Self-Assembly of Folic Acid Derivatives: Induction of Supramolecular Chirality by Hierarchical Chiral Structures

Yuko Kamikawa, Masayuki Nishii, and Takashi Kato*[a]

Abstract: Hierarchical chiral structures made up of dendritic oligo(L- or D-glutamic acid) moieties of folic acid derivatives induce supramolecular chirality in the self-assembled columnar structures of the folic acids. These folic acids self-assemble through the intermolecular hydrogen bonds of the pterin rings to form disklike tetramers. In the neat states, the stacked tetramers form thermotropic hexagonal columnar phases over wide temperature ranges, including room temperature. Addition of alkali metal salts induces chirality in the columnar phases. In dilute solution states in a relatively polar solvent (chloroform), the folic acid derivatives form non-chiral, self-assembled structures. In the presence of sodium triflate, the folic acid forms chiral columnar assemblies through the oligo(L-glutamic acid) moiety, similar to those formed in the liquid-crystalline (LC) states. The enantiomer of the folic acid induces columnar assemblies with reversed helicity. In the case of the diastereomer, no induced helicity is observed. Application of an apolar solvent (dodecane) drives the folic acid derivatives to form chiral assemblies in the absence of ions. In this case, lipophilic interactions promote nanophase segregation, which enhances the formation of chiral columns. Interestingly, the chiral supramolecular structure of the diastereomer induces the most intense circular dichroism. In both cases, the molecular chirality in the oligo(glutamate) moieties yields supramolecular chirality of the folic acids that self-assemble through cooperative molecular interactions.

Keywords: chirality · hydrogen bonds · liquid crystals · self-assembly · supramolecular chemistry

Introduction

Intensive studies have been focused on the development of molecular self-assembled materials obtained through noncovalent interactions.[1] Hydrogen bonding has been shown to be useful in molecular self-assembly, because this noncovalent interaction has moderate bonding energy, reversibility, and selectivity. Synthetic approaches to the construction of dynamically functional materials that use hydrogen bonds have been achieved for self-assembly in systems such as supramolecular liquid crystals,[2] ionophores,[3] nano-objects,[4] and supramolecular polymers.[5]

Our intention here is to develop functional materials based on biomolecules, because of their capability for molecular recognition and supramolecular association. Here we focus on folic acid, a vitamin, because of its self-assembling nature. The molecule consists of a pterin ring and a glutamic acid moiety, and self-assembly of folic acids and related molecules through intermolecular hydrogen bonds can result in the formation of self-organized materials.[6] We have previously developed thermotropic liquid-crystalline folic acids.[7] The addition of alkali metal salts to folic acid derivatives changes their self-assembled structures. Recently, we have found that folic acid derivatives form supramolecular liquid-crystalline cubic structures.[7a]

Another interesting feature of biomolecules is chirality. Folic acid is a useful candidate for such a chiral building block, because of its self-assembling nature and the molecular chirality in its amino acid component. Gottarelli, Spada, and co-workers reported that folic acids self-assembled in the presence of alkali metal salts to form chiral lyotropic liquid crystals.[6a–c] We have observed supramolecular chirality of folic acid derivatives in the thermotropic cubic phase. In these materials, π-stacked columnar assemblies play key roles in the induction of chirality.[7a,8] To date, a variety of supramolecular assemblies of chiral molecules have been reported.[9]

Columnar assemblies made up of stacked aromatic molecules have been explored widely in liquid-crystalline and dilute solution states. These π-stacked materials are basic structural motifs of discotic liquid crystals,[10] which are useful as electronic and photoconductive materials.[11] In

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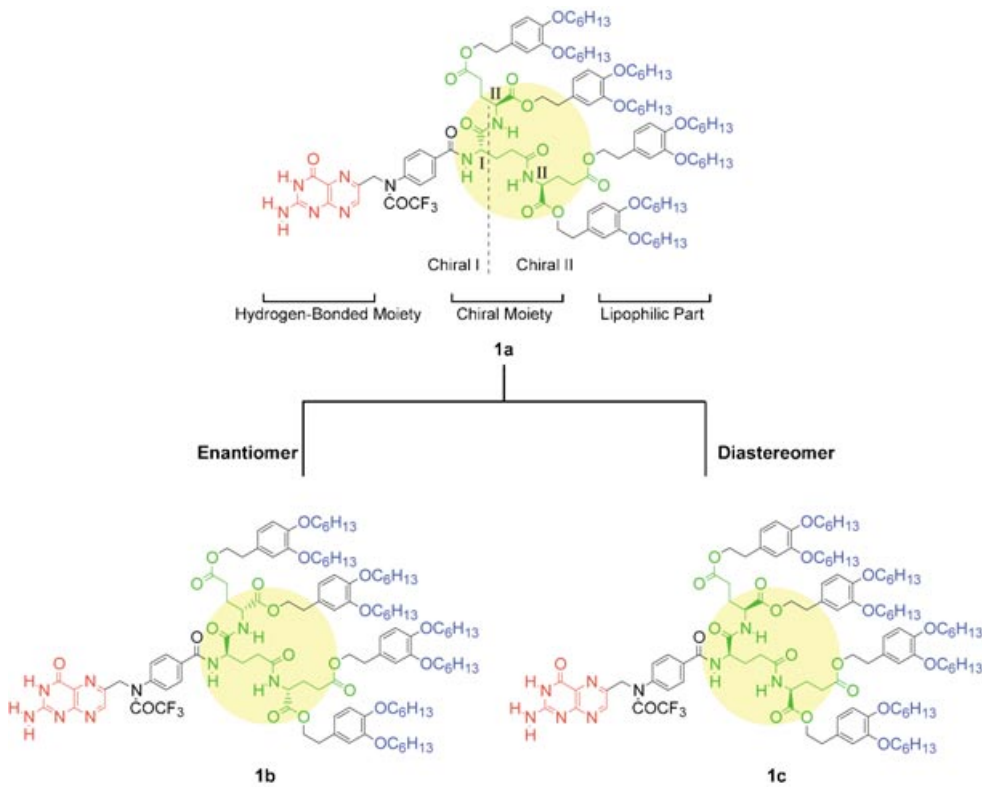
contrast, association of molecules in dilute solution is strongly influenced by solvent and temperature, since the attractive strengths of simple aromatic surfaces are generally weak. Several investigations into the creation of stable columnar assemblies through the use of cooperation between two or more secondary interactions, such as hydrogen bonds and lipophilic interactions, have been carried out.[12] Introduction of chirality into the side-chains of disk-shaped components induces helical stacked arrays that can be detected by CD spectroscopy. Molecular chirality is transferred to the central aromatic core, and is subsequently often amplified through the formation of supramolecular helical columns.[13] The potential for tuning of the supramolecular chirality of the columnar assemblies by external stimuli makes the development of new chiral architectures with dynamic properties particularly interesting.

