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Synthesis and duplex formation of the reverse amidohelicene tetramer

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ABSTRACT

The reverse amidohelicene (*P*)-tetramer containing (*P*)-helicenediamine and *m*-phenylenedicarboxylate was synthesized. The circular dichroism (CD) and vapor pressure osmometry (VPO) analysis revealed the dimeric aggregate formation in THF. It is notable that the reverse amide tetramer formed a duplex, as well as the original amidohelicene oligomers. In various solutions, mixtures of the reverse (*P*)-tetramer and amidohelicene (*P*)/(*M*)-tetramer formed homoaggregates instead of heteroaggregates.

1. Introduction

Synthetic aromatic amide oligomers have attracted interest in regard to the formation of ordered structures, such as zipperlike duplex, double helix, and single helix. The reported compounds include oligoamidopyridines,[1] methoxybenzamide oligomers,[2] dianilinocyclohexyl *m*-phenylenedicarbonyl oligomers,[3] *N*-methyl pyridinecarboxylate amide oligomers,[4] anthranilamide oligomers,[5] and phenanthrolinedicarboxyl *m*-diaminophenylene oligoamides.[6] Some of the compounds exhibit structural changes in response to a change in the environment.[1,2,5,6] In general, these synthetic oligomers are achiral, and optically active compounds have not been studied except for an optically active oligophenanthroline possessing one asymmetric carbon atom.[6]

We previously synthesized optically active amidohelicene oligomers containing (*P*)-1,12-dimethylbenzo[*c*]phenanthrene-5,8-dicarboxylate and *m*-phenylenediamine.[7] The amidohelicene trimer (*P*)-**4** to nonamer (*P*)-**7** formed stable helix dimers in nonpolar solvents, and the aggregate of (*P*)-**5** in chloroform did not dissociate between 5 and 60 °C even at the concentration of 5.0×10^{-6} M. The helix dimer of tetramer (*P*)-**5** dissociated to random-coil in hydrogen-bond-breaking solvents. It was also observed that the equilibrated states of the helix dimer and random-coil were not affected by temperature change. This is a notable aggregation phenomenon of chiral synthetic amide oligomers, and it was considered interesting to examine their derivatives in order to clarify the relationship between the structure and aggregation property.

In this study, we synthesized the reverse amidohelicene oligomers (*P*)-**1**, (*P*)-**2**, and (*P*)-**3**, as an analog of the amidohelicene oligomers. The arrangement of amine and carbonyl groups were reverted from the original oligomers (*P*)-**4** to (*P*)-**7**. The reversed oligomers (*P*)-**1** to (*P*)-**3** were synthesized from 1,12-dimethylbenzo[*c*]phenanthrene-5,8-diamine[8] and isophthalate. The tetramer (*P*)-**3** formed a duplex in THF, and was a random-coil in DMSO. The duplex structure of (*P*)-**3** was more stable than that of (*P*)-**5** in THF. The tetramer (*P*)-**3** did not form heteroaggregates with either (*P*)-**5** or (*M*)-**5**, and homoaggregate formation prevailed.

Such study to compare amide oligomers with the reversed amide structure was reported in the case of natural oligopeptides and peptide nucleic acid (PNA) oligomers but not for aromatic amide oligomers. An exception is the oligomer containing *m*-benzenedicarboxylate and aminoacetylaniline, and its reverse oligomers containing *m*-benzenediamine and benzoylaminoacetate.[9] In $CDCl_3$, the amide and the reverse amide oligomers formed a heteroduplex. A systematic study to compare the properties of the reversed amide compounds is interesting.

2. Result and discussion

2.1. Synthesis

In this study, the reverse amidohelicene oligomers were synthesized by repeating an amide coupling reaction using a building

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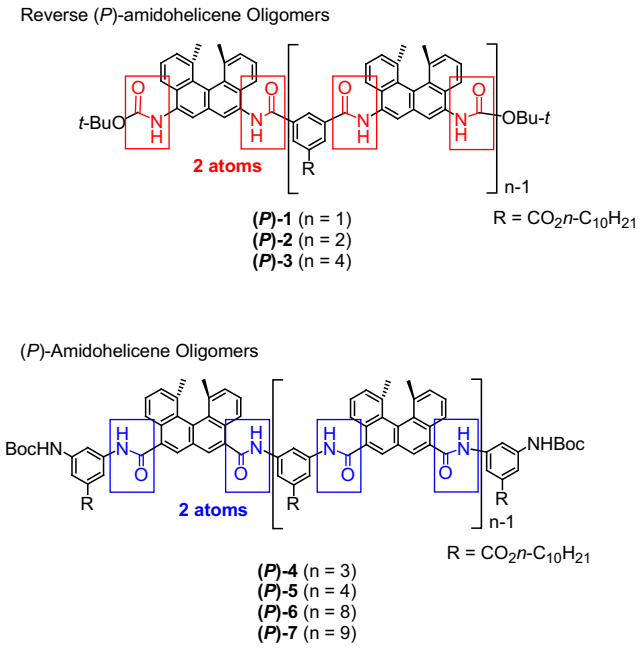

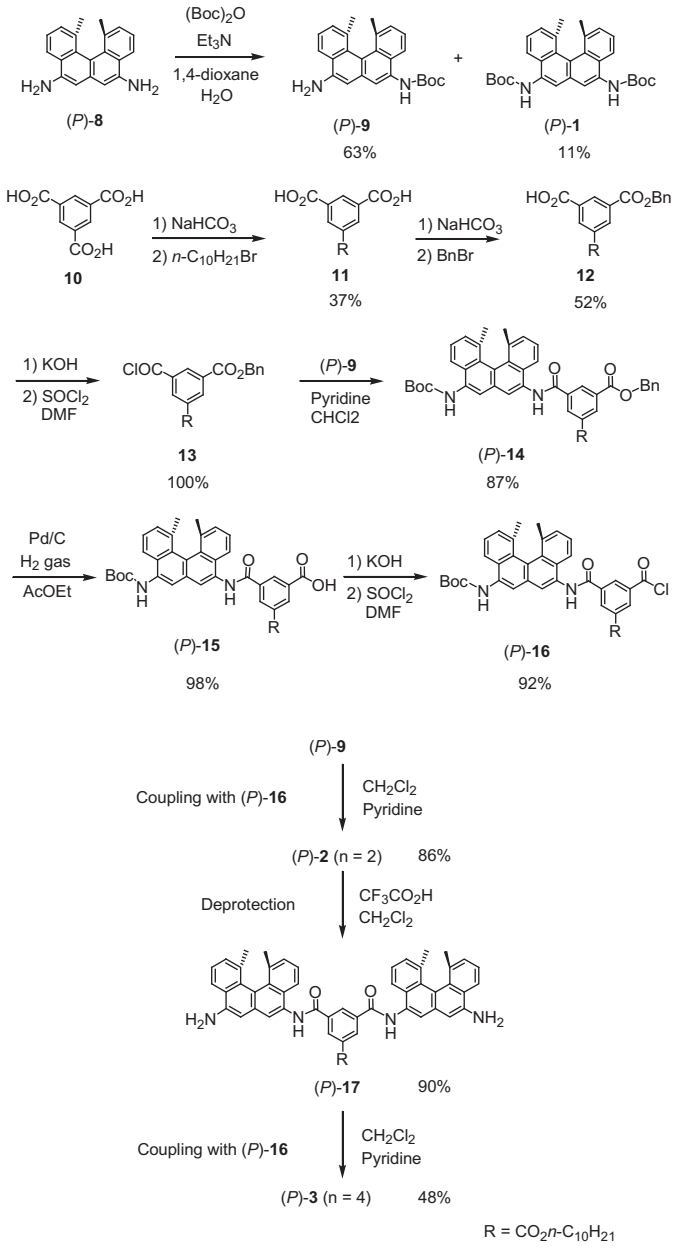

Scheme 1.

block acid chloride (*P*)-**16** containing a 1,12-dimethylbenzo[*c*]phenanthrene moiety and a *m*-phenylene moiety (Scheme 1). 1,3,5-Benzenetricarboxylate with three differentiated carboxylates was synthesized.[10] Monosodium salt of 1,3,5-benzenetricarboxylic acid **10** was reacted with 1-bromodecane in DMF at room temperature giving decyl ester **11** in 37% yield. The treatment of **11** sodium salt with benzyl bromide gave decyl benzyl ester **12** in 52% yield. Then, **12** was converted to acid chloride **13** with thionyl chloride in 100% yield.[7] An amino group of diaminohelicene (*P*)-**8**[8] was monoprotected with di(*tert*-butoxy)carbonyl anhydride giving carbamate (*P*)-**9** in 63% yield along with dicarbamate (*P*)-**1** (11%). Coupling of (*P*)-**9** and **13** gave (*P*)-**14**, and removal of the benzyl group gave carboxylic acid (*P*)-**15**. The building block acid chloride (*P*)-**16** was formed from (*P*)-**15** by treatment of its potassium salt with thionyl chloride at −20 °C in 92% yield. The low-temperature conditions were critical to obtain (*P*)-**16** in high yield. The reverse amide dimer (*P*)-**2** was synthesized by the reaction (*P*)-**9** and (*P*)-**16** in dichloromethane in the presence of pyridine in 88% yield. Then, dimer (*P*)-**2** was deprotected with trifluoroacetic acid giving diamine (*P*)-**17**, which was coupled with (*P*)-**16** to give the tetramer (*P*)-**3** in 48% yield. Attempts to synthesize trimer from (*P*)-**8** and (*P*)-**16** failed, because of the instability of (*P*)-**8** toward air oxidation.[10] Higher oligomers could not be obtained because of the low solubility of the deprotected diamine compound from tetramer (*P*)-**3**.

