DOI: 10.1002/chem.200500720

An Enantiomeric Nanoscale Architecture Obtained from a Pseudoenantiomeric Aggregate: Covalent Fixation of Helical Chirality Formed in Self-Assembled Discotic Triazine Triamides by Chiral Amplification

Tsutomu Ishi-i,*[a] Rempei Kuwahara,[b] Akihiko Takata,[b] Yeonhwan Jeong,[c] Kazuo Sakurai,[c] and Shuntaro Mataka[a]

Abstract: Covalent fixation of a chiral helical structure which is created in a self-assembling system by a chiral-amplification method based on the sergeants/soldiers principle is reported. Disk-shaped triazine triamides self-assembled to form columnar-type helical aggregates through π-stacking interactions among the central triphenyltriazine moieties, hydrogen-bonding interactions among the amide groups, and van der Waals interactions among the alkyl groups in nonpolar solvents such as hexane, octane, toluene, and *p*-xylene. When the achiral triazine triamide soldier component is mixed with a tiny amount of the chiral triazine triamide sergeant component, control of the intrinsic supramolecular helicity of the self-assembled soldier component by the sergeant component leads to chiral amplification and formation of a pseudoenantiomeric aggregate with only one handedness of the helix. The helicity can be preserved by ring-closing olefin metathesis polymerization mediated by Grubbs catalyst when an achiral component with terminal olefinic groups forms the pseudoenantiomeric aggregate in the presence of a tiny amount of the chiral component without olefinic groups. After polymerization and removal of the chiral component, the polymeric architecture obtained from the achiral soldier component is optically active and thus can be regarded as an enantiomeric object in which the chiral information transferred from the chiral sergeant component is preserved. The nanoscale chiral structure is fixed perfectly, as indicated by CD spectroscopic evidence obtained in a polar THF medium at high temperature and low concentration. AFM and TEM observations show a nanoscale fibrous structure with a diameter of 2–4 nm, which corresponds to the molecular size of the triazine triamide monomer.

Keywords: asymmetric amplification · circular dichroism · helical structures · self-assembly · supramolecular chemistry

Introduction

Chiral amplification is one of the most challenging targets of chemists in view of elucidating the origin of homochirality in L-amino acids and D-saccharides in natural systems.[1] In artificial architectures, chiral amplification was first found in covalent macromolecular systems incorporating tiny amounts of chiral components. In helical macromolecules without chiral centers such as polyisocyanates,[2,3] polyisocyanides,[4] polysilanes,[5] polythiophenes,[6] and a peptide nucleic acid,[7] even small amounts of the covalently incorporated chiral components govern the entire chiral structure of these macromolecule according to the so-called sergeants/soldiers principle.[2] The resulting helical species have much higher optical activity than expected from the chiral-to-achiral ratio. Similarly, macromolecular helicity in achiral poly-

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phenylacetylenes is governed by noncovalent synthesis, in which a chiral additive with low optical purity interacts with the macromolecule to achieve chiral amplification.[8] In a limited number of asymmetric reactions, chiral amplification was observed to produce chiral products with high enantiomeric excess by using a chiral auxiliary or catalyst with low optical purity.[9] Recently, chiral amplification has been extended to supramolecular assembled systems in finite aggregates with a capsule structure[10] and infinite aggregates with an extended columnar structure.[11–13] In these systems, tiny amounts of the chiral self-assembling components used as sergeants govern the manner of self-assembly of the excess of achiral components used as soldiers to create chirally ordered supramolecular systems. Generally, a supramolecular aggregate structure is constructed by weak noncovalent interactions such as van der Waals interactions, hydrogen-bonding interactions, π-stacking interactions, metal–ligand interactions, and so on.[14] The weak interactions are intensified in the self-assembly process to stabilize the supramolecular structure. Thus, a supramolecular self-assembled system is regarded as one of the most suitable media for chiral amplification, in which chiral information of the chiral sergeant component is transferred to the soldier-based aggregate via the noncovalent interactions and amplified to control the entire supramolecular chirality. The chiral aggregates produced by chiral amplification would provide an attractive medium for asymmetric reactions[15] and chiral recognition,[16] as well as applications as nanoscale functional materials with piezoelectric, pyroelectric, and ferroelectric properties,[17] although the low stability of the noncovalent architecture should be overcome by using chemical modification such as covalent fixation. Recently, Meijer et al. reported fixation of a chiral structure created in a columnar-type helical aggregate by a chiral-amplification method.[18] Chiral fixation was attributed to the creation of new chiral centers during the photopolymerization of the terminal sorbyl moieties introduced in the achiral components. The chiral architecture thus obtained has a kinetically stable helical structure which is retained in nonpolar media but collapses in polar media.

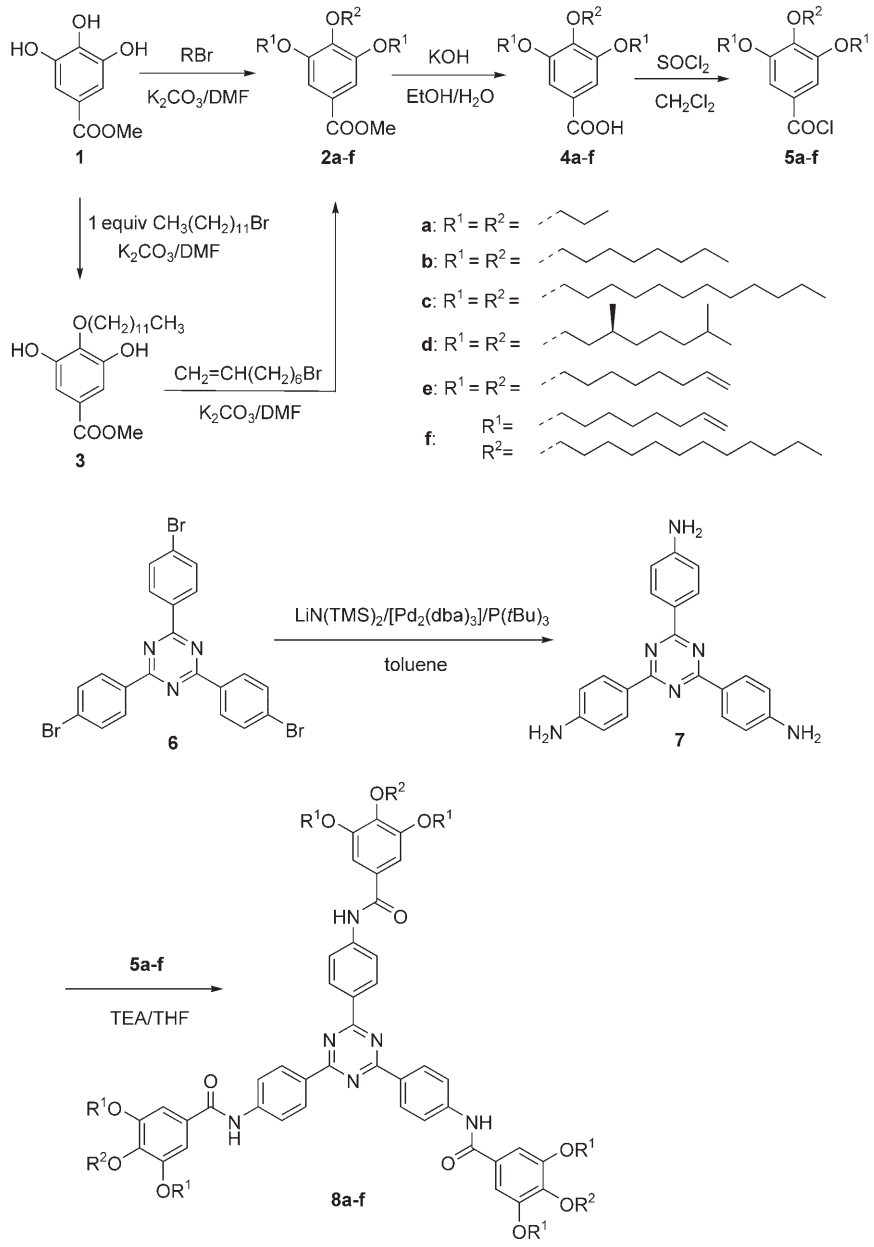
Previously, we reported that 1,3,5-tris[4-(1-naphthyl)phenyl]triazine shows an extremely high electron-drift mobility of $8\times10^{-3}\,cm^2V^{-1}s^{-1}$, which is one of the highest values in amorphous electron-transporting materials.[19] The electron is conventionally transported along a suitable π-stacking path between the molecules even in the amorphous state. This π stacking is ascribed to the flat conformation of the central triphenyltriazine core,[20] which tends to form a columnar-type stacking path.[21] This result led us to design new π-stacked columnar-type architectures based on self-assembling triazine-based discotic molecules. In addition to the π-stacking interactions among the triazine moieties, we have used hydrogen-bonding interactions to stabilize the new columnar-type architecture.[22] Here, we report chiral amplification in self-assembly of triazine derivatives with three amide groups and preservation of the chiral structure by ring-closing olefin metathesis. The helicity in the one-dimensional columnar-type aggregate composed of achiral triazine triamide soldiers is governed by a tiny amount of the chiral triazine triamide sergeant. After polymerization of the terminal olefinic moieties introduced in the achiral component, the polymeric architecture obtained from only the achiral component without any chiral centers completely preserves the chiral information, which can not be destroyed even in polar media.