Here we describe the induction and tuning of supramolecular chirality in the self-assembled folic acids **1a–c** in polar and apolar solution states and in bulk states (Scheme 1). Molecules **1a–c** are new chiral molecules with three-component structures consisting of pterin rings, chiral glutamate parts, and lipophilic alkyl parts, with the chiral glutamate part located between the pterin ring and the lipophilic part. We report on how such chiral molecular structures induce supramolecular chiral structures. We have synthesized the enantiomer of **1a** (**1b**) from D-glutamic acid, and also the diastereomer (**1c**). Their self-assembly properties have been examined. An analogous molecule of **1a** with undecyl chains forms a chiral cubic phase in the neat state.[7a] To the best of our knowledge, tuning of supramolecular chirality through these hierarchical chiral groups in one molecule has not yet been reported. We have found that molecular chirality greatly affects the supramolecular self-assembled structures in such hierarchical chirality.

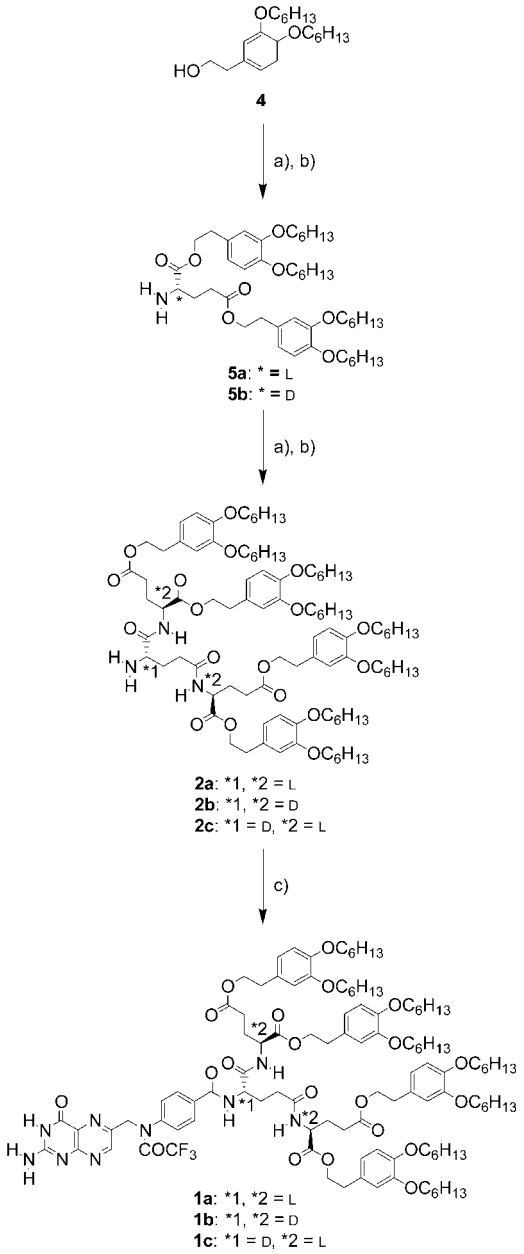
Results and Discussion

Synthesis of the folic acid derivative 1: Folic acid derivative **1** was prepared as shown in Scheme 2. 2-[3,4-Bis(hexyloxy)-phenyl]ethanol (**4**), *N*-Fmoc-glutamic acid, and N^{10}-(trifluoroacetyl)pteroic acid were synthesized according to the literature.[7d] Esterification of **4** with *N*-Fmoc-L-glutamic acid, followed by deprotection with piperidine as a base, gave **5a** in a yield of 67%. Similarly, esterification of **4** with *N*-Fmoc-D-glutamic acid and subsequent deprotection afforded **5b** in 75% yield. Oligo(glutamate) derivatives **2a–c** were obtained in moderate yields after repetition of the same procedure with **5a** and **5b** as starting materials. Finally, **1a–c** were prepared after coupling of compounds **2** with N^{10}-(trifluoroacetyl)pteroic acid.

Self-assembly of 1 in neat states and structural analysis: Compounds **1a–c** exhibit hexagonal columnar phases over wide temperature ranges (Table 1). Compounds **1a** and **1b** show identical thermal properties, while the diastereomer **1c** has a clearing point of 173 °C, 11 °C higher than that of **1a**. Interestingly, the chiral structural change between **1a** and **1c** induces thermal stabilization.

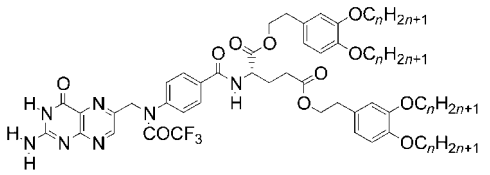


Scheme 1. Design and structures of folic acid derivatives **1a–c**.



Scheme 2. a) *N*-Fmoc-glutamic acid, DMAP, EDC, CH_2Cl_2, r.t., 1 d; b) piperidine, $CHCl_3$, RT, 1 h; c) N^{10}-(trifluoroacetyl)pteroic acid, *i*BuOCOCl, Et_3N, THF/DMF, 40 °C, 3 d, dark.

The isotropization temperature of **1a** and **1b** is 162 °C, while for folic acid derivatives **3** ($n=18$) with one glutamic acid moiety, more thermally stable columnar phases are observed over 200 °C.[7d] Steric repulsion of the bulky alkyl part of **1a** may suppress effective stacking, resulting in decreasing isotropization temperatures.



Variable-temperature infrared (IR) spectra show the formation of hydrogen bonds involving the pterin rings. The pterin ring N–H stretching bands show three broad peaks (3334, 3160, and 3054 cm^{-1}), indicating the disklike aggregation of the folic acid derivatives[7d] (see Supporting Information). Small-angle X-ray scattering (SAXS) measurements show that the diameters of the self-assembled columns of **1a** and **1c** are 48 and 49 Å, respectively (see Supporting Information). These values agree well with that estimated by the MM2 method for the tetramer (50 Å). Folic acid is known to form disklike tetramers through these intermolecular hydrogen bonds.[6a–c,7] The current observations suggest that compounds **1a–c** self-assemble into disklike tetramers through intermolecular pterin ring hydrogen bonds, and that these tetramers stack to form hexagonal columnar structures.

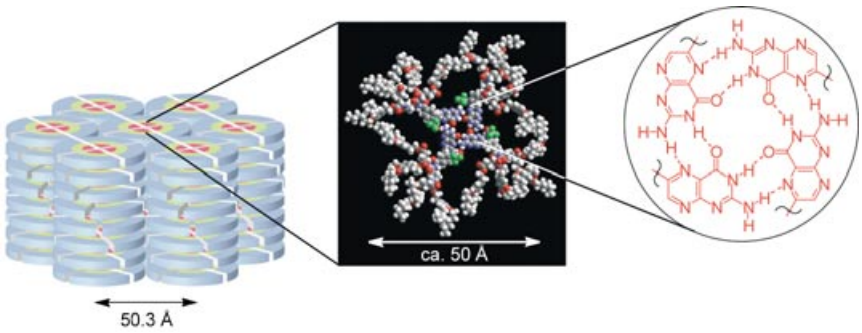
For **1a** and **1b**, the addition of sodium triflate ($NaOSO_2CF_3$, 25 mol%) increases their clearing points from 162 to 169 °C, and also induces the cubic phases above 143 °C (Table 1). No thermal stabilization of the mesophases is observed for the complex of diastereomer **1c** and sodium triflate (25 mol%). We have recently reported that a compound analogous to **1a** but possessing undecyl chains shows a chiral cubic phase.[7a] We focus here on the columnar phase relevant to self-assembled structures in the solution state. The SAXS profiles of **1a–c** forming columnar phases in the presence of $NaOSO_2CF_3$ show the same trends as those of **1a–c** alone (see Supporting Information); these results suggests that diastereomer **1c** and its complex with sodium salts forms stacked structures similar to compounds **1a** and **1b** (Scheme 3).