2.2. Duplex formation

The aggregate formation of monomer (*P*)-**1**, dimer (*P*)-**2**, and tetramer (*P*)-**3** (5.0×10^{-6} M, 25 °C) in dimethyl sulfoxide (DMSO) and tetrahydrofuran (THF) was examined by CD (Fig. 1). In DMSO, the intensity of the Cotton effect increased with the increase in the helicene numbers. In THF, (*P*)-**1** and (*P*)-**2** showed similar spectra with those in DMSO, and (*P*)-**3** provided a different spectrum with a strong positive Cotton effect at 318 nm. UV absorption of (*P*)-**3** in THF at 309 nm was weaker than that in DMSO, and the absorption maximum shifted from 309 nm in DMSO to 313 nm in THF (Fig. 2). The CD and UV spectra in THF did not change by changing the concentration between 5.0×10^{-5} M and 2.5×10^{-7} M and the temperature between 5 and 60 °C (Figs. 3 and 4, and S1). Vapor pressure osmometry (VPO) study of (*P*)-**3** in THF (1.0×10^{-3} M, 45 °C) showed bimolecular aggregate (N=2.2±0.1) formation. The results indicated that the tetramer (*P*)-**3** formed duplex in THF and random-coil in DMSO. While the ^{1}H NMR spectrum of (*P*)-**3** in DMSO showed sharp peaks, that in THF was broadened and shifted to a higher field (Fig. 5).

IR analysis of (*P*)-**3** was conducted in solution (1.0×10^{-3} M) at room temperature. The original (*P*)-**5** is helix dimer in chloroform as shown by CD and VPO,[7] and showed amide IR absorptions at 1654 and 1648 cm^{-1}. In THF, (*P*)-**5** is a random-coil,[7] and provided an amide absorption at 1682 cm^{-1} (Fig. 6). It is known that hydrogen-bonded amide carbonyl absorption shifts to lower frequency by 20–40 cm^{-1},[11] and the observations are consistent with helix dimer formation of (*P*)-**5** by hydrogen-bonding. In THF (1.0×10^{-3} M), (*P*)-**3** was a pure duplex as indicated by CD and VPO (Fig. 3, and 4), and showed amide absorptions at 1643 and 1687 cm^{-1}. The duplex of (*P*)-**3** appeared to possess hydrogen-bonded amides as well as nonhydrogen-bonded amides.

Note that both amidohelicene tetramer (*P*)-**5** and the reverse amidohelicene tetramer (*P*)-**3** formed dimeric aggregate in solution. We previously described that optically active acetylene oligomers

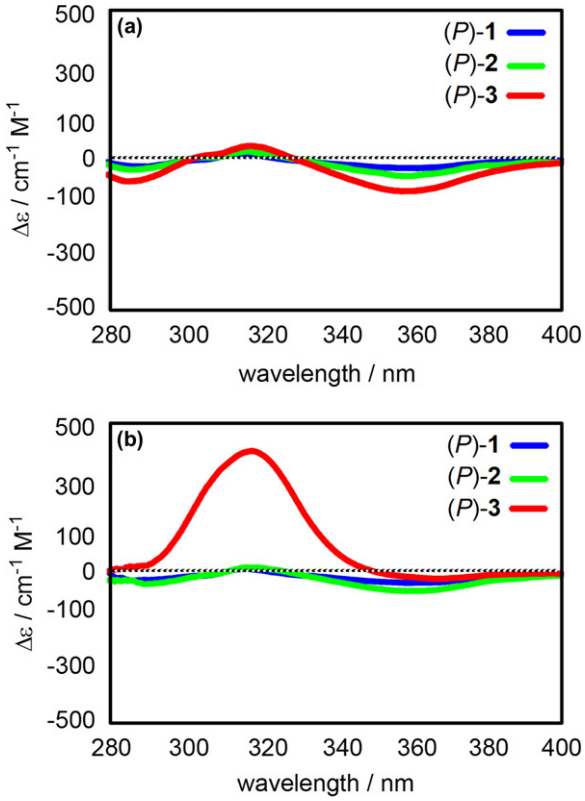

Fig. 1. CD spectra (5.0×10^{-6} M, 25 °C) of reverse amidohelicene oligomers: (a) in DMSO, (b) in THF.

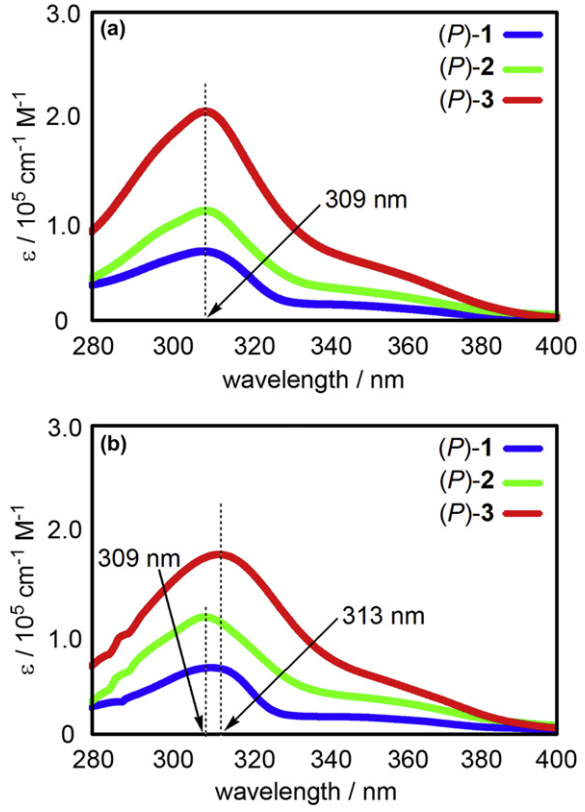

Fig. 2. UV spectra (5.0×10^{-6} M, 25 °C) of reverse amidohelicene oligomers: (a) in DMSO, (b) in THF.

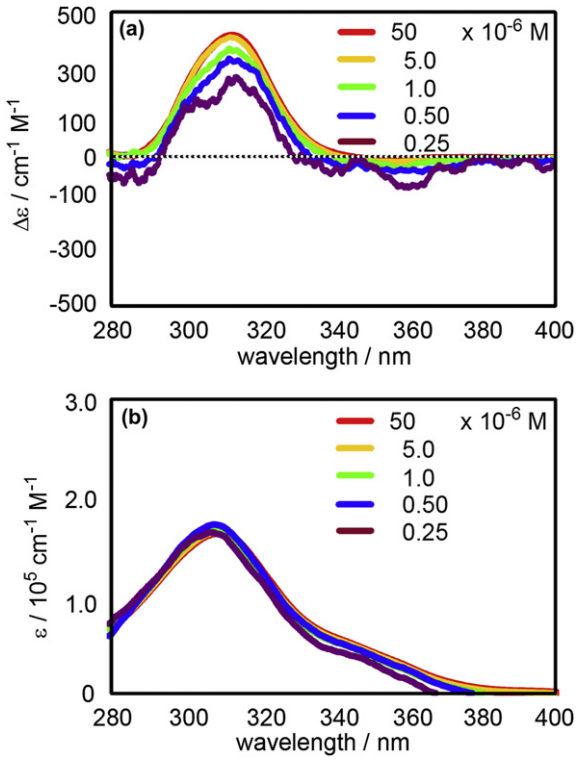

Fig. 3. (a) CD spectra, (b) UV spectra of tetramer (*P*)-**3** at 25 °C at various concentrations in THF.

containing helicene and *m*-phenylene formed double helix in solution.[12] All these oligomers possessing two-atom linkages between helicene and *m*-phenylene formed dimeric aggregates.

The solvent effect on the aggregate formation was examined by CD (5.0×10^{-6} M, 25 °C) (Fig. 7). The spectrum of (*P*)-**3** in pyridine was similar to that in DMSO. In THF/chloroform (70/30) and chloroform/DMSO (95/5), similar spectra to that in THF were obtained. The CD spectrum, therefore, was considered to be that of pure duplex. The results also indicated that the driving force of duplex formation of (*P*)-**3** is hydrogen-bonding. Since the solubility of (*P*)-**3** was low in chloroform and toluene, CD analysis was not conducted in these solvents.