Results and Discussion

3,4,5-Trialkoxybenzoic acid methyl esters **2a–e** with 1-propyl, 1-octyl, 1-dodecyl, 3-(*S*)-3,7-dimethyl-1-octyl, and oct-7-enyl groups, respectively, were prepared by alkoxylation of methyl 3,4,5-trihydroxybenzoate **1** with three equivalents of the corresponding bromide.[23] In contrast, **2f** with two different alkoxyl groups (one dodecyloxy group at the 4-position and two oct-7-enyloxy groups at the 3- and 5-positions) was obtained by selective alkoxylation of one hydroxyl group at the 4-position of **1** with one equivalent of 1-bromododecane to give **3** and subsequent alkoxylation of the remaining hydroxyl groups with two equivalents of 8-bromo-1-octene. Compounds **2a–f** were converted to the corresponding aroyl chlorides **5a–f** by treatment with aqueous potassium hydroxide to give the corresponding carboxylic acids **4a–f** and subsequent treatment with thionyl chloride.[23] Triazine triamides **8a–f** were prepared by condensation reactions of the aroyl chlorides **5a–f** with 2,4,6-tris(4-aminophenyl)-1,3,5-triazine (**7**) in the presence of triethylamine (Scheme 1). The key synthetic intermediate **7** was derived from the corresponding tribromide **6**[19] by coupling with lithium bis(trimethylsilyl)amide in the presence of a palladium(0) catalyst.[24] Triazine triamides **8a–f** were characterized on the basis of spectroscopic methods and elemental analysis.

To elucidate the effect of the central triazine core in **8a–f**, the corresponding benzene-core derivative **11** with chiral substituents was prepared by a similar condensation reaction of **5d** with **10** (Scheme 2). The key synthetic intermediate **10** was obtained from 1,3,5-tribromobenzene by coupling with *N*-Boc-4-aminophenylboronic acid in the presence of a palladium(0) catalyst and subsequent deprotection of the obtained **9** by treatment with trifluoroacetic acid.

In aliphatic hydrocarbon solvents such as hexane, cyclohexane, and octane at 10 mM, **8b**, **8c**, and **8d** can form viscoelastic fluid organogels (Table 1), in which one-dimensional aggregates composed of **8b**, **8c**, and **8d** molecules are entangled into three-dimensional network structures that prevent the solvents from flowing.[25,26] Triazine **8a** with short *n*-propyl chains is insoluble in these solvents, but it can form viscous solutions in aromatic hydrocarbons such as benzene, toluene, and *p*-xylene (Table 1). Interestingly, benzene-core derivative **11** shows similar gelation ability to **8b**, **8c**, and **8d** (Table 1). The organogel aggregate structure of **8b** and **8d** can be visualized by SEM observations. The SEM images of the xerogels obtained from **8b** and **8d** in cyclohexane at



Scheme 1. Preparation of triazine triamides **8a–f**. TMS = trimethylsilyl, dba = dibenzylideneacetone, TEA = triethylamine.

−15 °C/0.1 Torr showed a fibrous structure with 500–2000 nm diameters (Figure 1).[27] The aggregate structures of **8b**, **8c**, and **8d** can be maintained even at a low concentration of about 0.01 mM in aliphatic hydrocarbons and about 0.1 mM in aromatic hydrocarbons (see below).

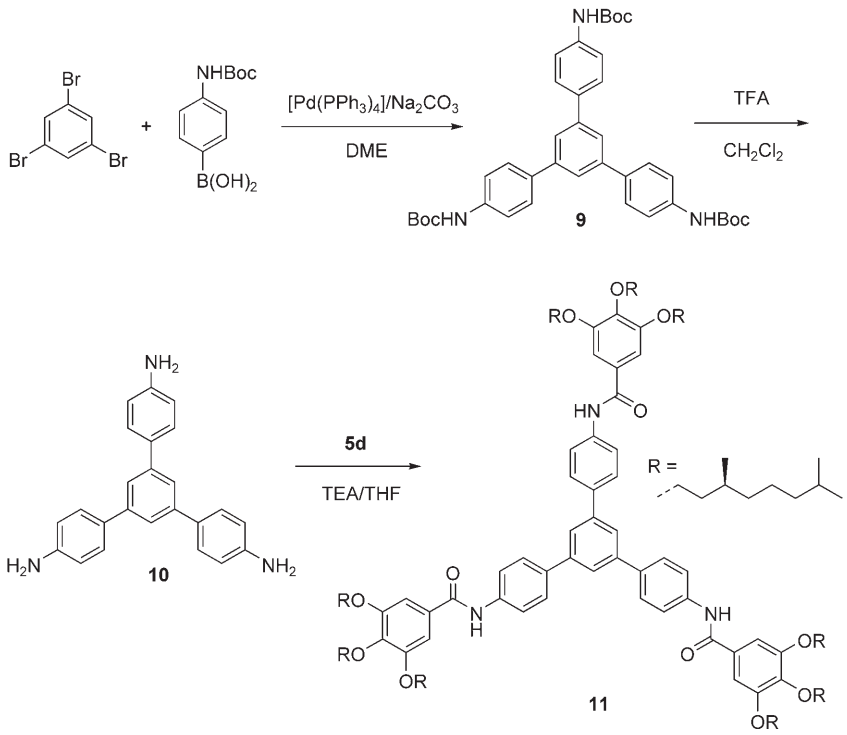
In octane and *p*-xylene solutions of **8b** (1.0 mM), NH stretching vibrations at 3299 and 3302 cm^{-1}, respectively, were observed at almost the same wavenumber (3317 cm^{-1}) in the solid state (KBr), whereas they shifted to lower wavenumber compared to that in a dichloromethane solution (3424 cm^{-1}, Table 2). A similar trend was observed in C=O stretching vibrations: 1649 cm^{-1} in KBr, 1645 cm^{-1} in octane, 1645 cm^{-1} in *p*-xylene, and 1681 cm^{-1} in dichloromethane. The results indicate that hydrogen-bonding interactions among amide moieties contribute to formation of the aggregates. In octane solutions of **8b**, the NH and C=O stretching vibrations do not change between gel (10 mM) and sol (1.0 mM) phases, that is, the aggregates in both gel and sol phases have the same hydrogen-bonding network structure. Evidence for hydrogen bonding was observed in the other triazine derivatives **8a**, **8c**, and **8d** as well as in benzene-core derivative **11** (Table 2).