Table 1. Liquid-crystalline behavior of **1** and complexes of **1**/$NaOSO_2CF_3$ on the second heating.

Compounds[a]	Phase transition behavior[c]							Lattice parameter [Å][e]
1a			G	−28	Col_h	162 (4.4)	Iso	48.3
1b			G	−28	Col_h	162 (6.4)	Iso	47.7
1c			G	−19	Col_h	173 (5.3)	Iso	48.8
1a+**1b**[b]			G	−28	Col_h	162 (6.7)	Iso	48.5
1a/$NaOSO_2CF_3$	G	−22	Col_h	143 (–[d])	Cub	169 (6.9)	Iso	51.0
1b/$NaOSO_2CF_3$	G	−22	Col_h	143 (–[d])	Cub	169 (6.4)	Iso	51.3
1c/$NaOSO_2CF_3$	G	−16	Col_h	143 (–[d])	Cub	171 (11)	Iso	51.2
(**1a**+**1b**)/$NaOSO_2CF_3$[b]	G	−22	Col_h	143 (–[d])	Cub	169 (2.8)	Iso	50.2

[a] Molar ratio of **1**/$NaOSO_2CF_3$ = 0.25. [b] Racemic mixture of **1a** and **1b**. [c] Transition temperatures [°C] and enthalpy changes [kJ mol^{-1}] in parentheses. G: glassy; Col_h: hexagonal columnar; Cub: cubic; Iso: isotropic. [d] Transitions from columnar to cubic phases were not detected on DSC thermograms. [e] Col_h phase at 60 °C.

Circular dichroism (CD) and UV/Vis spectra of thin films of **1a** and **1a**/$NaOSO_2CF_3$ were measured in the hexagonal columnar states (Figure 1). The samples were prepared on quartz plates by casting solutions of the compounds prepared in chloroform. The CD spectrum of pure **1a** is inactive (Figure 1a), indicating that the columnar structures formed do



Scheme 3. Schematic representation of self-assembled **1a**/$NaOSO_2CF_3$ in hexagonal columnar phases.

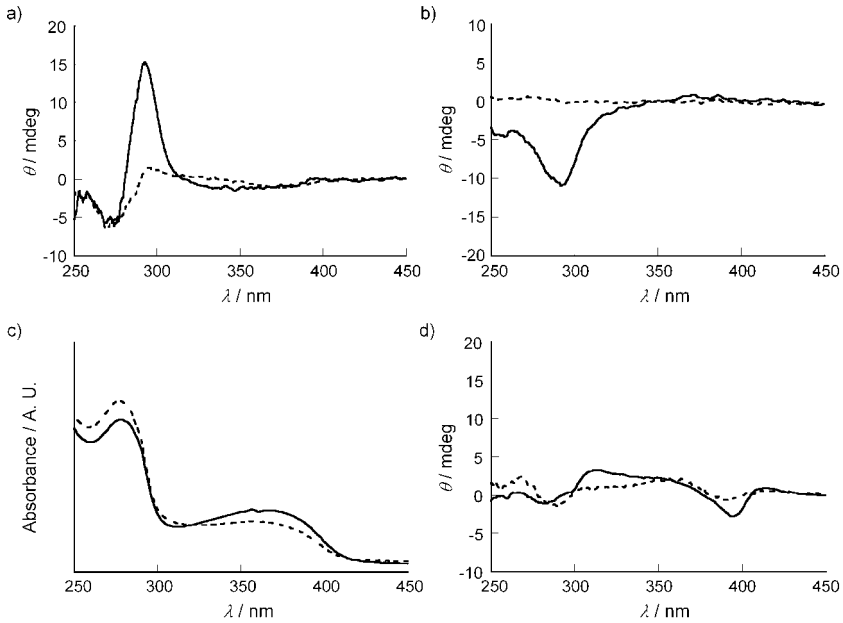


Figure 1. a) CD spectra of **1a** (broken line) and **1a**/$NaOSO_2CF_3$ (solid line; molar ratio = 0.25); b) CD spectra of **1b** (broken line) and **1b**/$NaOSO_2CF_3$ (solid line; molar ratio = 0.25); c) UV spectra of **1a** (broken line) and **1a**/$NaOSO_2CF_3$ (solid line; molar ratio = 0.25); d) CD spectra of **1c** (broken line) and **1c**/$NaOSO_2CF_3$ (solid line). All spectra were measured in the hexagonal columnar phase at 60 °C.

not have chiral order. In contrast, the addition of sodium triflate to **1a** gives rise to a positive CD spectrum in the absorption wavelength ranges of pterin rings (Figure 1a,c). These results show that the introduction of sodium ions into the columnar assemblies leads to the formation of supramolecular chiral structures along the columnar axis. Sodium salts play important roles not only in the stabilization of the self-assembled structures, but also in the induction of the supramolecular chiral assemblies, in which helical stacking may be induced. For **1c**, less active CD spectra are seen both in the presence and in the absence of sodium ions (Figure 1 d), suggesting that the molecular structure of **1c** is not suitable for the formation of chiral columnar structures.

Self-assembly of 1 in solution: We have examined the self-assembly behavior of **1** in dilute solution states and have found that supramolecular chirality in solution is induced by the salt for self-assembled **1**. Particularly interesting are the effects of polar and apolar environments on supramolecular chirality induction of **1**.

The CD and UV/Vis spectra of **1a** in chloroform are shown in Figure 2. The absorption of the pterin rings of **1a** appears at 280 and 352 nm (Figure 2b), and an inactive CD spectrum is observed (Figure 2a). The **1a**/$NaOSO_2CF_3$ complex (molar ratio of **1a**/$NaOSO_2CF_3$ = 1:0.25) induces a coupled CD curve centered at 280 nm with a positive extreme at 293 nm, a negative extreme at 272 nm, and a broad negative CD band around 360 nm (Figure 2a).