The CD spectra of (*P*)-**3** in a mixed solvent of THF and DMSO (5.0×10^{-6} M) were used to obtain the ratio of random-coil to duplex (Fig. 8). The CD spectra in DMSO (5.0×10^{-6} M) did not change between 5 and 60 °C (Fig. 9c), and the same spectra were obtained in pyridine. The spectrum therefore was considered to be that of a pure random-coil state. Then, the $\Delta\varepsilon$ values at 318 nm for the pure duplex ($+410$ cm^{-1} M^{-1}) and pure random-coil ($+40$ cm^{-1} M^{-1}) were obtained. The ratio of duplex to random-coil of (*P*)-**3** in the mixed solutions was estimated from the $\Delta\varepsilon$ values at 318 nm (Figs. 8–10, and S2). For example, $\Delta\varepsilon$ $+339$ cm^{-1} M^{-1} at 318 nm was obtained in THF/DMSO (99/1), from which the equilibrium of (*P*)-**3** between the duplex and random-coil was calculated to be 81/19. With increasing amount of DMSO, the amount of duplex decreased. From the results, equilibria of the reversed amidohelicene tetramer (*P*)-**3** and (*P*)-**5** were compared. In chloroform/DMSO (95/5), the ratio of duplex to random-coil of (*P*)-**3** was calculated to be 77/23 from the $\Delta\varepsilon$ $+325$ cm^{-1} M^{-1} (Fig. 10a). Under the same solvent conditions, (*P*)-**5** was in equilibrium between the helix dimer and random-coil with a 20/80 ratio.[7] In toluene/DMSO (99/1), the equilibrium ratio of (*P*)-**3** was 75/25 (Fig. 10b), and that of (*P*)-**5** was 5/95.[7] The results indicated the stable duplex formation of (*P*)-**3** compared with that of (*P*)-**5**.

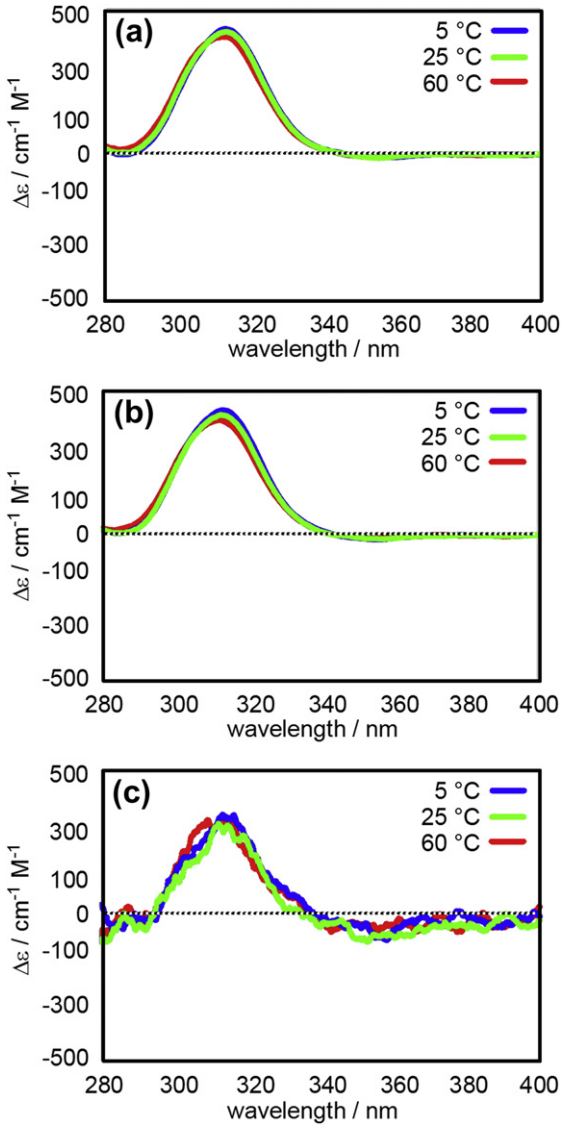

Fig. 4. CD spectra of tetramer (*P*)-**3** in THF: (a) 50×10^{-6} M, (b) 5.0×10^{-6} M, (c) 0.25×10^{-6} M.

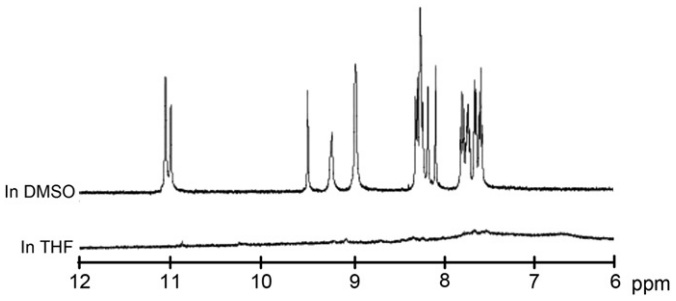

Fig. 5. ^{1}H NMR spectra of tetramer (*P*)-**3** at 1.0×10^{-3} M in DMSO and THF.

The CD study was conducted at different temperatures. In THF at the concentration between 1.0×10^{-6} and 2.5×10^{-7} M, (*P*)-**3** is a pure duplex (Figs. 4, and S1). No change in the CD spectrum was observed between 60 and 5 °C. In DMSO, where (*P*)-**3** was a random-coil, no temperature effect was observed. In THF/DMSO (99/1, 98/2, 97/3, 95/5), chloroform/DMSO (95/5), and toluene/DMSO (99/1) at 5.0×10^{-6} M, equilibria between the duplex and random-coil were 81/19, 64/36, 20/80, <5/95, 77/23, and 75/25, respectively (Figs. 9,

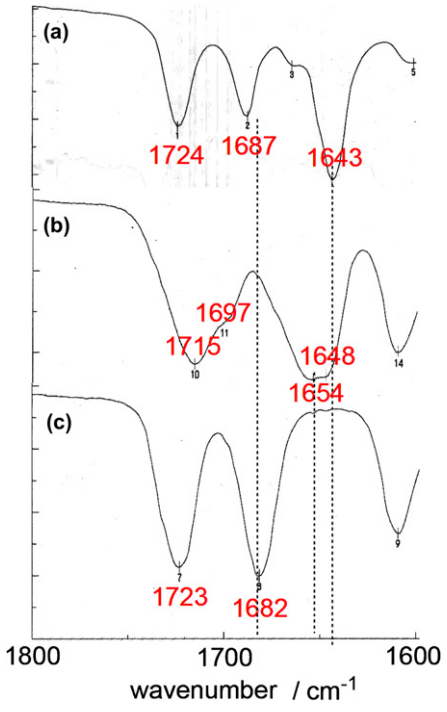

Fig. 6. IR spectra of (*P*)-**3** and (*P*)-**5** (1.0×10^{-3} M). (a) (*P*)-**3** in THF: duplex, (b) (*P*)-**5** in chloroform: helix dimer, (c) (*P*)-**5** in THF: random-coil.

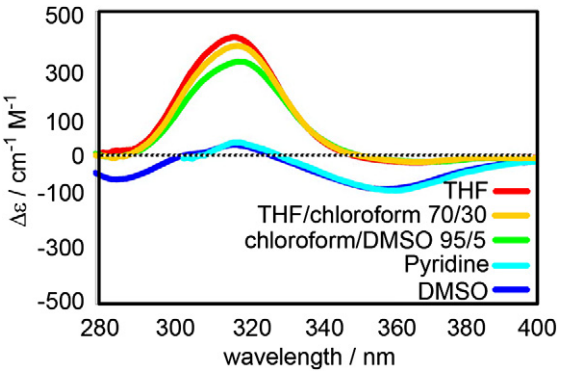

Fig. 7. CD spectra (5.0×10^{-6} M, 25 °C) of tetramer (*P*)-**3** in various solvents.

and S2). CD spectra were again not affected by the temperature change in these mixed solvents. An exception was in toluene/DMSO (99/1) at 100 °C, in which a slight decrease was observed (Fig. 10b).

Both the amidohelicene tetramer (*P*)-**5** and the reverse amidohelicene tetramer (*P*)-**3** formed duplex in nonpolar solvents and random-coil in hydrogen-bond-breaking solvents. The equilibrium between the duplex and random-coil for both (*P*)-**5** and (*P*)-**3** was also not affected by temperature changes. Different properties were noted concerning the stability of the duplex. (*P*)-**3** formed a stable duplex in THF, whereas (*P*)-**5** did not form dimeric aggregate in the same solvent. Solubility in chloroform also differed. Whereas (*P*)-**5** was soluble in chloroform up to 1.0×10^{-2} M, (*P*)-**3** was not soluble even at 5.0×10^{-6} M. Both oligomers showed similar CD spectra of random-coil but different spectra of duplex (Fig. 11), which may be due to the difference in the three-dimensional structures of (*P*)-**3** and (*P*)-**5**. Based on the report that similar linear helicene oligomer formed helix conformation,[7,12] we guess the tetramer (*P*)-**3** have also helix formation in the aggregations. Direct experimental data for helix conformation of (*P*)-**3** was not obtained by any analysis in this paper.