In **8b**, **8c**, and **8d**, π-stacking interaction to form one-dimensional aggregates was confirmed by UV/Vis spectroscopy. In polar solvents at 1.0 mM and 20 °C, **8b** shows an absorption band at 329 nm in dichloromethane and around 333–344 nm in THF. In contrast, the absorption band shifted hypsochromically to 308 nm in octane and to 310 nm in *p*-xylene (Figure 2). The hypsochromic shift in the nonpolar solvents could be attributed to self-assembled **8b** molecules in an H-type aggregation mode, which is rationalized by the exciton-coupling theory.[28] The stability of the **8b**-based aggregate can be monitored by temperature- and concentration-dependent UV/

Table 1. Organic solvents tested for gelation by **8a–d** and **11**.[a]

Solvent	**8a**	**8b**	**8c**	**8d**	**11**
hexane	I	G	vS (G)[b]	G	G
cyclohexane	I	G	S (vS)[b]	G	vS
octane	I	G	vS (G)[b]	G	G
benzene	vS (R)[b]	R	S	R	S
toluene	vS (R)[b]	R	S	R	S
p-xylene	tG (R)[b]	S	S (pG)[b]	S	S
dichloromethane	R	S	S	S	S
chloroform	S	S	S	S	S
diethyl ether	I	S	S	S	S
THF	S	S	S	S	S
1,4-dioxane	S	R	R	R	S
ethanol	R	R	R	R	I
ethyl acetate	R	R	R	R	S
acetone	R	R	R	R	S

[a] [gelator] = 10 mM, at room temperature. G = gel, pG = partial gel, tG = turbid gel, R = recrystallization, S = solution, vS = viscous solution, I = insoluble. [b] The data in parentheses are for 5 °C.



Scheme 2. Preparation of benzene triamide **11**. DME = dimethoxyethane, TFA = trifluoroacetic acid.

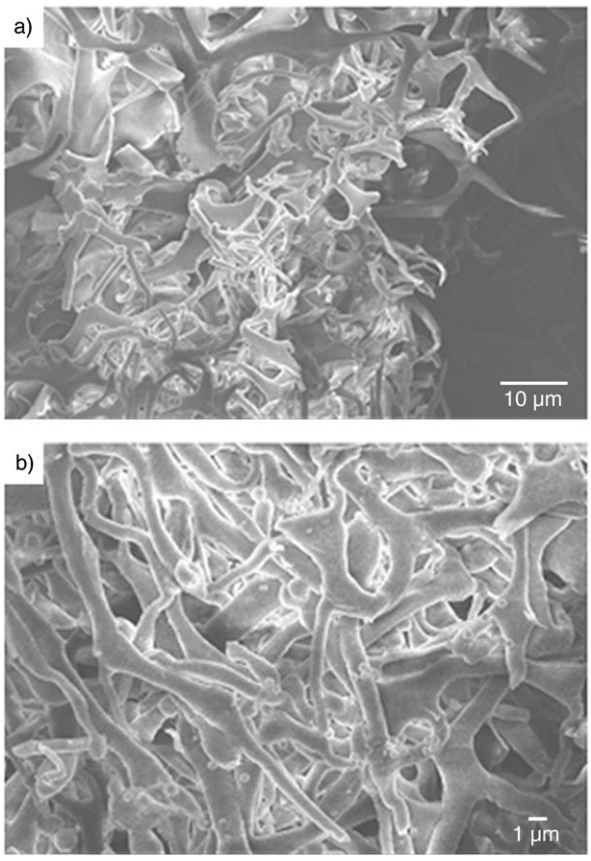


Figure 1. SEM images of cyclohexane xerogels of **8b** (a) and **8d** (b), prepared at −15 °C/0.1 Torr.

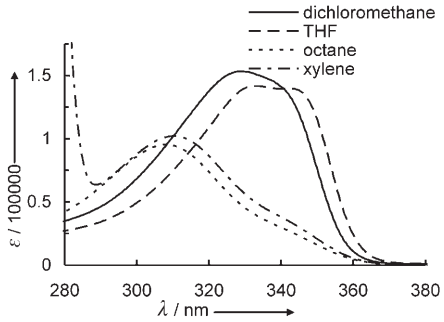


Figure 2. UV/Vis spectra of **8b** in octane, *p*-xylene, dichloromethane, and THF at 1.0 mM (0.01 cm width cell) at 20 °C.

Table 2. NH and C=O stretching vibrations of **8b** and **11**.

Compound	Conditions	ν_{NH}	$\nu_{C=O}$
8b	KBr	3317	1649
	octane (10 mM, gel)	3295	1645
	octane (1.0 mM, sol)	3299	1645
	p-xylene (1.0 mM)	3302	1645
	dichloromethane (1.0 mM)	3424	1681
11	KBr	3303	1645
	octane (1.0 mM)	3303	1647
	dichloromethane (1.0 mM)	3429	1674

Vis spectroscopy at 20–75 °C and 1.0–0.01 mM. Under these conditions, the UV/Vis spectra scarcely changed in octane, that is, the aggregate formed in octane solution is quite stable and does not dissociate. In contrast, in *p*-xylene the aggregate dissociates at a low concentration of about

0.01 mM (Figure 3) and at a high temperature of about 75 °C (Figure 4a), since the UV/Vis spectra changed with changing conditions, and the resulting spectra were very similar to those observed in dichloromethane and THF solutions. Comparison of the spectral shapes of **8b**, **8c**, and **8d** indicates the order of aggregate stability to be **8b** > **8c** > **8d** (Figure 4 and S-Figure 1–3 in Supporting Information). The inferior stability of aggregated **8d** could be ascribed to unfavorable packing of the chiral alkyl groups arising from the branched structure.[29]

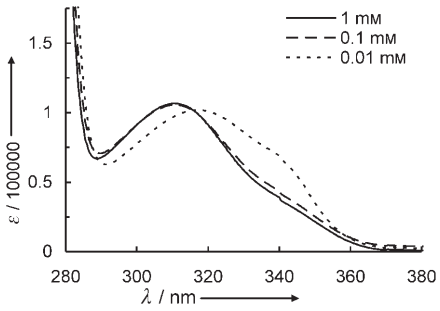


Figure 3. Concentration-dependent change of UV/Vis spectra of **8b** in *p*-xylene (20 °C): 1.0 mM (0.01 cm width cell), 0.1 mM (0.1 cm width cell), and 0.01 mM (1 cm width cell).