It is considered that disklike tetramers of **1** stack to form columnar assemblies in the presence of $NaOSO_2CF_3$ for the following reasons:

1) In our previous work on folic acid derivatives in neat states,[7a] we reported that an analogous folic acid compound possessing undecyl chains formed the disklike tetramer in the presence of alkali metal ions.
2) The infrared spectrum (3000–3500 cm^{-1}) of **1** in concentrated chloroform is almost identical to those of

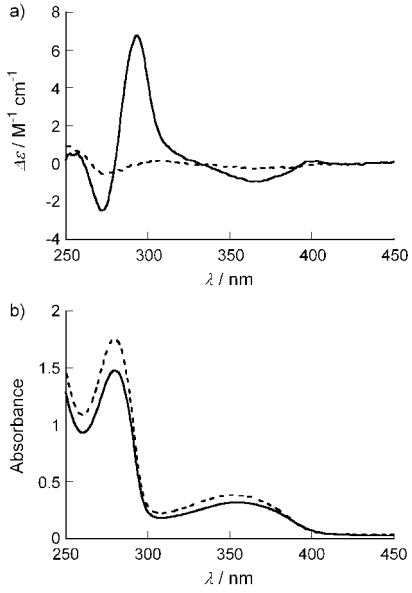


Figure 2. a) CD and b) UV/Vis spectra of **1a** (broken line) and **1a**/$NaOSO_2CF_3$ (solid line; molar ratio = 0.25) in chloroform (5.0×10^{-3} M) at 20 °C.

1 in the LC states and of the tetramer form of **3** ($n=11$)[7d] (see Supporting Information).

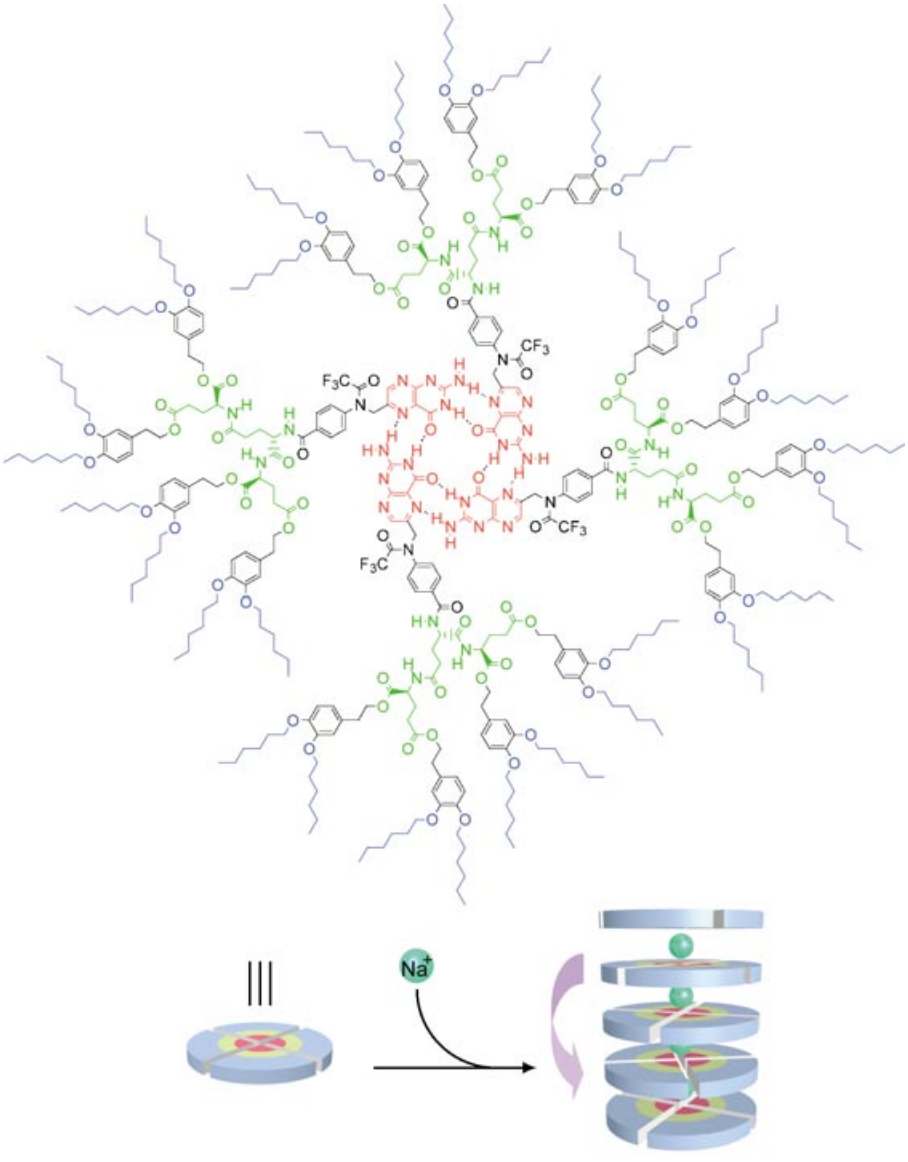
3) Moreover, an aqueous solution of a simple sodium folate exhibits an induced CD spectrum generated through helical stacking of self-assembled tetramers of folic acids.[6b,c]
4) For guanosine derivatives with the same hydrogen-bonded pattern as **1**, a single-crystal X-ray structure determination shows the formation of the same hydrogen-bonded pattern as seen in the stacked tetramer structure of **1** in the presence of alkali metal ions.[3a] When dissolved in tetrachloroethane, these G-quadruplex crystals produced a strong CD spectrum in the absorption ranges of the guanine chromophores, originating from helical stacking of tetramers.

These results suggest that compounds **1** self-assemble in chloroform to form disklike tetramers, which should stack to form columnar assemblies through ion–dipolar interactions between sodium salts and the carbonyl groups of the pterin rings (Scheme 4).

Compound **1a** has three chiral groups, and we are interested in how the molecular chirality of these three amino acids in **1a** affects its self-assembled structures in solution. The CD spectra of **1b** and **1c** and their complexes are compared with those of **1a** and its complex in Figure 3. Each of the single components of **1a–c** has only a weak CD spectrum (Figure 3a), while the complex of the enantiomer **1b** and $NaOSO_2CF_3$ shows a negative Cotton effect (Figure 3b), which is a mirror image of the induced CD spectrum of **1a**/$NaOSO_2CF_3$. These results indicate the formation of the same chiral columnar assemblies of **1b** as in **1a**, but with reversed helicity. In contrast, no supramolecular chirality is observed for **1c** either in the presence or in the absence of sodium salts, and the diastereomer **1c**/$NaOSO_2CF_3$ shows only an inactive CD spectrum. Thus, compound **1c** may form columnar structures consisting of randomly stacked tetramers.

A racemic mixture of equimolar **1a** and **1b** was also prepared; Figure 3b shows that no CD effect is observed for the racemic mixture in the presence of sodium salts.

When **1a**/$NaOSO_2CF_3$ was mixed with **1b**/$NaOSO_2CF_3$ in a different molar ratio, the CD intensity decreased in proportion to the added amount of **1b** (within experimental error), indicating that no specific cooperative interactions were occurring. The ^1H NMR spectrum of an equimolar mixture of (**1a**+**1b**)/$NaOSO_2CF_3$ is identical to those of **1a** or **1b** alone in the presence of the salts (see Supporting Information). These results suggest that homochiral tetramers are formed and that no cooperative interactions exist between the columns.[9f,14] It is difficult to distinguish by spectroscopic methods whether a column consists of pure enantiomers or stacks of segmented homochiral columns. For neat columnar materials, a racemic mixture of **1a** and **1b** shows the same thermal properties as **1a** alone, both in the presence and in the absence of sodium salts (Table 1). Moreover, XRD profiles are identical for the columnar liquid crystals of the racemic mixture and the enantio-



Scheme 4. Schematic representation of self-assembled **1a**/$NaOSO_2CF_3$ in chloroform solution state.