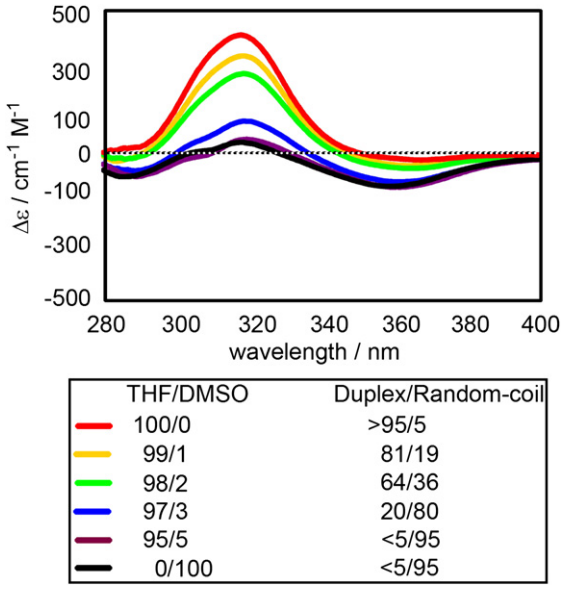

Fig. 8. CD spectra (5.0×10^{-6} M, 25 °C) of tetramer (*P*)-**3** in THF/DMSO at various ratios. The ratio of duplex to random-coil was also noted.

2.3. Aggregation in mixed systems of (*P*)-3 and (*P*)/(*M*)-5

Since both amidohelicene oligomers and the reverse amidohelicene tetramer (*P*)-**3** formed duplex, it was considered interesting to determine whether they could form heteroaggregates. The reversed tetramer (*P*)-**3** and amidohelicene tetramer (*P*)-**5** were mixed at a 1/1 ratio (each 2.5×10^{-6} M) in various solvents. The mixture of tetramer (*P*)-**3** and tetramer (*P*)-**5** has the advantage of being CD active. When a heteroaggregate is formed, the CD spectra should be different from those obtained by the addition of the spectrum of each compound in the same solvent. It was also considered important to control the initial states of both oligomers, duplex or random-coil, because the initial states can affect the process of heteroaggregate formation. The mixing experiments therefore were conducted under different conditions, where different compositions of duplex or random-coil were obtained.

In DMSO, both (*P*)-**3** and (*P*)-**5** were in random-coil states at 5.0×10^{-6} M.[7] The solutions were mixed, and the CD spectrum (each 2.5×10^{-6} M) was obtained. The experimental spectrum coincided with the calculated spectrum (Fig. 12a), which was obtained by the addition of the spectra of (*P*)-**3** and (*P*)-**5** in DMSO at 5.0×10^{-6} M. The results indicated that the mixture of (*P*)-**3** and (*P*)-**5** in DMSO did not produce aggregates, and both were in random-coil states. In THF (5.0×10^{-6} M), (*P*)-**5** was random-coil and (*P*)-**3** formed duplex. The experimental CD spectra (each 2.5×10^{-6} M) obtained by mixing the solutions coincided with the calculated spectrum (Fig. 12b).

Heteroaggregate formation was examined for equilibrated mixtures of homoaggregate and random-coil. Under the same equilibrated conditions, four combinations of interactions between (*P*)-**3** and (*P*)-**5** can occur, namely, duplex/helix dimer, duplex/random-coil, random-coil/helix dimer, and random-coil/random-coil, and the probability of heteroaggregate formation can increase. In chloroform/DMSO (95/5) at 5.0×10^{-6} M, the equilibrium ratios between homoduplex and random-coil were 77/23 for (*P*)-**3** and 20/80 for (*P*)-**5**. The experimental CD spectrum (each 2.5×10^{-6} M) in the mixed solution coincided with the calculated spectrum, which was obtained by adding the CD spectra (5.0×10^{-6} M) of (*P*)-**3** and (*P*)-**5** in the same solvents (Fig. 13a). In toluene/DMSO (99/1), (*P*)-**3** and (*P*)-**5** showed 75/25 and 5/95 ratios of duplex and random-coil, respectively. The CD spectrum in the mixed solution again coincided with the calculated one (Fig. 13b). The results indicated that the heteroaggregates of (*P*)-**3** and (*P*)-**5** did not form under these equilibrium states.

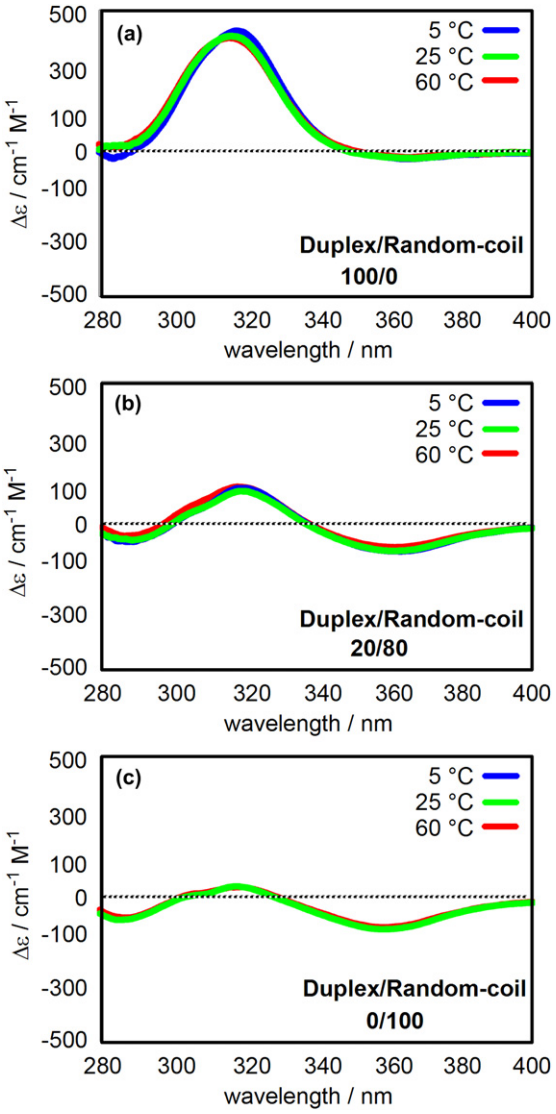

Fig. 9. CD spectra of tetramer (*P*)-**3** at 5.0×10^{-6} M at various temperatures in THF/DMSO: (a) 100/0, (b) 97/3, (c) 0/100. The ratio of duplex to random-coil was also noted.

The same mixing experiments using (*P*)-**3** and the enantiomeric (*M*)-**5** were conducted. In chloroform/DMSO (95/5) and toluene/DMSO (99/1), the CD spectra showed no sign of heteroaggregate formation between (*P*)-**3** and (*M*)-**5** (Fig. 14).

Attempts were made to change the solvent ratio. Solutions containing (*P*)-**3**/(*P*)-**5** or (*P*)-**3**/(*M*)-**5** in chloroform/DMSO (95/5) (each 2.5×10^{-6} M) were prepared, and chloroform was evaporated in vacuo. To the residual DMSO solution was added chloroform to make a chloroform/DMSO (95/5) solution, and CD spectra were obtained. The spectra coincided with the calculated one (5×10^{-6} M) obtained from (*P*)-**3**/(*P*)-**5** and (*P*)-**3**/(*M*)-**5** (Fig. 15).

The results showed that, in the mixtures of amidohelicene tetramer (*P*)-**5**/(*M*)-**5** and the reverse amidohelicene tetramer (*P*)-**3**, homoaggregates prevailed over heteroaggregates (Fig. 16). It may be noted that (*P*)-**3** recognized (*P*)-**3** as the counterpart rather than (*P*)-**5** or (*M*)-**5** in these mixed systems. The difference in the relative three-dimensional arrangement of the hydrogen-bonded secondary amides may be playing an important role.

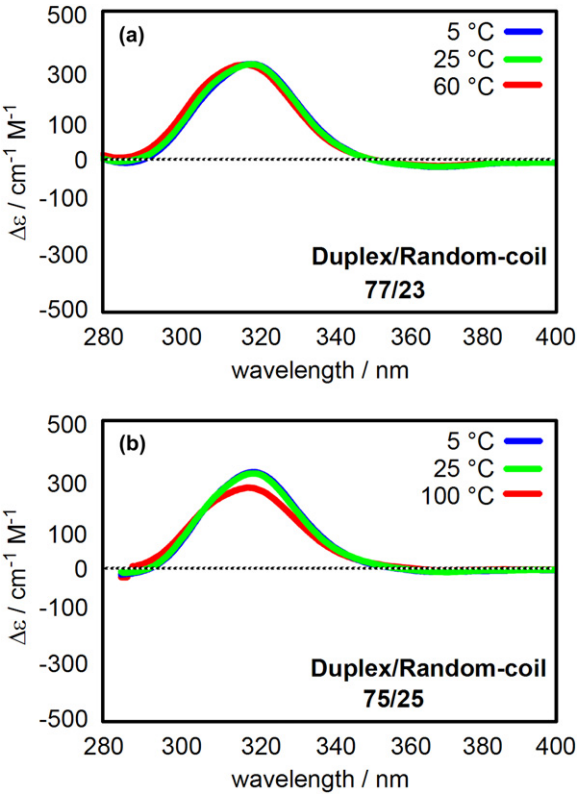

Fig. 10. CD spectra of tetramer (*P*)-**3** at 5.0×10^{-6} M at various temperatures: (a) in DMSO/chloroform 5/95, (b) in DMSO/toluene 1/99. The ratio of duplex to random-coil was also noted.

