg, 0.0332 mmol) as was (*P*,*P*,*P*,*P*)-**14**, except that tetrahydrofuran (0.6 mL) and methanol (0.3 mL) were used for the solvent in the coupling reaction, and the mixture was reacted for 18 h. mp 230–233 °C (methanol). $[\alpha]^{29}_{D}$ +20.8 (*c* 0.25, $CHCl_3$). MALDI-TOF MS Calcd for $^{13}C^{12}C_{166}H_{173}N_7O_{14}$: 2502.2. Found: 2525.1 (M^+ + Na). Anal. Calcd for $C_{167}H_{173}N_7O_{14}\cdot H_2O$: C, 79.59; H; 7.00, N, 3.89%. Found: C, 79.47; H, 6.99; N, 3.72%. IR (KBr) 3720–3150, 1692 cm^{-1}. ^{1}H NMR (DMSO-d_6, 600 MHz, 60 °C) δ 1.22 (30H, brs), 1.36 (45H, brs), 1.39 (18H, brs), 1.68 (6H, brs), 4.61–5.09 (26H, br), 7.06–7.28 (24H, br), 7.42–7.50 (12H, br), 7.90–8.12 (12H, br). ^{13}C NMR (DMSO-d_6, 150 MHz, 60 °C) δ 22.0 (2 peaks), 22.1, 22.2 (2 peaks), 22.5, 27.7, 40.0, 47.7 (3 peaks), 120.0 (8 peaks), 123.3 (3 peaks), 123.4, 123.5 (5 peaks), 125.3 (2 peaks), 125.5, 127.4 (2 peaks), 127.5 (2 peaks), 127.6, 128.6, 129.7, 129.8 (2 peaks), 130.1, 130.2, 130.5 (2 peaks), 130.6 (2 peaks), 130.7, 132.0 (2 peaks), 132.1 (2 peaks), 132.2 (4 peaks), 134.1, 135.5 (2 peaks), 154.9 (2 peaks).

(*P*,*P*,*P*,*P*,*P*,*P*)-Hexamer Heptahydrochloride, (*P*,*P*,*P*,*P*,*P*,*P*)-5. (*P*,*P*,*P*,*P*,*P*,*P*)-**5** (28.4 mg, 0.0138 mmol, quant.) was prepared from (*P*,*P*,*P*,*P*,*P*,*P*)-**16** (34.4 mg, 0.0138 mmol), as was (*P*,*P*,*P*)-**2**. mp 180 °C dec. (ethanol–hexane). $[\alpha]^{27}_{D}$ +15.0 (*c* 0.2, methanol). MALDI-TOF MS Calcd for $^{13}C^{12}C_{131}H_{117}N_7$ [M^+ − 7HCl]: 1801.4. Found: 1824.1 [M^+ − 7HCl + Na]. IR (KBr) 3580–2720 cm^{-1}. ^{1}H NMR (CD_3OD, 600 MHz, 5.0 mM) δ 1.79 (6H, s), 1.79 (12H, s), 1.80 (6H, s), 1.80 (6H, s), 1.82 (6H, s), 4.61(2H, d, J = 14.5 Hz), 5.05–5.12 (10H, m), 7.42–7.44 (8H, m), 7.48 (2H, d, J = 7.9 Hz), 7.51 (2H, d, J = 12 Hz), 7.54 (10H, t, J = 7.9 Hz), 7.71 (2H, t, J = 7.9 Hz), 7.97–8.02 (18H, m), 8.06 (2H, d, J = 5.8 Hz), 8.10 (2H, d, J = 7.9 Hz), 8.16 (2H, s). ^{1}H NMR (D_2O/CD_3OD = 2:1, 600 MHz, 0.5 mM) δ 1.39 (6H, s), 1.43 (6H, s), 1.48 (12H, s), 1.49 (6H, s), 1.53 (6H, s), 3.89 (2H, d, J = 14.8 Hz), 4.07 (2H, d, J = 13.4 Hz), 4.12 (2H, d, J = 14.8 Hz), 4.34 (2H, d, J = 13.7 Hz), 4.48–4.60 (5H, m), 4.68 (2H, d, J = 15.1 Hz), 6.55 (4H, s), 6.76 (2H, s), 6.77 (2H, s), 7.15–7.77 (38H, m), 7.99 (2H, d, J = 6.0 Hz). ^{13}C NMR (CD_3OD, 150 MHz) δ 23.6 (2 peaks), 23.7 (2 peaks), 49.2, 49.3 (2 peaks), 49.4, 121.4 (2 peaks), 121.5 (4 peaks), 128.0, 128.4 (3 peaks), 128.5 (2 peaks), 128.6, 128.7, 129.9 (5 peaks), 130.0, 130.1, 130.3 (3 peaks), 130.4, 130.5, 131.5, 131.7 (3 peaks), 131.8 (2 peaks), 132.6 (2 peaks), 138.5.

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