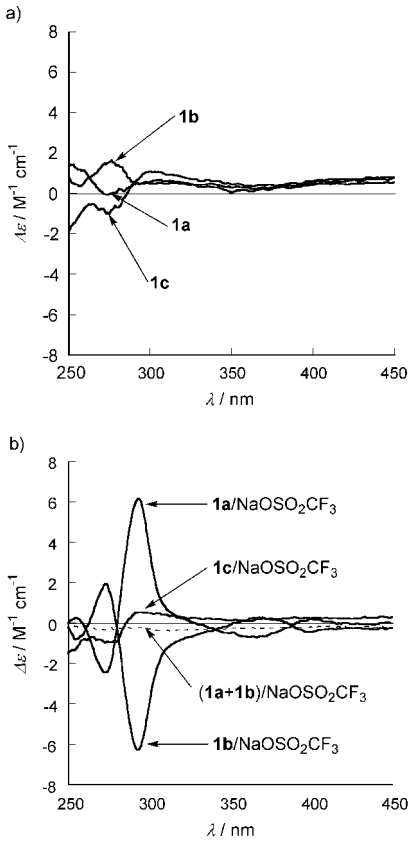


Figure 3. CD spectra of **1a–c** a) in the absence and b) in the presence of $NaOSO_2CF_3$ (molar ratio = 0.25) in chloroform (5.0×10^{-3} M, 20 °C).

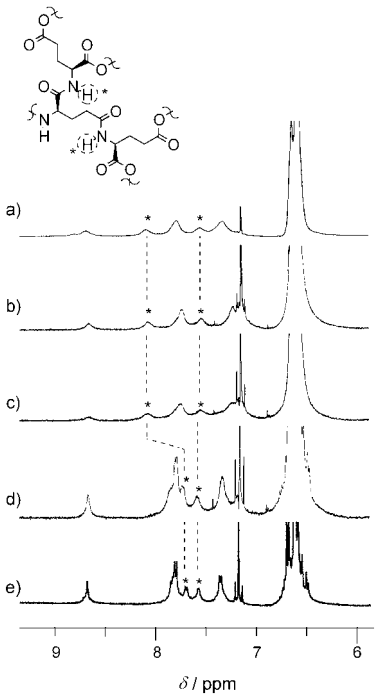
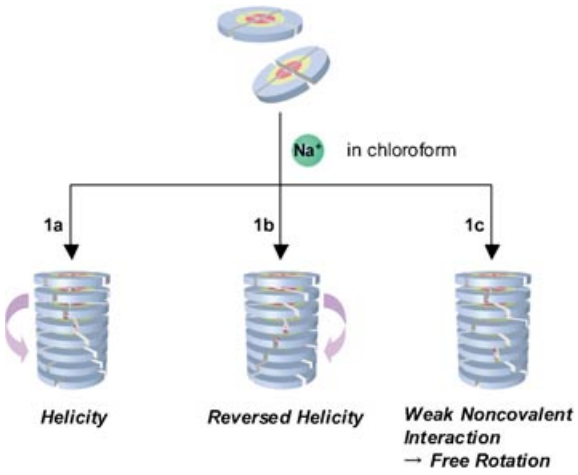


Figure 4. a) ^{1}H NMR spectrum of **1a**; b) ^{1}H NMR spectrum of **1a**/$NaOSO_2CF_3$; c) ^{1}H NMR spectrum of **1b**/$NaOSO_2CF_3$; d) ^{1}H NMR spectrum of **1c**/$NaOSO_2CF_3$; e) ^{1}H NMR spectrum of **1c**. Asterisks denote amide protons of oligo(glutamate) parts. All spectra were measured in chloroform-d (5.0×10^{-3} M).



Scheme 5. Schematic representation of the formation of chiral columnar assemblies in chloroform solution.

merically pure components. These results are consistent with our proposed formation of homochiral columns.

The ^{1}H NMR spectrum of **1** in $CDCl_3$ at the same concentration as used in the CD measurements is shown in Figure 4. No difference in the spectrum of **1** is observed in the absence or in the presence of $NaOSO_2CF_3$ (Figure 4a,b). The two complexes of **1a** and **1b** with $NaOSO_2CF_3$ have identical spectra, as would be expected (Figure 4b,c), while for **1c**/$NaOSO_2CF_3$, the amide proton peaks appear at 7.8 ppm (Figure 4d), due to weak hydrogen bonding. The hydrogen-bonded structures of self-assembled **1c**/$NaOSO_2CF_3$ are different from those of **1a** and **1b**, although these hydrogen-bonding properties are the same for the complex of **1c**/$NaOSO_2CF_3$ and compound **1c** alone (Figure 4d,e).

These results suggest that supramolecular chirality induced in the aggregates of **1a–c** is dependent on the chirality of the oligo(glutamate) parts (Scheme 5). Moreover, cooperative interactions such as ion–dipolar interactions and hydrogen bonds play key roles in transferring the molecular chirality of the oligo(glutamate) parts to the supramolecular chirality of the assemblies.

Self-assembly of 1 in a lipophilic environment: In apolar solvents we expected that molecular assembly of the columnar structures for **1a–c** should proceed due to lipophilic interactions between the alkyl chains of **1** and the solvent (dodecane). The three components of the molecules undergo microphase segregation at the nanometer scale and the lipophilic units surround the column. Self-assembly behavior in dodecane was examined for **1a–c**. The UV/Vis and CD spectra of **1a** alone in dodecane are compared with those in chloroform in Figure 5. A strong negative CD spectrum is induced for **1a** in dodecane, whereas no appreciable CD is observed in chloroform (Figure 5a). The red shift from 357 nm to 367 nm in the UV/Vis spectra indicates that the tetramers of **1a** stack in dodecane, resulting in π–π interactions between the pterin rings (Figure 5b). These results suggest that use of dodecane as solvent results in self-organiza-

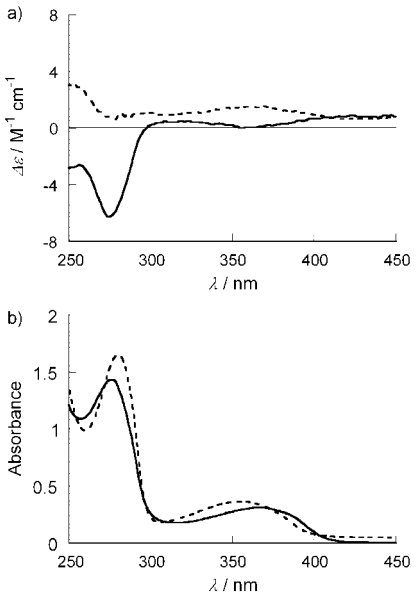


Figure 5. a) CD and b) UV/Vis spectra of **1a** in chloroform (broken line) and in dodecane (solid line) solution (5.0×10^{-4} M at 20 °C).

tion of compound **1a** in the absence of salts, the chiral assemblies being formed solely through cooperative hydrogen bonds and lipophilic interactions. In this case, the lipophilic fraction of the material increases and the microphase-segregated structures are enhanced, resulting in the induction of supramolecular chirality without the need for the ion. The IR spectrum (3000–3500 cm^{-1}) of a concentrated solution of **1a** in dodecane (1.0×10^{-2} M) is similar to those in chloroform in the presence of salts and in the LC state; these results indicate that compound **1a** undergoes disklike aggregation in hydrocarbon solvents.