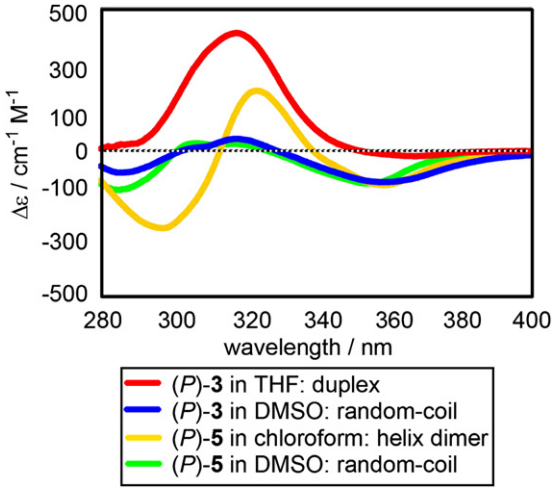

Fig. 11. CD spectra of (*P*)-**3** and (*P*)-**5** (each 2.5×10^{-6} M) in various solvents at 25 °C.

3. Conclusion

To summarize, the reversed tetramer (*P*)-**3** was synthesized from 1,12-dimethylbenzo[*c*]phenanthrene-5,8-diamine and isophthalate. The tetramer (*P*)-**3** formed a duplex in THF, and was a random-coil in DMSO. The equilibrium between the duplex and random-coil was not affected by temperature change between 5 and 60 °C. The duplex structure of (*P*)-**3** was stable in THF, whereas (*P*)-**5** did not form dimeric aggregate in the same solvent. The tetramer (*P*)-**3** did not form heteroaggregates with either (*P*)-**5** or (*M*)-**5**, and formed only homoaggregates.

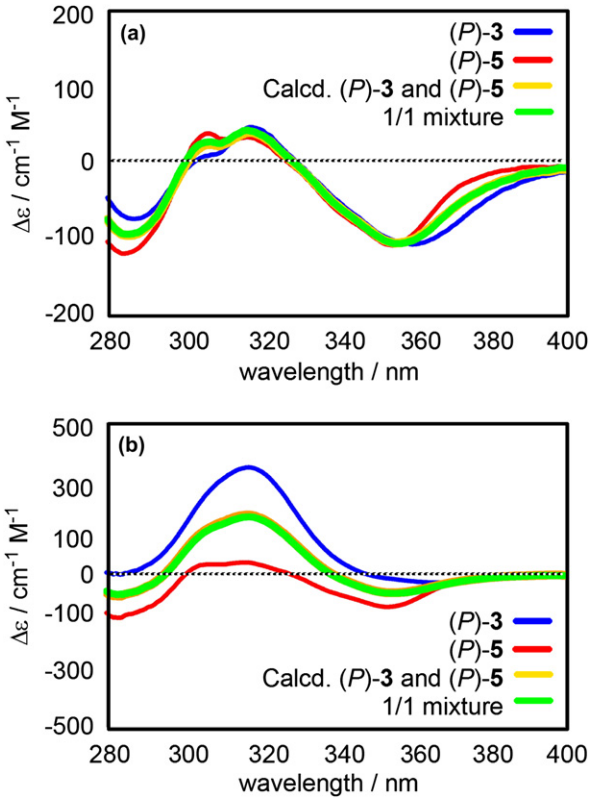

Fig. 12. CD spectra of a 1/1 mixture of (*P*)-**3** and (*P*)-**5** (each 2.5×10^{-6} M), (*P*)-**3**, and (*P*)-**5** (5.0×10^{-6} M) in various solvents at 25 °C: (a) DMSO, (b) THF. The spectrum calculated by adding those of (*P*)-**3** and (*P*)-**5** is also shown.

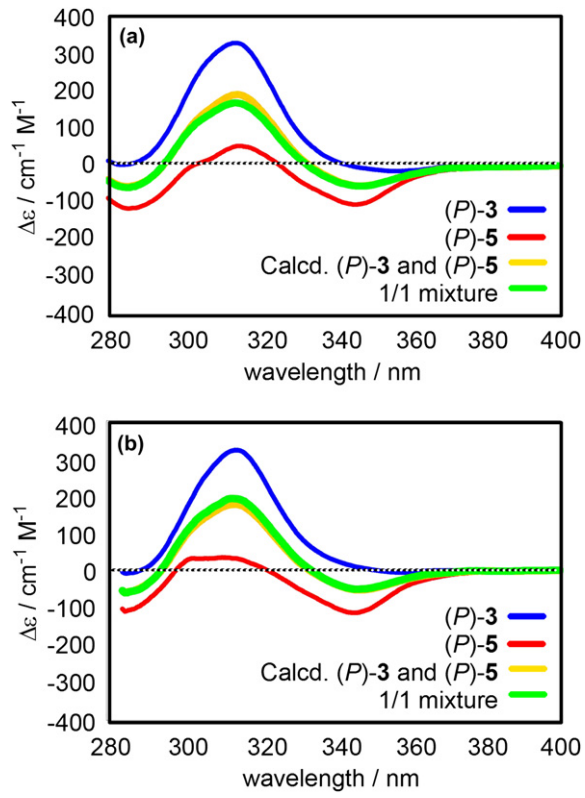

Fig. 13. CD spectra of a 1/1 mixture of (*P*)-**3** and (*P*)-**5** (each 2.5×10^{-6} M), (*P*)-**3**, and (*P*)-**5** (5.0×10^{-6} M) in various solvents at 25 °C: (a) chloroform/DMSO 95/5, (b) toluene/DMSO 99/1. The spectrum calculated by adding those of (*P*)-**3** and (*P*)-**5** is also shown.

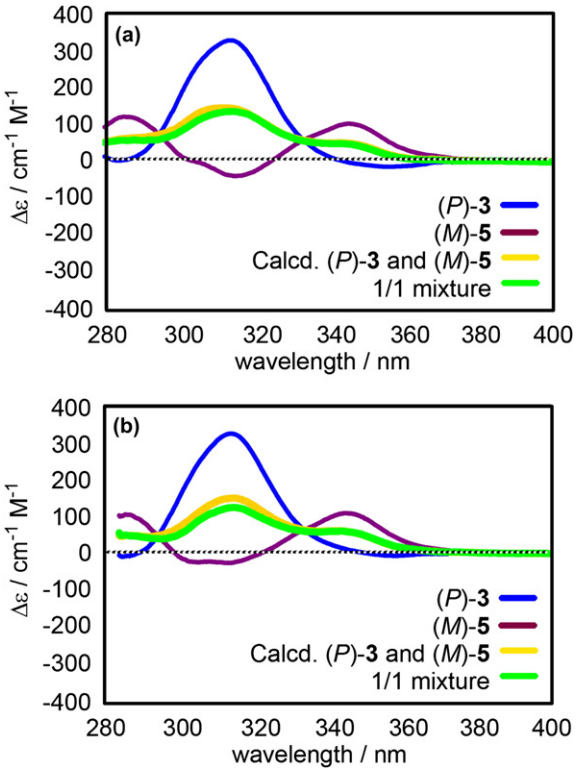

Fig. 14. CD spectra of a 1/1 mixture of (*P*)-**3** and (*M*)-**5** (each 2.5×10^{-6} M), (*P*)-**3**, and (*M*)-5 (5.0×10^{-6} M) in various solvents at 25 °C: (a) chloroform/DMSO 95/5, (b) toluene/DMSO 99/1. The spectrum calculated by adding those of (*P*)-**3** and (*M*)-**5** is also shown.

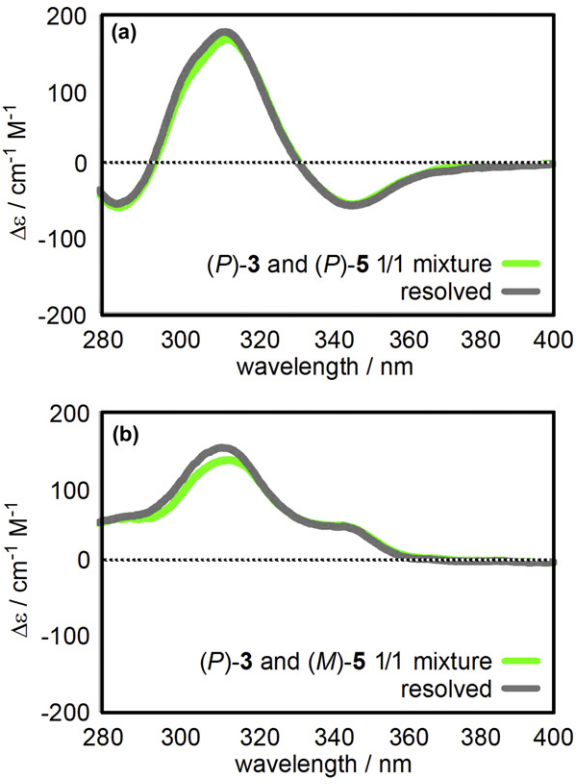

Fig. 15. CD spectra at 25 °C in chloroform/DMSO 95/5: (a) 1/1 mixture of (*P*)-**3** and (*P*)-**5** (each 2.5×10^{-6} M), (b) 1/1 mixture of (*P*)-**3** and (*M*)-**5** (each 2.5×10^{-6} M). Once their samples were evaporated in vacuo, they were resolved in the same solvent and observed as gray lines.