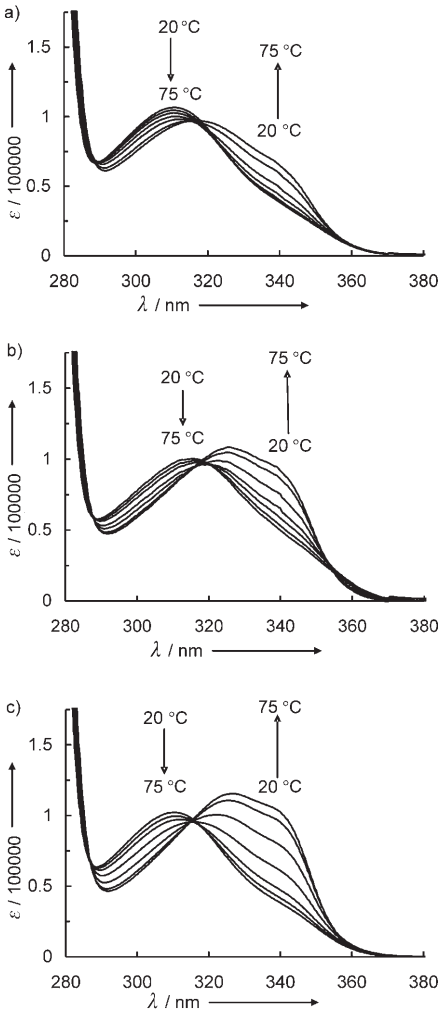


Figure 4. Temperature-dependent change of UV/Vis spectra of **8b** (a), **8c** (b), and **8d** (c) in *p*-xylene at 1.0 mM (0.01 cm width cell) at 20, 30, 40, 50, 60, 70, and 75 °C.

The CD spectra of **8d** with chiral alkyl groups in octane and *p*-xylene at 1.0 mM at 20 °C exhibited a negative exciton-coupling pattern with negative first Cotton effect and positive second effect (321 ($\Delta\varepsilon = -181.4\ cm^2\,mmol^{-1}$) and 302 nm ($\Delta\varepsilon = 81.0\ cm^2\,mmol^{-1}$) in octane, and 324 ($\Delta\varepsilon = -150.5\ cm^2\,mmol^{-1}$) and 304 nm ($\Delta\varepsilon = 122.5\ cm^2\,mmol^{-1}$) in *p*-xylene), and the intersections at $\lambda_{\theta=0}$ of 309 nm in octane and 313 nm in *p*-xylene were in accord with the absorption maxima (Figure 5). In contrast, **8d** is CD-inactive in dichloromethane and THF. The exciton-splitting pattern found in the octane sol samples (0.01–1.0 mM) is observable also in the gel sample (10 mM) without any shifts and changes in the CD spectrum, that is, the aggregates in gel and sol phases have the same helical stacking mode (Figure 5). In octane solution, the CD spectra scarcely changed even at low concentration (ca. 0.01 mM) and high temperature (ca. 75 °C; Figures 6a and 7a). In contrast, in *p*-xylene the magnitude of the Cotton effects decreased with decreasing concentration and increasing temperature (Figures 6b and 7b, and S-Figure 4 in Supporting Information); this indicates a reversible aggregation and dissociation equilibrium of **8d**. The trend is in accordance with that of the UV/Vis spectra.

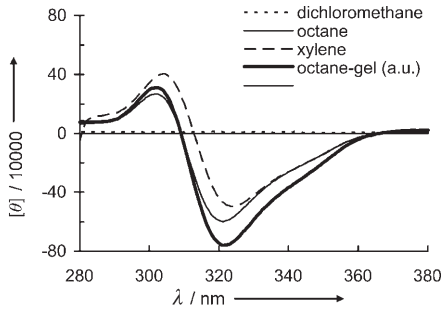


Figure 5. CD spectra of **8d** in octane, *p*-xylene, and dichloromethane at 1.0 mM (0.01 cm width cell) at 20 °C. The octane gel sample (10 mM) was measured between two quartz glass plates.

Here we propose a possible aggregate structure stabilized by cooperative π stacking, hydrogen bonding, and van der Waals interactions. When π stacking of the central triphenyltriazine moieties forms a one-dimensional aggregate, a triple helical network of hydrogen bonds among the amide groups propagates along the aggregate axis and enforces a helical mode of the aggregate (Figure 8).[22a] A subtle balance between packing and solvation of the alkyl groups is important to control the solubility and to prevent crystallization of the aggregate. In the absence of any sources of chirality, the aggregate exists as equal amounts of left- and right-handed enantiomeric helices in a racemic mixture. By introducing the chiral center in **8d**, a pair of two helical aggregates is

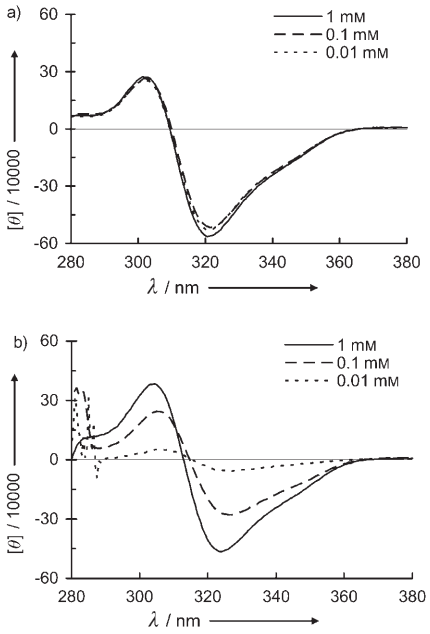


Figure 6. Concentration-dependent change of CD spectra of **8d** in octane (a) and *p*-xylene (b) at 20 °C: 1.0 mM (0.01 cm width cell), 0.1 mM (0.1 cm width cell), and 0.01 mM (1 cm width cell).

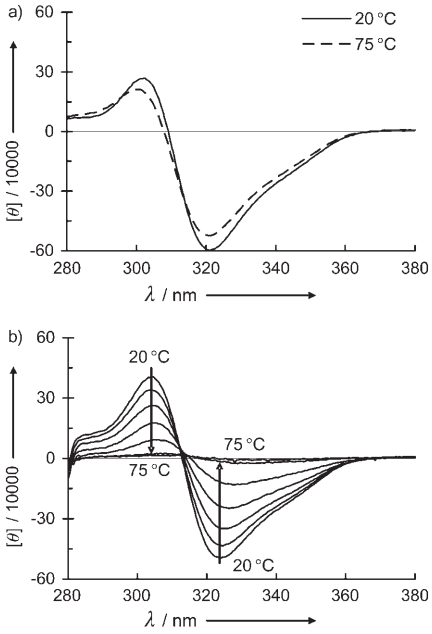


Figure 7. Temperature-dependent change of CD spectra of **8d** in octane (a) and *p*-xylene (b) at 1.0 mM (0.01 cm width cell) at 20, 30, 40, 50, 60, 70, and 75 °C.

changed from an enantiomeric relationship to a diastereomeric one, and the left-handed helical aggregate exists as a favored diastereoisomer under dynamic exchange conditions. Selective formation of left-handedness is explained by the negative exciton-coupling pattern found in the CD spectra.[30]

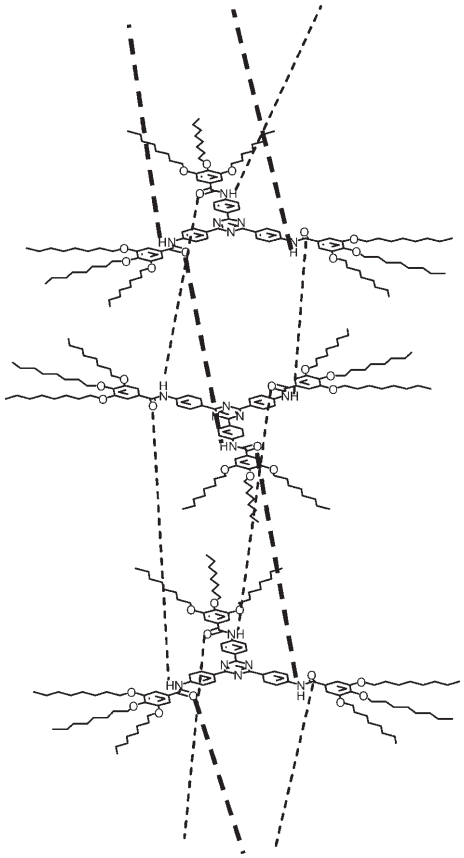


Figure 8. Stacking model for **8b**.