The effects of hierarchical molecular chirality on the self-assembled structures were also studied for **1a–c** in dodecane (Figure 6). The induced CD spectra of **1a** and **1b** are mirror images, as in the solutions prepared in chloroform. Compound **1b** induces a positive CD spectrum, in contrast to **1a**. It is of interest that the positive CD spectrum of **1c** is similar to that of **1b**, while its intensity is greater than that of **1b**. The stronger Cotton effect should be due to more stable chiral aggregates formed by **1c**. These results indicate that the supramolecular chirality of the assemblies depends on

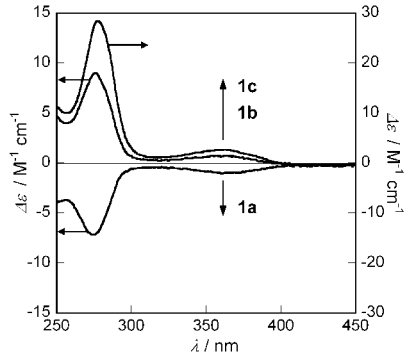
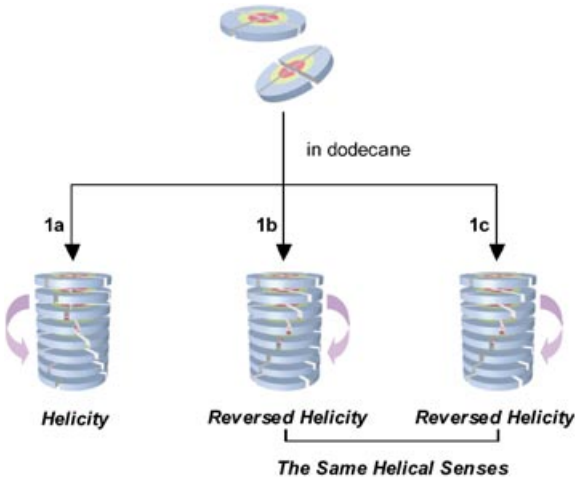


Figure 6. CD spectra of **1a–c** in dodecane solution (5.0×10^{-4} M at 20 °C).

the internal chirality (the Chiral I part of **1a–c** in Scheme 1) of the oligo(glutamic acid) parts; that is, the chirality closest to the pterin rings. The effects of the apolar environment on the self-assembly of **1a–c** are summarized in Scheme 6.



Scheme 6. Schematic representation of the formation of chiral columnar assemblies in dodecane solution.

It should be noted that **1c** adopts the same supramolecular chiral structures as **1b** in dodecane. However, **1c** forms a different structure both in chloroform and in columnar liquid crystal states, as shown in the CD spectra of **1** (Figures 1 and 3). These observations suggest that this series of molecules is capable of changing its supramolecular chiral structures depending on external environments.

Meijer reported that disk-shaped molecules helically assemble in an apolar hydrocarbon solvent, while they molecularly dissociate in chloroform.[13b] Unlike Meijer's compounds, the materials in this study—the disk-shaped folic acid tetramers in chloroform—helically assemble to exhibit Cotton effects in the presence of salts. In dodecane they assemble in a different manner, to induce circular dichroism in the absence of salts. It should be noted that the folic acid derivatives form chiral columnar structures both in polar and in apolar solvents.

The helical stacked disklike tetramers should be formed in dodecane solution. In the case of lyotropic liquid crystalline properties of compound **3** ($n=11$), which forms a thermotropic smectic phase in the bulk state, the compound shows hexagonal and nematic columnar phases without added ions.[7c] The formation of nematic columnar phases supports the involvement of the stacked tetramer. Without templating sodium salts, self-assembly of compounds **1a–c** should be strongly affected by hydrogen bonds of peripheral glutamic acid parts. The diastereomer **1c** forms the same chiral structure as **1b**, as shown in Figure 6. The inner chiral parts of the oligo(glutamate) moieties in **1b** and **1c** have the same stereoregularity. Thus, from this model we suggest that the chirality of the self-assembled columns is determined by the chiral part closest to the pterin ring (Scheme 6). Anoth-

er possible structure would be supramolecular pterin helices similar to guanosine helices, as recently suggested by Gottarelli and co-workers.[6d] These helices are formed through the same disklike hydrogen bonding of pterin rings in the absence of templating ions. Furthermore, the CD patterns of solutions of **1a–c** in chloroform and dodecane are similar to those of guanosine derivatives in dichloroethane and dodecane. According to modeling simulations,[6d] the energies of the two assembled structures are almost the same for guanosine materials.

Conclusion

This paper reports supramolecular chirality arising from hierarchical chiral structures in oligo(glutamate) moieties in folic acid derivatives **1a–c**. The self-assembled columns of the folic acid derivatives are formed through cooperative secondary interactions, such as hydrogen bonds, stacking interactions, ion–dipolar interactions, and nanophase segregation of molecular block structures. The addition of salts triggers chiral self-assembly of **1a–c** in the liquid-crystalline state and in polar environments, whereas chiral self-assembly in **1a–c** proceeds spontaneously in apolar environments, induced by lipophilic interactions. The chiral behavior of the compounds depends on their environments. This is the first example of tuning of supramolecular chirality through hierarchical chiral block structures. The results presented here may provide a new design strategy for developing chiral functional materials.

Experimental Section

General methods and materials: All starting materials were obtained from commercial suppliers and were used without further purification. Analytical thin-layer chromatography (TLC) was performed on 0.25 mm silica gel plates (E. Merck, Silica Gel F_{254}), and silica gel column chromatography was carried out with silica gel 60 (Kanto Chemicals, Silica Gel 60, spherical, 40–50 μm). Recycling preparative GPC was carried out with a Japan Analytical Industry LC-908 chromatograph. IR measurements were conducted on a JASCO FT/IR-660 Plus instrument in KBr. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA400 instrument, while ^{19}F NMR spectra were recorded on a Varian Mercury 300 machine at 282 MHz. Chemical shifts of ^{1}H, ^{13}C, and ^{19}F NMR signals are expressed in parts per million (δ) with use of the internal standards Me_4Si ($\delta = 0.00$ ppm), $CDCl_3$ ($\delta = 77.00$ ppm), and $CFCl_3$ ($\delta = 0.00$ ppm), respectively. Coupling constants (J) are reported in Hertz (Hz). Mass spectra were recorded on a PerSeptive Biosystems Voyager-DE STR spectrometer. Elemental analyses were carried out on a Perkin–Elmer CHNS/O 2400 apparatus. DSC measurements were conducted on a Mettler DSC 30 to determine the thermal transitions (scanning rate: 10 °C min^{-1}). An Olympus BH-2 polarizing optical microscope fitted with a Mettler FP82HT hot stage was used for visual observation. X-ray diffraction measurements were carried out on a Rigaku RINT 2100 diffractometer with a heating stage and with use of Ni-filtered $Cu_{K\alpha}$ radiation.