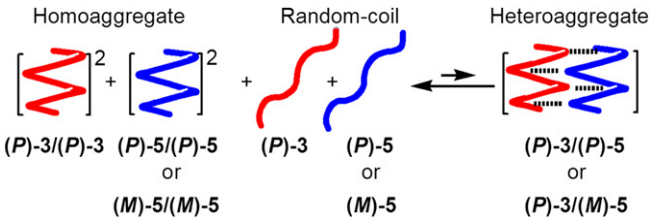

Fig. 16. Homoaggregation in mixed systems of (*P*)-**3** and (*P*)/(*M*)-**5**.

4. Experimental section

4.1. General methods

Melting points were determined with a Yanagimoto micro melting point apparatus without correction. Elemental analyses were conducted with Yanaco CHN CORDER MT-6. Optical rotations were measured on a JASCO P-1010 digital polarimeter. IR spectra were measured on a JASCO FT/IR-400 spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury (^{1}H, 400 MHz; ^{13}C, 100 MHz) with tetramethylsilane as an internal standard. ^{1}H NMR spectra taken in acetone-d_6 (δ 2.04), DMSO-d_6 (δ 2.49), CD_3OD (δ 3.30), and THF-d_8 (δ 3.58) were referenced to the residual solvents. ^{13}C NMR spectra taken in $CDCl_3$ (δ 77.0), acetone-d_6 (δ 206.5), DMSO-d_6 (δ 39.7), and CD_3OD (δ 49.0) were referenced to the residual solvents. Low- and high-resolution mass spectra were recorded on a JEOL JMS DX-303, or a JEOL JMS AX-700 spectrometer. FAB mass spectra were recorded on a JEOL JMS DX-303, or a JEOL JMS AX-700 spectrometer by using 3-nitrobenzyl alcohol (NBA) matrix. MALDI-TOF MS spectra were recorded on a Perseptive Biosystems Voyager™ DE observing with negative ion mode and using 2-amino-5-nitropyridine as a matrix. CD spectra were measured on a JASCO J-720 spectropolarimeter. Vapor pressure osmometry (VPO) was conducted with a KNAUER K-7000 molecular weight apparatus using benzyl as a standard. Gel permeation chromatography (GPC) was conducted with a Recycling Preparative HPLC LC-908 or LC-918 (Japan Analytical Industry, Co. Ltd.).

4.2. Synthesis and characterization

*4.2.1. (P)-5-Amino-8-(tert-butoxycarbonyl)amino-1,12-dimethylbenzo[c]phenanthrene, (P)-**9** and (P)-5,8-di-(tert-butoxycarbonylamino)-1,12-dimethylbenzo[c]phenanthrene, (P)-**1**.* To a solution of (*P*)-5,8-diamino-1,12-dimethylbenzo[*c*]phenanthrene[8] (226.0 mg, 0.789 mmol) in 1,4-dioxane (3.38 mL) and water (0.56 mL) were added triethylamine (0.229 mL, 1.64 mmol) and di(*tert*-butyl)dicarbonate (0.217 mL, 0.945 mmol) at 0 °C. The mixture was stirred vigorously at room temperature for 24 h.[13] The reaction was quenched by adding 10% citric acid, and the organic materials were extracted with ethyl acetate twice. The combined organic layers were washed with water twice, brine, and dried over magnesium sulfate. The solvents were removed in vacuo, and separation by silica gel chromatography (ethyl acetate/hexane=1/3) gave (*P*)-**9** (191.5 mg, 63%), (*P*)-**1** (40.8 mg, 0.084 mmol, 11%) and recovered diaminohelicene (56.9 mg, 25%).

Compound (*P*)-**9**. Mp 205–207 °C (hexane/diethyl ether). $[\alpha]_D^{21}$ −430 (*c* 0.50, $CHCl_3$). LRMS (EI, 70 eV) *m*/*z* 386 (M^+, 18%), 330 ($M^+-{}^t$Bu, 41%), 312 (M^+-O^tBu, 40%), 286 (M^+−Boc, 100%). HRMS *m*/*z* calcd for $C_{25}H_{26}N_2O_2$: 386.1993. Found: 386.1992. IR (KBr) 3448, 3369, 2960, 2868, 1709, 1630 cm^{-1}. Anal. ($C_{25}H_{26}N_2O_2$) Calcd: C, 77.69; H, 6.78; N, 7.25%. Found: C, 77.29; H, 6.96; N, 7.17%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.59 (9H, s), 1.91 (3H, s), 1.93 (3H, s), 4.35 (2H, br), 7.00 (2H, s), 7.36 (1H, d, *J*=7 Hz), 7.39 (1H, d, *J*=7 Hz), 7.49 (1H, dd, *J*=7, 9 Hz) 7.54 (1H, dd, *J*=7, 9 Hz), 7.84 (2H, t, *J*=9 Hz), 8.07 (1H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.5, 23.6, 28.4, 80.7, 107.0, 115.7,

117.1, 117.4, 117.9, 124.3, 124.5, 124.7, 128.2, 128.4, 131.7, 132.2, 132.4, 134.0, 136.2, 136.7, 141.3, 153.5.

Compound (*P*)-**1**. Mp 199–200 °C (ethyl acetate). $[\alpha]_D^{21}$ −354 (*c* 0.35, $CHCl_3$). LRMS (EI, 70 eV) *m*/*z* 486 (M^+, 11%), 386 (M^+−Boc+H, 38%). HRMS *m*/*z* calcd for $C_{30}H_{34}N_2O_4$: 486.2517. Found: 486.2525. IR (KBr) 3318, 2978, 2868, 1686 cm^{-1}. Anal. ($C_{30}H_{34}N_2O_4$) Calcd: C, 74.04; H, 7.05; N, 5.76%. Found: C, 73.90; H, 7.09; N, 5.69%. ^1H NMR (400 MHz, $CDCl_3$) δ 1.59 (18H, s), 1.91 (6H, s), 6.99 (2H, s), 7.39 (2H, d, *J*=7 Hz), 7.56 (2H, t, *J*=8 Hz) 7.88 (2H, d, *J*=8 Hz), 8.21 (2H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.4, 28.3, 80.6, 117.0, 117.6, 120.0, 125.2, 125.9, 128.2, 131.7 (two peaks), 132.7, 136.7, 153.5.

4.2.2. 5-Decyloxycarbonylbenzene-1,3-dicarboxylic acid, ***11****.* A mixture of 1,3,5-benzenetricarboxylic acid **10** (210 mg, 1.0 mmol) and sodium bicarbonate (84 mg, 1.0 mmol) were suspended in *N*,*N*-dimethylformamide (5 mL), and the mixture was stirred at room temperature for 12 h. 1-Bromodecane (0.42 mL, 2.0 mmol) was added, and stirring was continued for another 7 h at 90 °C.[10] Then, aqueous sodium carbonate (212 mg in 25 mL) was added, and the resulting mixture was extracted three times with diethyl ether. The organic layers were discarded. The aqueous layer was acidified with saturated aqueous potassium bisulfate, and extracted three times with ethyl acetate. The combined organic layers were washed with water and brine, and dried over magnesium sulfate. The solvents were removed in vacuo, and separation by silica gel chromatography (ethyl acetate/hexane=1/2) gave **11** (128.6 mg, 37%) and recovered benzenetricarboxylic acid (104 mg, 50%). Mp 194–195 °C (toluene). LRMS (EI, 70 eV) *m*/*z* 350 (M^+, 1%), 332 (M^+-H_2O, 1%), 211 (M^+−decyl+H, 100%). HRMS *m*/*z* calcd for $C_{19}H_{26}O_6$: 350.1728. Found: 350.1729. IR (KBr) 3084, 2956, 2920, 2852, 1735, 1701 cm^{-1}. Anal. ($C_{19}H_{26}O_6$) Calcd: C, 65.11; H, 7.48%. Found: C, 64.96; H, 7.31%. ^1H NMR (400 MHz, CD_3OD) δ 0.88 (3H, t, *J*=7 Hz), 1.26–1.51 (14H, m), 1.81 (2H, quint, *J*=7 Hz), 4.38 (2H, t, *J*=7 Hz), 8.80 (2H, d, *J*=2 Hz), 8.82 (1H, t, *J*=2 Hz). ^{13}C NMR (100 MHz, CD_3OD) δ 14.4, 23.7, 27.1, 29.7, 30.3, 30.4, 30.6, 33.1, 66.9, 132.7, 133.3, 135.2, 135.7, 166.4, 167.8.