In contrast to triazine derivative **8d**, benzene-core derivative **11** was CD-inactive even in nonpolar solvents. In addition, the UV/Vis spectra of **11** scarcely changed between polar dichloromethane and nonpolar octane solutions (Figure 9). These results show that the central 1,3,5-triphenylbenzene moiety in **11** is not suitable for intermolecular π-stacking because of its nonplanar structure. Thus, molecules of **11** can self-assemble only through hydrogen-bonding interactions among the amide groups but not by π stacking interactions, and hence a less-ordered aggregate is formed in a nonchiral manner. A comparison of **8d** with **11** provides the valuable information that the planar structure of the central 2,4,6-triphenyl-1,3,5-triazine moiety in **8d** is very suitable for π stacking. The planar structure in **8d** was elucidated not only on the basis of the single-crystal structure of 2,4,6-triphenyl-1,3,5-triazine[20] but also by molecular modeling (Spartan, Hartree–Fock 6-31G*, Figure 10). Probably, the electron-deficient nature of the central triazine core contributes to the π-stacking interactions that stabilize the one-dimensional aggregate.[31]

Chiral amplification of the present aggregate system was monitored by CD spectroscopy. When a total concentration of achiral **8b** and chiral **8d** was kept constant at 1.0 mM, the magnitude of the Cotton effects increased nonlinearly with increasing amount of **8d**. The Cotton effects are observable even in the presence of a tiny amount of **8d**. In octane solu-

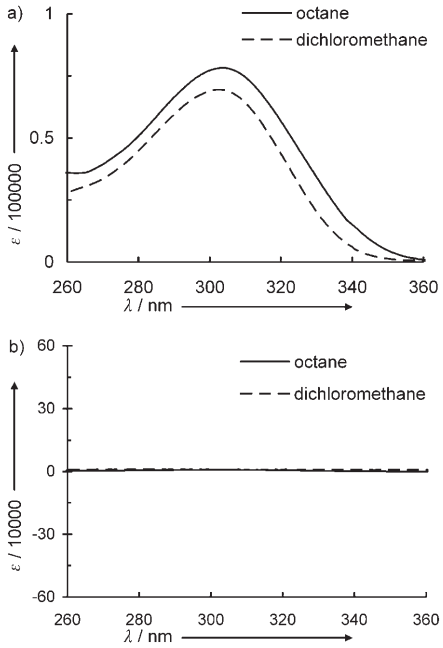


Figure 9. UV/Vis (a) and CD spectra (b) of **11** in octane and dichloromethane at 1.0 mM (0.01 cm width cell) at 20 °C.

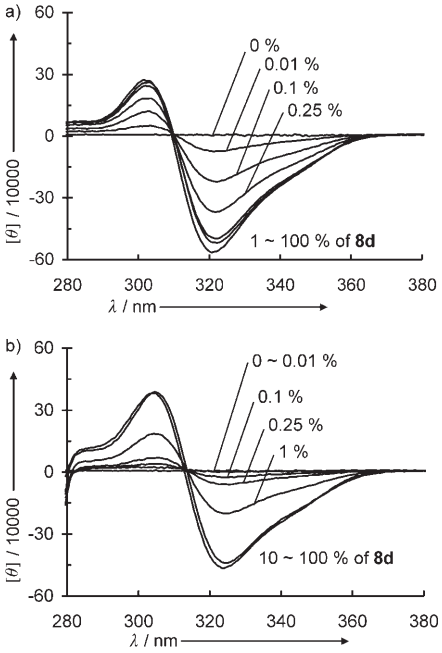


Figure 11. CD spectra of the mixture of **8b** and **8d** in octane (a) and *p*-xylene (b) at [**8b**+**8d**] = 1.0 mM (0.01 cm width cell): [**8d**]/{[**8b**]+[**8d**]}×100 = 0, 0.01, 0.1, 0.25, 1, 10, and 100 mol%.

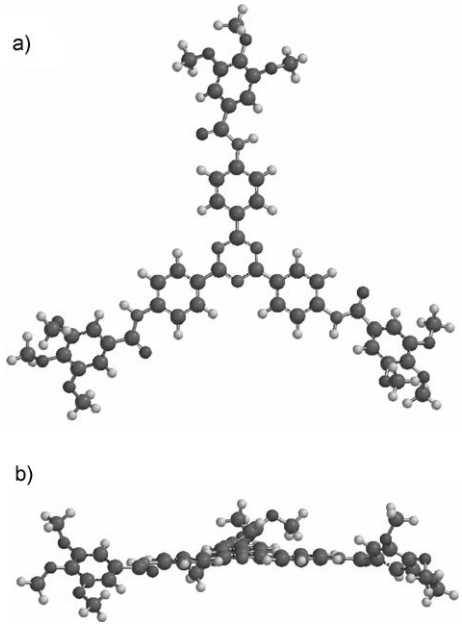


Figure 10. Computer-simulated structure of the methyl ether derivative of **8** by a MO calculation (Spartan, Hartree–Fock 6-31G*): top view (a) and side view (b).

tion, the **8b**-based aggregate is CD-active in the presence of 0.01 mol% of **8d**. With only 1 mol% of **8d** the magnitude of CD intensity is as strong as that of the diastereomeric aggregate composed only of **8d**, that is, chiral amplification really does occur to preferentially form one of the two helical aggregates (Figure 11a). Even at a low concentration of 0.01 mM, chiral amplification can be achieved without any decrease in optical activity (S-Figure 5 in Supporting Information). A similar trend was observed in *p*-xylene, although the efficiency is reduced by one order of magnitude compared to that in octane (Figure 11b). In octane, one molecule of the chiral sergeant **8d** controls the helical stacking mode of 100 molecules of achiral soldier **8b**, whereas in *p*-xylene ten molecules of **8b** are governed by one molecule of **8d** (Figure 12). In the chiral-amplification process, the racemic mixture of left- and right-handed helical aggregates composed of achiral component **8b** is converted to a pseudoenantiomeric aggregate with left-handed helicity including a tiny amount of chiral component **8d** under dynamic exchange conditions (Figure 13).

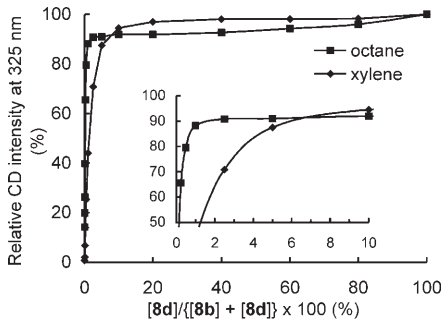


Figure 12. Plots of relative CD intensity at 325 nm ($CD_{obs}/CD_{100\,mol\%}$ of **3d**×100) vs mole percentage of **8b** ([**8d**]/([**8b**]+[**8d**])×100) for the mixture of **8b** and **8d** in octane and *p*-xylene. The total concentration of **8b** and **8d** was kept at 1.0 mM.