Absorbance and circular dichroism measurements: The UV/Vis absorption spectra were recorded on an Agilent 8453 spectrophotometer in 1 mm and 100 μm rectangular quartz cells. Circular dichroism spectra were recorded on a Jasco J-700 spectropolarimeter fitted with a Jasco PTC-423 L temperature controller in 1 mm and 100 μm rectangular quartz cells. UV/Vis and CD measurements in LC states were conducted on the same spectrometer fitted with a Mettler FP82HT hot stage in 200 μm quartz plates.

Synthesis

Bis{2-[3,4-bis(hexyloxy)phenyl]ethyl} L-glutamate (5a): 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC, 6.65 g, 34.7 mmol), dissolved in dry CH_2Cl_2 (30 mL), was added to a mixture of **4** (8.69 g, 26.9 mmol), *N*-Fmoc-L-glutamic acid (4.81 g, 13.0 mmol), and 4-dimethylaminopyridine (DMAP, 0.244 g, 2.00 mmol) dissolved in dry CH_2Cl_2 (100 mL). The solution was stirred under an Ar atmosphere at room temperature for 12 h. The reaction mixture was extracted three times with ethyl acetate, the collected organic fractions were washed with saturated aqueous NaCl and dried over $MgSO_4$, and the solvent was removed in vacuo. The residue was dissolved in $CHCl_3$ (100 mL), piperidine (5.0 mL) was added, and the mixture was left stirring at room temperature for 1 h. The reaction mixture was poured into saturated aqueous NH_4Cl (150 mL) and was extracted with $CHCl_3$ (3×100 mL). The collected organic fractions were washed with saturated aqueous $NaHCO_3$ and dried over $MgSO_4$, and the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography (hexane/ethyl acetate 1:1) to afford **5a** (6.86 g, 9.08 mmol, 67%) as a pale yellow oil.Spectroscopic data for **5a** are given in our previous paper.[7d]

Bis{2-[3,4-bis(hexyloxy)phenyl]ethyl} D-glutamate (5b): *N*-Fmoc-D-glutamic acid (2.51 g, 6.80 mmol) and DMAP (0.163 g, 1.33 mmol) were added to a solution of **4** (4.31 g, 13.4 mmol) and dry CH_2Cl_2 (100 mL). EDC (6.65 g, 34.7 mmol) dissolved in dry CH_2Cl_2 (30 mL) was added to the mixture, followed by constant stirring under an Ar atmosphere at room temperature for 12 h. The procedure was the same as that used for **5a**. Yield: 3.79 g, 5.02 mmol, 75%. The spectroscopic data for **5b** were identical to those for **5a**.

Tetra{2-[3,4-di(hexyloxy)phenyl]ethyl} ester of α,γ-bis(L-glutamoyl)-L-glutamic acid (2a): *N*-Fmoc-L-glutamic acid (0.545 g, 1.48 mmol) and DMAP (35.4 mg, 0.290 mmol) were added to a solution of **5a** (2.18 g, 2.88 mmol) and dry CH_2Cl_2 (100 mL). EDC (0.693 g, 3.62 mmol), dissolved in dry CH_2Cl_2, (30 mL) was added to the solution, which was heated at reflux under an Ar atmosphere at 50 °C for 3 h. The reaction mixture was extracted with ethyl acetate (3×50 mL), the collected organic fractions were washed with saturated aqueous NaCl and dried over $MgSO_4$, and the solvent was removed under reduced pressure. The residue was dissolved in $CHCl_3$ (100 mL), piperidine (5 mL) was added, and the reaction mixture was stirred at room temperature for 1 h. The reaction mixture was poured into saturated aqueous NH_4Cl (150 mL) and extracted with $CHCl_3$ (3×50 mL). The collected organic fractions were washed with saturated aqueous $NaHCO_3$ and dried over $MgSO_4$, and the solvent was removed in vacuo. The crude product was purified by flash column chromatography (silica gel, gradient hexane/ethyl acetate/chloroform 2:5:3 followed by $CHCl_3$/MeOH 10:1) to give **2a** (1.30 g, 0.804 mmol, 56%) as a colorless solid. $R_f = 0.20$ (hexane/ethyl acetate 2:5); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.02$ (d, $J = 9$ Hz, 1H), 7.60 (d, $J = 8$ Hz, 1H), 6.68–6.83 (m, 12H), 4.70–4.71 (m, 1H), 4.59–4.64 (m, 1H), 4.20–4.32 (m, 8H), 3.92–3.98 (m, 16H), 3.23–3.32 (m, 1H), 2.80–2.89 (m, 8H), 2.30–2.41 (m, 6H), 2.13–2.19 (m, 4H), 1.77–1.84 (m, 18H), 1.22–1.47 (m, 48H), 0.90 ppm (t, $J = 6$ Hz, 24H); IR: $\tilde{\nu} = 3444$, 3312, 3217, 3048, 2956, 2931, 2859, 1732, 1686, 1652, 1590, 1519, 1468, 1428, 1392, 1264, 1236, 1171, 1140, 1071, 1017, 799 cm^{-1}; MS (MALDI): *m/z*: 1623.06 $[M+H]^+$; calcd 1623.11; elemental analysis calcd (%) for $C_{95}H_{151}N_3O_{18}$: C 70.29, H 9.38, N 2.59; found: C 70.67, H 9.47, N 2.93.

Tetra{2-[3,4-di(hexyloxy)phenyl]ethyl} ester of α,γ-bis(D-glutamoyl)-D-glutamic acid (2b): *N*-Fmoc-D-glutamic acid (0.781 g, 2.12 mmol) and DMAP (52.4 mg, 0.429 mmol) were added to a solution of **5b** (3.14 g, 4.15 mmol) and dry CH_2Cl_2 (100 mL). EDC (0.944 g, 4.92 mmol) dissolved in dry CH_2Cl_2 (30 mL) was added to the solution, which was heated at reflux under an Ar atmosphere at 50 °C for 3 h. The procedure was the same as that used for **2a**. Yield: 2.27 g, 1.40 mmol, 67%. The spectroscopic data for **2b** were identical to those for **2a**.