4.2.3. 3-Benzyloxycarbonyl-5-decyloxycarbonyl-1-benzoic acid, ***12****.* A mixture of **11** (2.42 g, 6.9 mmol) and sodium bicarbonate (580 mg, 6.9 mmol) was suspended in *N*,*N*-dimethylformamide (24 mL), and the mixture was stirred at room temperature for 12 h. Benzyl bromide (1.7 mL, 13.9 mmol) was added, and stirring was continued for another 2.5 h at 90 °C.[10] The reaction was quenched by adding saturated aqueous potassium bisulfate at 0 °C, and the organic materials were extracted with ethyl acetate twice. The combined organic layers were washed with water and brine, and dried over magnesium sulfate. The solvents were removed in vacuo, and purification by silica gel chromatography (ethyl acetate/hexane=1/7) gave **12** (1.58 g, 52%) and recovered **11** (724 mg, 30%). Mp 82 °C (hexane). LRMS (EI, 70 eV) *m*/*z* 440 (M^+, 35%), 422 (M^+-H_2O, 14%), 333 (M^+−benzyloxy, 100%), 283 (M^+−decyloxy, 30%). HRMS *m*/*z* calcd for $C_{26}H_{32}O_6$: 440.2197. Found: 440.2199. IR (KBr) 3087, 2954, 2924, 2852, 1728, 1697 cm^{-1}. Anal. ($C_{26}H_{32}O_6$) Calcd: C, 70.89; H, 7.32%. Found: C, 70.87; H, 7.29%. ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (3H, t, *J*=7 Hz), 1.27–1.48 (14H, m), 1.80 (2H, quint, *J*=7 Hz), 4.38 (2H, t, *J*=7 Hz), 5.44 (2H, s), 7.35–7.49 (5H, m), 8.92 (1H, d, *J*=2 Hz), 8.94 (2H, t, *J*=2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.6, 25.9, 28.6, 29.2, 29.3, 29.5 (two peaks), 31.9, 66.0, 67.5, 128.4, 128.5, 128.7, 130.2, 131.4, 131.8, 135.1, 135.2, 135.4, 135.5, 164.7, 164.8, 170.3.

4.2.4. 3-Benzyloxycarbonyl-5-decyloxycarbonyl-1-benzoyl chloride, ***13****.* Potassium salt was prepared by mixing **12** (132 mg, 0.30 mmol) in THF/methanol (1/1, 3.0 mL) and 1.0 M potassium hydroxide in methanol (0.27 mL) at 0 °C. After being stirred for 5 min, the solvents were removed, and the residue was dried at room temperature for 18 h in vacuo. Under an argon atmosphere, the potassium salt was suspended in dichloromethane (3.0 mL), to which thionyl chloride (0.24 mL) and *N*,*N*-dimethylformamide (3 drops) were added. The mixture was stirred at room temperature for 1 h. Excess thionyl chloride was removed in vacuo, and the residue was azeotropically dried twice by adding toluene (1.0 mL) and evaporated in vacuo. The resulted acid chloride **13** (136.8 mg, 100%) was purified by rapid silica gel chromatography.[7] Mp 36–37 °C (hexane). LRMS (EI, 70 eV) *m*/*z* 460 ($C_{26}H_{31}{}^{37}ClO_5{}^+$, 10%), 458 ($C_{26}H_{31}{}^{35}ClO_5{}^+$, 26%), 423 ($C_{26}H_{31}O_5{}^+$, 37%), 368 ($M^+$−benzyloxy+H, 49%). HRMS *m*/*z* calcd for $C_{26}H_{31}{}^{35}ClO_5$: 458.1860. Found: 458.1843. IR (neat) 2954, 2925, 2854, 1765, 1733 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (3H, t, *J*=7 Hz), 1.27–1.48 (14H, m), 1.81 (2H, quint, *J*=7 Hz), 4.39 (2H, t, *J*=7 Hz), 5.44 (2H, s), 7.33–7.48 (5H, m), 8.90 (1H, t, *J*=2 Hz), 8.92 (1H, t, *J*=2 Hz), 8.97 (1H, t, *J*=2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 22.6, 25.9, 28.5, 29.2 (two peaks), 29.4 (two peaks), 31.8, 66.2, 67.6, 128.4, 128.5, 128.6, 131.8, 132.2, 134.2, 135.1, 135.6, 135.7, 136.4, 164.0, 164.1, 167.0.

*4.2.5. (P)-5-{3-(Benzyloxycarbonyl)-5-(decyloxycarbonyl)benzoylamino}-8-(tert-butoxycarbonylamino)-1,12-dimethylbenzo[c]phenanthrene, (P)-****14****.* Under an argon atmosphere, to a solution of (*P*)-**9** (217 mg, 0.56 mmol) in dichloromethane (50 mL) and pyridine (0.56 mL) was added acid chloride **13** (319 mg, 0.70 mmol) in dichloromethane (45 mL), and the mixture was stirred at room temperature for 12 h. Then, 2 M hydrochloric acid was added, and the organic materials were extracted with dichloromethane twice. The combined organic layers were washed with water and brine, and dried over magnesium sulfate. Purification by silica gel chromatography (ethyl acetate/hexane=1/6) gave (*P*)-**14** (394 mg, 87%). Mp 91–94 °C (hexane/THF). $[\alpha]_D^{21}$ −242 (*c* 0.25, $CHCl_3$). MS (FAB, NBA) *m*/*z* calcd for $C_{51}H_{56}N_2O_7$: 808.4084. Found: 808.4075. IR (KBr) 3242, 2954, 2925, 2854, 1728, 1684, 1649, 1523 cm^{-1}. Anal. ($C_{51}H_{56}N_2O_7$) Calcd: C, 75.72; H, 6.98; N, 3.46%. Found: C, 75.54; H, 6.95; N, 3.43%. ^1H NMR (400 MHz, acetone-d_6) δ 0.84 (3H, t, *J*=7 Hz), 1.25–1.51 (14H, m), 1.55 (9H, s), 1.81 (2H, quint, *J*=7 Hz), 1.91 (3H, s), 1.92 (3H, s), 4.39 (2H, t, *J*=7 Hz), 5.47 (2H, s), 7.35–7.63 (5H, m), 8.07 (1H, s), 8.08 (1H, s), 8.18 (1H, d, *J*=8 Hz), 8.24 (1H, d, *J*=8 Hz), 8.59 (1H, s), 8.80 (1H, s), 8.96 (1H, s), 8.98 (1H, s), 10.21 (1H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.6, 23.4, 23.5, 25.9, 28.3, 28.6, 29.3, 29.5 (two peaks), 31.8, 65.9, 67.3, 80.7, 118.2, 118.3, 118.7, 120.7, 121.6, 125.5, 125.6, 126.8, 126.9, 128.4, 128.5, 128.6, 130.7, 130.9, 131.3, 131.6, 131.7, 132.5, 132.7, 133.3, 135.4, 135.5, 136.6, 136.7, 153.9, 164.6, 164.9, 165.1.

*4.2.6. (P)-3-(Decyloxycarbonyl)-5-{1,12-dimethyl-8-(tert-butoxycarbonylamino)-benzo[c]phenanthrenyl}carbamoyl-benzoic acid, (P)-****15****.* Under a hydrogen atmosphere, a mixture of (*P*)-**14** (266 mg, 0.33 mmol) and palladium carbon (67 mg) in ethyl acetate (27 mL) was vigorously stirred at room temperature for 3 h. Then, the mixture was filtered, and filtrate was concentrated. Silica gel chromatography (ethyl acetate/hexane=1/2) gave (*P*)-**15** (231 mg, 98%). Mp 142–143 °C (hexane/ethyl acetate). $[\alpha]_D^{21}$ −239 (*c* 0.86, $CHCl_3$). MS (FAB, NBA) calcd for $C_{44}H_{50}N_2O_7$: 718.3615. Found: 718.3633. IR (KBr) 3253, 3066, 2954, 2925, 2854, 1728, 1703, 1660, 1599, 1523 cm^{-1}. Anal. ($C_{44}H_{50}N_2O_7$) Calcd: C, 73.51; H, 7.01; N, 3.90%. Found: C, 73.33; H, 7.03; N, 3.71%. ^1H NMR (400 MHz, acetone-d_6) δ 0.84 (3H, t, *J*=7 Hz), 1.25–1.52 (14H, m), 1.55 (9 H, s), 1.83 (2H, quint, *J*=7 Hz), 1.94 (3H, s), 1.95 (3H, s), 4.41 (2H, t, *J*=7 Hz), 7.49 (2H, t, *J*=6 Hz), 7.58–7.65 (2H, m), 8.23 (2H, d, *J*=7 Hz), 8.26 (2H, d, *J*=8 Hz), 8.62 (1H, s), 8.84 (1H, s), 9.00 (1H, s), 9.02 (1H, s), 10.26 (1H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.6, 23.4, 23.5, 25.9, 28.3, 28.6, 29.3, 29.5 (two peaks), 31.8, 65.9, 67.3, 80.7, 118.2, 118.3, 118.7, 120.7, 121.6, 125.5, 125.6, 126.8, 126.9, 128.4, 128.5, 128.6, 130.7, 130.9, 131.3, 131.6, 131.7, 132.5, 132.7, 133.3, 135.4, 135.5, 136.6, 136.7, 153.9, 164.6, 164.9, 165.1.