To preserve the helical aggregate structure, we polymerized the pseudoenantiomeric aggregate by ring-closing metathesis (RCM) mediated by the Grubbs catalyst

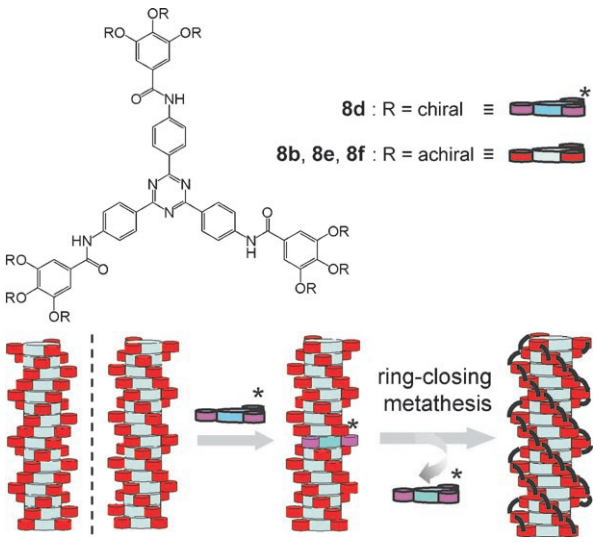


Figure 13. Schematic explanation of chiral amplification for the one-dimensional stacking of achiral **8b,e,f** in the presence of tiny amounts of chiral **8d**, and subsequent preservation of the chiral structure by ring-closing metathesis.

(Figure 13).[32,33] For this, new triazine triamides **8e** and **8f** with terminal olefinic groups were designed and prepared (Scheme 1).

Like **8b**, **8e** with nine terminal olefinic groups is CD-active in the presence of chiral **8d** (10 mol%). Due to the low solubility of **8e**, chiral amplification was only achieved in toluene solution at a concentration of about 0.1 mM (Figure 14). Thus, the RCM reaction was performed at a

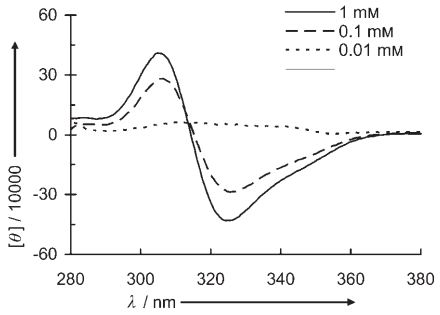


Figure 14. CD spectra of the mixture of **8e** and **8d** (90/10 mol/mol) in toluene at 20°C: [**8e**+**8d**]=0.01, 0.1, and 1.0 mM, in 1.0, 0.1, and 0.01 cm width cells, respectively.

moderate concentration of 0.1 mM. To facilitate the chiral amplification, the reaction was carried out at a low temperature of 5°C. After addition of the Grubbs catalyst to a toluene solution of **8e**/**8d** (90/10 mol/mol), the reaction solution was quenched by oxygen and diluted with THF to a concentration of 0.01 mM. The diluted THF solution, which was subjected directly to CD measurement without purification, showed retention of the exciton-coupling pattern in the CD spectrum even in the polar medium (Figure 15), in which monomer **8e** and sergeant **8d** dissolved molecularly to be

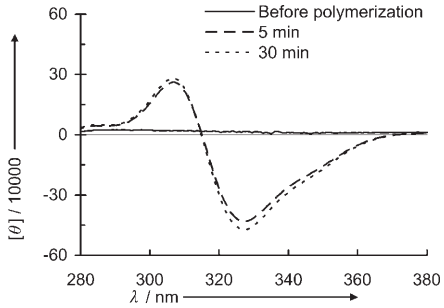


Figure 15. CD spectra of the mixture of **8e** and **8d** (90/10 mol/mol) in THF at 0.01 mM, before and after polymerization (5 and 30 min). After the polymerization of the mixture of **8e** and **8d** in toluene (0.1 mM) at 5°C in the presence of Grubbs catalyst, the reaction mixture was diluted with THF to 0.01 mM and subjected to the CD measurement.

CD-inactive, as outlined above. Time-dependent CD monitoring indicated that the RCM polymerization proceeds rapidly in around 5 min (Figure 15). However, after evaporation of the solvents, the resulting polymeric material (poly-1) shows significantly poor solubility in common organic solvents. Thus, further characterization of poly-1 could not be performed. The poor solubility of poly-1 could be ascribed to the moderate reaction concentration of 0.1 mM, where intercolumnar polymerization could compete with the desired intracolumnar polymerization to produce a three-dimensional network structure. In addition, the presence of nine multiple bonds groups in **8e** is disadvantageous for preventing intercolumnar polymerization.

To overcome the undesired intercolumnar polymerization, three of the nine olefinic groups in **8e** were replaced with three long dodecyl groups, which also act as soluble chains. Thus, triazine triamide **8f** with six terminal olefinic groups was designed and prepared (Scheme 1). As expected, **8f** dissolves in aliphatic hydrocarbons such as hexane and octane. Similar to **8b** without olefinic groups, **8f** shows chiral amplification on self-assembling in the presence of 1 mol% of **8d** (Figure 16). The degree of chiral amplification is strong

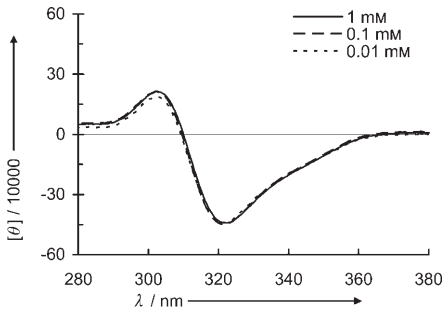


Figure 16. CD spectra of the mixture of **8f** and **8d** (99/1 mol/mol) in hexane at 20°C: [**8f**+**8d**]=0.01, 0.1, and 1.0 mM in 1.0, 0.1, and 0.01 cm width cells, respectively.

enough even at a low concentration of 0.01 mM. The dilute conditions are very suitable for facilitating intracolumnar RCM polymerization and avoiding intercolumnar polymeri-

zation. The RCM reaction of the **8f/8d** (99/1 mol/mol) system was performed in hexane at 0.01 mM. After evaporation, the soluble and insoluble polymeric components in chloroform were separated by filtration. Finally, the soluble polymeric product poly-2 was purified by size-exclusion chromatography (SEC) with chloroform as eluant, by which chiral component **8d** was recovered quantitatively. Thus, the obtained poly-2 is composed of only achiral units without any chiral centers.