Tetra{2-[3,4-di(hexyloxy)phenyl]ethyl} ester of α,γ-bis(L-glutamoyl)-D-glutamic acid (2c): *N*-Fmoc-D-glutamic acid (0.622 g, 1.68 mmol) and DMAP (68.2 mg, 0.558 mmol) were added to a solution of **5a** (2.48 g, 3.28 mmol) and dry CH_2Cl_2 (100 mL). EDC (1.10 g, 5.74 mmol), dissolved in dry CH_2Cl_2, (100 mL) was added to the solution, which was heated at reflux under an Ar atmosphere at 50 °C for 3 h. The procedure was the same as that used for **2a**. Yield: 1.26 g, 0.780 mmol, 48%; $R_f = 0.20$ (hexane/ethyl acetate 2:5); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.17$ (d, $J =$

8 Hz, 1H), 7.38 (d, $J=8$ Hz, 1H), 6.69–6.81 (m, 12H), 4.62–4.67 (m, 2H), 4.21–4.33 (m, 8H), 3.92–3.99 (m, 16H), 3.61 (t, $J=5$ Hz, 1H), 2.81–2.90 (m, 8H), 2.22–2.40 (m, 6H), 2.03–2.15 (m, 4H), 1.74–1.83 (m, 18H), 1.24–1.47 (m, 48H), 0.90 ppm (t, $J=7$ Hz, 24H); MS (MALDI): *m/z*: 1622.68 $[M+H]^+$; calcd 1623.11; elemental analysis calcd (%) for $C_{95}H_{151}N_3O_{18}$: C 70.29, H 9.38, N 2.59; found: C 70.26, H 9.38, N 2.70.

Tetra{2-[3,4-di(hexyloxy)phenyl]ethyl} ester of α,γ-bis(L-glutamoyl)-*N*-[N^{10}-(trifluoroacetyl)pteroyl]-L-glutamic acid (1a): N^{10}-(Trifluoroacetyl)pteroic acid (0.556 g, 1.36 mmol) was dried over P_2O_5 for 24 h in vacuo, dry DMF (10 mL) was added, and the mixture was stirred under an Ar atmosphere. Triethylamine (230 μL, 1.66 mmol) and isobutyl chloroformate (198 μL, 1.51 mmol) were added dropwise to the resulting dark red solution, which was stirred for 1 h at room temperature. Compound **2a** (1.18 g, 0.730 mmol), dissolved in dry THF (20 mL), was then added, and the mixture was left stirring for 3 days in the dark at 40 °C under an Ar atmosphere. The reaction mixture was filtered through a Celite pad and was washed with $CHCl_3$ (50 mL) and EtOH (10 ml), and the solvent was removed in vacuo. The residue was purified by flash column chromatography (silica gel, $CHCl_3$/EtOH/benzene 13:1:1), followed by GPC to yield **1a** (0.572 g, 0.284 mmol, 39%) as a yellow wax. $R_f=0.56$ (CH_2Cl_2/MeOH 10:1); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=8.78$ (br s, 1H), 8.09–8.29 (m, 1H), 7.88 (d, $J=8$ Hz, 2H), 7.55–7.76 (m, 1H), 7.42 (d, $J=8$ Hz), 6.69–6.79 (m, 12H), 5.14 (br s, 2H), 4.64–4.81 (m, 1H), 4.43–4.60 (m, 1H), 4.10–4.43 (m, 8H), 3.78–4.03 (m, 16H), 3.64–3.69 (m, 1H), 2.67–3.00 (m, 8H), 2.28–2.57 (m, 6H), 1.90–2.26 (m, 6H), 1.64–1.90 (m, 16H), 1.17–1.55 (m, 48H), 0.74–1.06 ppm (m, 24H); ^{19}F NMR (300 MHz, $CDCl_3$): $\delta=-67.7$ ppm; IR: $\tilde{\nu}=3366$, 2956, 2932, 2860, 1734, 1699, 1653, 1540, 1517, 1473, 1429, 1395, 1263, 1212, 1163, 1141, 1018, 802, 668 cm^{-1}; MS (MALDI): *m/z*: 2013.28 $[M+H]^+$; calcd 2013.17; elemental analysis calcd (%) for $C_{111}H_{160}F_3N_9O_{21}$: C 66.21, H 8.01, F 2.83, N 6.26, found: C 66.25, H 8.17, N 6.70.

Tetra{2-[3,4-di(hexyloxy)phenyl]ethyl} ester of α,γ-bis(D-glutamoyl)-*N*-[N^{10}-(trifluoroacetyl)pteroyl]-D-glutamic acid (1b): N^{10}-(Trifluoroacetyl)pteroic acid (0.608 g, 1.49 mmol) was dried over P_2O_5 for 24 h in vacuo, dry DMF (10 mL) was added, and the mixture was stirred under an Ar atmosphere. Triethylamine (238 μL, 1.72 mmol) and isobutyl chloroformate (215 μL, 1.64 mmol) were added dropwise to the solution, and the mixture was left to stir for 1 h at room temperature. Compound **2b** (1.87 g, 1.15 mmol), dissolved in dry THF (20 mL), was then added to the mixture, which was left to stir for 3 days in the dark at 40 °C under an Ar atmosphere. The workup procedure was the same as that used for **1a**. Yield: 0.965 g, 0.479 mmol, 42%. The spectroscopic data for **1b** were identical to those for **1a**.

Tetra{2-[3,4-di(hexyloxy)phenyl]ethyl} ester of α,γ-bis(L-glutamoyl)-*N*-[N^{10}-(trifluoroacetyl)pteroyl]-D-glutamic acid (1c): N^{10}-(Trifluoroacetyl)pteroic acid (0.386 g, 0.945 mmol) was dried over P_2O_5 for 24 h in vacuo, dry DMF (10 mL) was added, and the mixture was stirred under an Ar atmosphere. Triethylamine (151 μL, 1.09 mmol) and isobutyl chloroformate (137 μL, 1.04 mmol) were added dropwise to the solution, which was stirred for 1 h at room temperature. Compound **2c** (1.16 g, 0.72 mmol), dissolved in dry THF (20 mL), was then added to the reaction mixture, which was stirred for 3 days in the dark at 40 °C under an Ar atmosphere. The workup procedure was the same as that used for **1a**. Yield: 0.685 g, 0.340 mmol, 47%; $R_f=0.56$ (CH_2Cl_2/MeOH, 10:1); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=8.78$ (s, 1H), 7.90 (d, $J=7$ Hz, 2H), 7.75–7.83 (m, 1H), 7.60–7.69 (m, 1H), 7.45 (d, $J=7$ Hz, 2H), 6.59–6.87 (m, 12H), 4.94–5.11 (m, 2H), 4.75–4.86 (m, 1H), 4.48–4.66 (m, 1H), 4.07–4.34 (m, 8H), 3.87–3.97 (m, 16H), 2.77–2.85 (m, 8H), 2.28–2.54 (m, 6H), 2.07–2.27 (m, 6H), 1.63–1.90 (m, 16H), 1.17–1.54 (m, 48H), 0.72–0.97 ppm (m, 24H); MS (MALDI): m/z 2013.44 $[M+Na]^+$; calcd = 2013.17; elemental analysis calcd (%) for $C_{111}H_{160}F_3N_9O_{21}$: C 66.21, H 8.01, F 2.83, N 6.26; found: C 66.42, H 8.08, N 6.53.

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