4.2.7. (P)-5-(tert-Butoxycarbonylamino)-8-{3-(chlorocarbonyl)-5-(decyloxycarbonyl)benzoylamino}-1,12-dimethylbenzo[c]

*phenanthrene, (P)-**16**.* Potassium salt was prepared by mixing (*P*)-**15** (22 mg, 0.031 mmol) in THF/methanol (1/1, 0.30 mL) and 1.0 M potassium hydroxide in methanol (0.028 mL) at 0 °C. After being stirred for 5 min, the solvents were removed, and the residue was dried at room temperature for 18 h in vacuo. Under an argon atmosphere, to a suspension of the potassium salt in dichloromethane (0.31 mL) were added thionyl chloride (0.024 mL) and DMF (3 drops). The mixture was stirred at −20 °C for 1 h. Excess thionyl chloride was removed in vacuo, and the residue was azeotropically dried twice by added toluene (1.0 mL) and evaporated in vacuo. The resulted acid chloride (*P*)-**16** (18 mg, 92%) was purified by rapid silica gel chromatography.[7] Mp 103–105 °C (hexane). $[\alpha]_D^{22}$ −220 (*c* 0.65, $CHCl_3$). MS (FAB, NBA) *m*/*z* calcd for $C_{44}H_{49}N_2O_6{}^{35}Cl$: 736.3279. Found: 736.3317. IR (KBr) 3246, 2956, 2925, 2854, 1766, 1730, 1691, 1655, 1525 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 0.84 (3H, t, *J*=7 Hz), 1.25–1.52 (14H, m), 1.55 (9 H, s), 1.83 (2H, quint, *J*=7 Hz), 1.94 (3H, s), 1.95 (3H, s), 4.41 (2H, t, *J*=7 Hz), 7.49 (2H, t, *J*=6 Hz), 7.58–7.65 (2H, m), 8.23 (2H, d, *J*=7 Hz), 8.26 (2H, d, *J*=8 Hz), 8.62 (1H, s), 8.84 (1H, s), 9.00 (1H, s), 9.02 (1H, s), 10.26 (1H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.6, 23.4, 23.5, 25.9, 28.3, 28.6, 29.3, 29.5 (two peaks), 31.8, 65.9, 67.3, 80.7, 118.2, 118.3, 118.7, 120.7, 121.6, 125.5, 125.6, 126.8, 126.9, 128.4, 128.5, 128.6, 130.7, 130.9, 131.3, 131.6, 131.7, 132.5, 132.7, 133.3, 135.4, 135.5, 136.6, 136.7, 153.9, 164.6, 164.9, 165.1.

*4.2.8. Dimer (P)-**2**.* Under an argon atmosphere, to a solution of (*P*)-**9** (7.9 mg, 0.020 mmol) in pyridine (0.06 mL) was added (*P*)-**16** (18 mg, 0.025 mmol) in dichloromethane (4.9 mL), and the mixture was stirred at room temperature for 1 h. Then, 2 M hydrochloric acid was added, and the organic materials were extracted with ethyl acetate twice. The combined organic layers were washed with water, brine, and dried over magnesium sulfate. Purification by silica gel chromatography and GPC (THF) gave dimer (*P*)-**2** (22.8 mg, 86%). Mp 244 °C decomposed (hexane/THF). $[\alpha]_D^{22}$ −363 (*c* 0.033, THF). MS (MALDI-TOF, 2-amino-5-nitropyridine) calcd for $C_{69}H_{74}N_4O_8$: 1086.5502. Found: 1086.2154. ($[M-H]^-$). IR (KBr) 3261, 2956, 2925, 2854, 1724, 1689, 1647, 1523 cm^{-1}. Anal. ($C_{69}H_{74}N_4O_8$) Calcd: C, 76.20; H, 6.86; N, 5.16%. Found: C, 76.16; H, 6.77; N, 4.91%. ^1H NMR (400 MHz, DMSO-d_6) δ 0.80 (3H, t, *J*=7 Hz), 1.20–1.46 (14H, m), 1.53 (18H, s), 1.79 (2H, quint, *J*=7 Hz), 1.89 (6H, s), 1.90 (6H, s), 4.41 (2H, t, *J*=6 Hz), 7.50 (4H, t, *J*=7 Hz), 7.64 (2H, t, *J*=8 Hz), 7.65 (2H, t, *J*=8 Hz), 8.00 (2H, s), 8.09 (2H, s), 8.17 (4H, t, *J*=7 Hz), 8.89 (2H, s), 9.16 (1H, s), 9.44 (2H, s), 10.98 (2H, s). ^{13}C NMR (100 MHz, DMSO-d_6) δ 14.1, 22.2, 23.2 (two peaks), 25.7, 28.4, 28.8, 28.9, 29.1 (two peaks), 31.4, 65.6, 79.4, 119.0, 120.6, 121.1, 122.4, 125.8, 125.9, 127.8, 128.2, 128.6, 128.7, 130.9, 131.3, 131.4, 131.5, 131.8, 131.9, 132.8, 133.6, 135.8, 154.3, 165.1, 165.4.

*4.2.9. Diamine (P)-**17**.* Under an argon atmosphere, to a solution of (*P*)-**2** (58 mg, 0.053 mmol) in dichloromethane (2.1 mL) was added trifluoroacetic acid (0.40 mL) at 0 °C. The mixture was stirred vigorously at room temperature for 1 h. The reaction was quenched by adding saturated aqueous sodium bicarbonate at 0 °C, and the organic materials were extracted with ethyl acetate twice. The combined organic layers were washed with water and brine, and dried over magnesium sulfate. The solvents were removed in vacuo, and purification by silica gel chromatography and GPC (THF) gave diamine (*P*)-**17** (43 mg, 90%). Mp 180–185 °C (hexane/ethyl acetate). $[\alpha]_D^{22}$ −691 (*c* 0.69, DMSO). MS (FAB, NBA) calcd for $C_{59}H_{58}N_4O_4$: 886.4455. Found: 886.4448. IR (KBr) 3354, 3248, 2952, 2924, 2852, 1718, 1670, 1520 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ 0.80 (3H, t, *J*=7 Hz), 1.20–1.47 (14H, m), 1.79 (2H, quint, *J*=7 Hz), 1.85 (6H, s), 1.89 (6H, s), 4.40 (2H, t, *J*=6 Hz), 6.10 (4H, s), 7.38–7.49 (6H, m), 7.55 (2H, t, *J*=8 Hz), 7.82 (2H, s), 8.04 (2H, d, *J*=8 Hz), 8.17 (2H, d, *J*=8 Hz), 8.87 (2H, s), 9.13 (1H, s), 10.83 (2H, s). ^{13}C NMR (100 MHz, DMSO-d_6) δ 14.1, 22.3, 23.4, 25.7, 28.4, 28.9, 29.1, 31.5, 65.6, 115.7, 120.0, 120.9, 122.0, 123.8, 124.6, 124.8, 126.6, 128.3, 128.4, 130.8, 131.4, 131.8, 132.1, 132.4, 134.3, 134.6, 135.6, 135.8, 165.2, 165.3.

*4.2.10. Tetramer, (P)-**3**.* Under an argon atmosphere, to a solution of (*P*)-**17** (23 mg, 0.026 mmol) in dichloromethane (1.0 mL) and pyridine (0.16 mL) was added (*P*)-**16** (50 mg, 0.068 mmol) in dichloromethane (8.6 mL), and the mixture was stirred at room temperature for 1 h. Then, 2 M hydrochloric acid was added, and the organic materials were extracted with ethyl acetate twice. The combined organic layers were washed with water, brine, and dried over magnesium sulfate. Purification by silica gel chromatography and GPC (THF) gave tetramer (*P*)-**3** (28 mg, 48%). Mp 235 °C decomposed (hexane/THF). $[\alpha]_D^{22}$ +1345 (*c* 0.032, THF). MS (MALDI-TOF, 2-amino-5-nitropyridine) calcd for $C_{147}H_{154}N_8O_{16}$: 2287.1474. Found: 2286.7969 ($[M-H]^-$). IR (KBr) 3222, 2952, 2925, 2854, 1726, 1689, 1645, 1523 cm^{-1}. Anal. ($C_{147}H_{154}N_8O_{16}$) Calcd: C, 77.13; H, 6.79; N, 4.90%. Found: C, 76.73; H, 6.80; N, 4.70%. ^1H NMR (400 MHz, DMSO-d_6) δ 0.78 (9H, t, *J*=7 Hz), 1.19–1.45 (42H, m), 1.51 (18H, s), 1.79 (6H, quint, *J*=7 Hz), 1.88 (12H, s), 1.94 (12H, s), 4.40 (6H, t, *J*=6 Hz), 7.48 (4H, t, *J*=7 Hz), 7.55 (4H, d, *J*=7 Hz), 7.63 (4H, m), 7.69 (4H, t, *J*=8 Hz), 7.99 (2H, s), 8.08 (2H, s), 8.14–8.22 (10H, m), 8.90 (6H, s), 9.16 (3H, s), 9.43 (2H, s), 10.97 (2H, s), 11.03 (4H, s). ^{13}C NMR (100 MHz, DMSO-d_6) δ 14.1, 22.3, 23.2, 25.7, 28.4, 28.9, 29.1, 31.4, 65.6, 79.4, 119.0, 120.6, 121.1, 121.2, 122.4, 125.8, 126.2, 127.8, 128.2, 128.6, 128.8, 128.9, 130.9, 131.3, 131.4, 131.5, 131.6, 131.8, 131.9, 132.9, 133.1, 133.6, 135.7, 135.8, 136.0, 154.3, 165.1, 165.4.

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Supplementary data

These data include CD spectra of (*P*)-**3**. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2011.05.059. These data include MOL files and InChIKeys of the most important compounds described in this article.

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