The preservation of the chirally-ordered helical structure in poly-2 is indicated by retention of the exciton-coupling pattern in the CD spectra even in polar media such as THF, in which monomer **8f** and sergeant **8d** did not form CD-active aggregates. The magnitude of the Cotton effects in THF did not change under conditions of extreme dilution of 0.001 mM and a high temperature of 60 °C (Figure 17), and

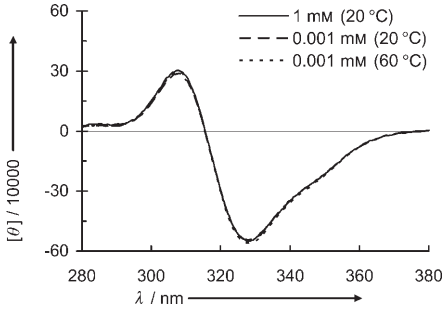


Figure 17. CD spectra of poly-2 in THF at 1.0 mM (at 20 °C, in 0.01 cm width cell) and 0.001 mM (at 20 and 60 °C, in 10 cm width cell): the concentration was calculated on the basis of monomer unit **8f**. The poly-2 was obtained by polymerization of a mixture of **8f** and **8d** (99/1 mol/mol) in hexane (0.01 mM) at 20 °C in the presence of Grubbs catalyst and purified by SEC.

hence the observed Cotton effects are ascribed to an intramolecular organization within molecularly dissolved poly-2. Compared to the chiral aggregate of **8f/8d** before polymerization, poly-2 shows comparable magnitude of the Cotton effects. This indicates that the RCM reaction is performed without dissociation of the aggregate and the helical information is retained completely in the poly-2 structure. In poly-2, hydrogen-bonding interactions among the amide groups are effective in the polar THF and dichloromethane solutions, as indicated by the stretching vibrations for hydrogen-bonded NH and C=O groups (Table 3). The RCM reaction fixes the triazine triamide units at specific positions to facilitate the π-stacking and hydrogen-bonding interactions.

Table 3. NH and C=O stretching vibrations of **8f** and poly-2.

Compound	Conditions	ν_{NH}	$\nu_{C=O}$
8f	KBr	3302	1645
	octane (1.0 mM)	3299	1645
	dichloromethane (1.0 mM)	3424	1681
poly-2[a]	film	3299	1648
	dichloromethane (1.0 mM)	3292	1647
	THF (1.0 mM)	3292	1647

[a] Poly-2 was obtained by RCM of **8f** in hexane (0.01 mM) in the presence of **8d** (1 mol%).

A nanoscale fibrous structure of poly-2 was monitored by TEM and AFM. A TEM image shows an amoeba-like structure with 10–100 nm size, which would be ascribed to reag-

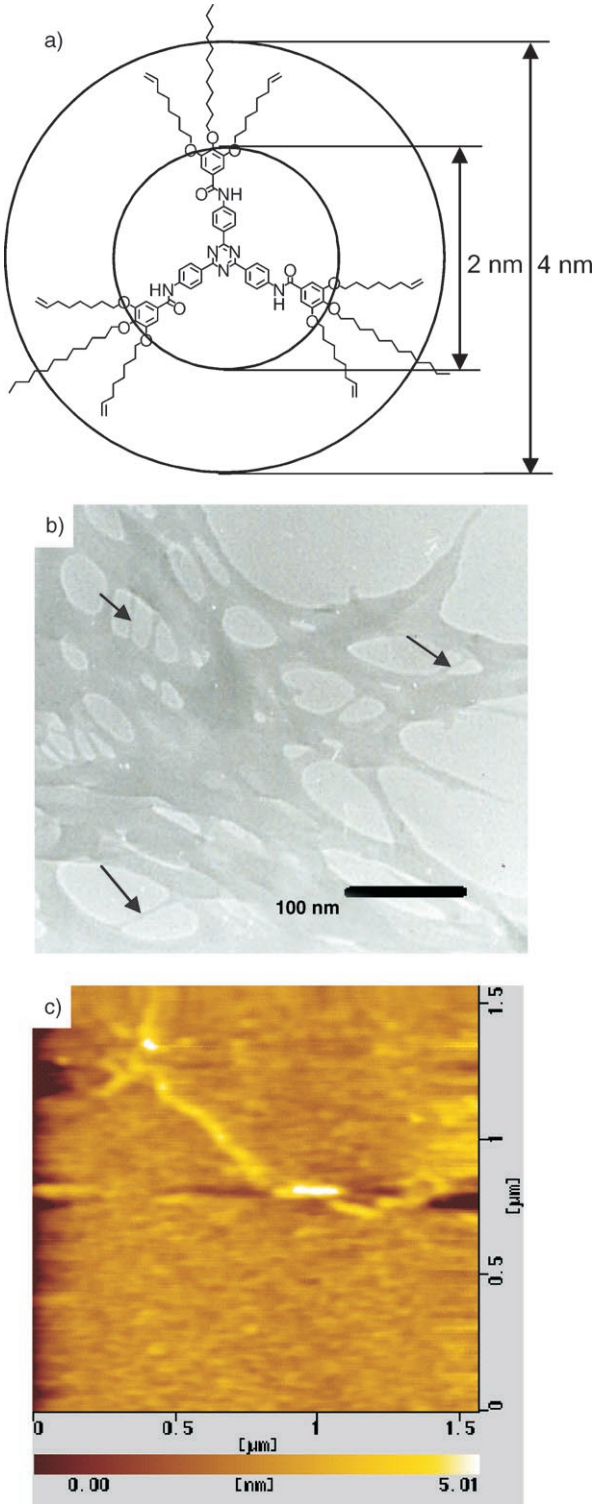


Figure 18. a) Molecular size of monomer **8f**. b) TEM image on carbon-coated copper grid. c) AFM images of poly-2 on HOPG.

gregation of poly-2 during drop casting on a carbon-coated copper grid and the subsequent solvent-evaporation process. However, by careful observation, one can find several narrow fibrous parts with a diameter of 2–3 nm, which are comparable to the molecular size of monomer **8f** (extended molecular size of ca. 4 nm and aromatic core size of ca. 2 nm; Figure 18a and b). An AFM image of poly-2 on highly oriented pyrolytic graphite (HOPG) also reveals a nanoscale fibrous structure with a height of 3–4 nm (Figure 18c). The nanoscale fibrous structure was not observed at all before RCM polymerization.

Conclusion

We have demonstrated that a chirally ordered helical structure created in a columnar-type supramolecular aggregate by chiral amplification is preserved by covalent fixation of the aggregate. In the chiral amplification, the chiral triazine triamide sergeant governs the manner of self-assembly of the achiral triazine triamide soldiers to form a pseudoenantiomeric aggregate with only one handedness of the helix. The helical structure is fixed perfectly by ring-closing metathesis of the terminal olefinic groups introduced in the achiral component. The resulting polymeric architecture obtained from only the achiral component is optically active and is regarded as an enantiomeric helical object without any chiral centers. We believe that the present study will provide new valuable information for creating a nanoscale chiral architectures without chiral centers and could be developed to design a specific nanoscale environment for asymmetric reaction and chiral recognition as well as nanoscale functional materials.

Experimental Section

General: All melting points are uncorrected. IR spectra were recorded on a JASCO FT/IR-470 plus FTIR spectrometer as KBr pellets. ^{1}H NMR spectra were determined in $CDCl_3$ or $(CD_3)_2SO$ with a JEOL EX-270 or LA 400 spectrometer. Residual solvent protons were used as internal standard, and chemical shifts δ are given relative to tetramethylsilane (TMS). The coupling constants J are reported in hertz. Elemental analysis was performed at the Elemental Analytical Center, Kyushu University. EI-MS spectra were recorded with a JEOL JMS-70 mass spectrometer at 70 eV using a direct inlet system. FAB-MS were recorded with a JEOL JMS-70 mass spectrometer with *m*-nitrobenzyl alcohol (NBA) as matrix. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) was performed on a PerSeptive Biosystems Voyager-DE spectrometer in delayed extraction mode with an acceleration voltage of 20 keV. Samples were prepared from a solution of THF with α-cyano-4-hydroxycinnamic acid (CHCA) as matrix. UV/Vis spectra were measured on a JASCO V-560 spectrophotometer between two quartz plates (10.0 mm), and in a 0.01 cm width quartz cell (1.0 mm), a 0.1 cm width quartz cell (0.1 mm), a 1.0 cm width quartz cell (0.01 mm), and a 10 cm width quartz cell (0.001 mm). CD spectra were measured on a JASCO J-720W spectropolarimeter between two quartz plates (10.0 mm), and in a 0.01 cm width quartz cell (1.0 mm), a 0.1 cm width quartz cell (0.1 mm), a 1.0 cm width quartz cell (0.01 mm), and a 10 cm width quartz cell (0.001 mm). Size-exclusion chromatography (SEC) was performed with a Japan Analytical Industry LC-908 using JAIGEL-1H (20×600 mm) and JAIGEL-2H columns (20×600 mm) with chloroform (3.0 mL min^{-1}) as eluant. Analytical TLC was carried out on silica gel coated on aluminum foil (Merck 60 F_{254}). Column chromatography was carried out on silica gel (Wako C-300 or KANTO 60N). THF, hexane, and toluene were distilled from sodium and benzophenone under an argon atmosphere just before use. Dichloromethane was distilled from calcium hydride under an argon atmosphere just before use. Compounds **2a–d, 4a–d**, and **5a–d** were prepared according to methods reported previously.[23] Preparation of triazine derivative **6** was reported previously.[19]

Gelation test: The gelators **8a–d** and **11** and the solvent (10 mm) were put in a screw-capped test tube and heated until the solid dissolved. The solution was cooled at 5 °C or 20 °C. If a stable and transparent gel was observed at this stage, the system classified as a gel.

SEM measurements: A JSM 6340-F scanning electron microscope was used for recording SEM images. A thin gel, prepared in a sample tube at 10 mm and −15 °C, was evaporated by a vacuum pump (0.1 torr) for 1 h. The dry sample thus obtained was shielded by Pt. The accelerating voltage of SEM was 5 kV and the emission current was 12 μA.

Methyl 3,4,5-tris(oct-7-enyloxy)benzoate (2e): Gallic acid methyl ester (**1**, 146 mg, 0.79 mmol) and 8-bromo-1-octene (500 mg, 2.62 mmol) were added to a suspension of potassium carbonate (1.1 g, 7.9 mmol) in DMF (6 mL) at room temperature under an argon atmosphere. After the reaction mixture was stirred for 12 h at 70 °C, it was poured into water (50 mL) and neutralized with aqueous 1.2 N hydrochloric acid solution. The reaction mixture was extracted with dichloromethane (10 mL×2), dried over anhydrous magnesium sulfate, and evaporated in vacuo to dryness. The oily residue was purified by column chromatography on silica gel (WAKO C-300) with hexane/chloroform (1/1) as eluant to give **2e** in 86% yield (352 mg, 6.83 mmol) as colorless oil; ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.29–1.59 (m, 18H; CH_2), 1.63–1.90 (m, 6H; $ArOCH_2CH_2CH_2$), 1.93–2.16 (m, 6H; $ArOCH_2CH_2$), 3.89 (s, 3H; $COOCH_3$), 4.01 (t, J = 6.5 Hz, 6H; $ArOCH_2$), 4.94 (d, J = 11.3 Hz, 3H; olefinic H), 4.99 (d, J = 18.6 Hz, 3H; olefinic H), 5.74–5.89 (m, 3H; olefinic H), 7.26 ppm (s, 2H; ArH); IR (NaCl): $\tilde{\nu}$ = 3076, 2928, 2856, 1722 (C=O), 1640, 1587, 1499, 1386, 1336, 1218, 1118, 996, 909, 863, 766 cm^{-1}; FAB-MS (NBA): *m/z*: 514 [M^+]; HR-FAB-MS (NBA): *m/z* calcd for $C_{32}H_{50}O_5$ [M^+]: 514.3658; found: 514.3652.

Methyl 4-dodecyloxy-3,5-dihydroxybenzoate (3): Compound **1** (1.50 g, 8.15 mmol) and 1-bromododecane (2.03 g, 1.97 mL, 8.15 mmol) were added to a suspension of potassium carbonate (3.38 g, 24.45 mmol) in DMF (50 mL) at room temperature under an argon atmosphere. After the reaction mixture was stirred at room temperature for 10 h, it was poured into water (200 mL), neutralized with aqueous 1.2 N hydrochloric acid solution, and extracted with chloroform (50 mL×2). The organic layer was dried over anhydrous magnesium sulfate and evaporated in vacuo to dryness. The residue was purified by column chromatography on silica gel (WAKO C-300) with chloroform/ethyl acetate (3/1) as eluant and recrystallized from chloroform/hexane (1/5) to give **3** in 61% yield (812 mg, 1.42 mmol) as a white powder; m.p. 81–85 °C; ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.6 Hz, 3H; CH_3), 1.26–1.30 (m, 16H; $ArOCH_2CH_2CH_2(CH_2)_8$), 1.39–1.45 (m, 2H; $ArOCH_2CH_2CH_2$), 1.74–1.81 (m, 2H; $ArOCH_2CH_2$), 3.88 (s, 3H; $COOCH_3$), 4.11 (t, J = 6.8 Hz; 2H, $ArOCH_2$), 5.62 (s, 2H; OH), 7.24 ppm (s, 2H; ArH); IR (KBr): $\tilde{\nu}$ = 3533 (OH), 3304 (OH), 2954, 2915, 2851, 1686 (C=O), 1604, 1529, 1462, 1367, 1325, 1272, 1188, 1094, 1058, 1017, 1006, 990, 972, 873, 768, 759, 715, 666, 451 cm^{-1}; EI-MS (70 eV): *m/z*: 352 [M^+]; elemental analysis calcd (%) for $C_{20}H_{32}O_5$ (352.5): C 68.15; H 9.15; found: C 68.12; H 9.17.

Methyl 4-dodecyloxy-3,5-bis(oct-7-enyloxy)benzoate (2f): Compound **3** (829 mg, 2.35 mmol) and 8-bromo-1-octene (1.00 g, 875 μL, 5.18 mmol) were added to a suspension of potassium carbonate (2.15 g, 15.5 mmol) in DMF (12 mL) at room temperature under an argon atmosphere. After the reaction mixture was stirred at 70 °C for 12 h, it was poured into water (150 mL), neutralized with aqueous 1.2 N hydrochloric acid solution, and extracted with dichloromethane (50 mL×2). The organic layer was dried over anhydrous magnesium sulfate and evaporated in vacuo to dryness. The oily residue was purified by column chromatography on

silica gel (WAKO C-300) with chloroform/hexane (1/1) as eluant to give **2f** in 60% yield (812 mg, 1.42 mmol) as colorless oil; ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 0.88$ (t, $J = 6.6$ Hz, 3H; CH_3), 1.21–1.36 (m, 24H; CH_2), 1.37–1.54 (m, 6H; $ArOCH_2CH_2CH_2$), 1.69–1.87 (m, 6H; $ArOCH_2CH_2$), 2.06 (q, $J = 6.5$ Hz, 4H; CH_2=$CHCH_2$), 3.89 (s, 3H; $COOCH_3$), 4.01 (t, $J = 6.3$ Hz, 6H; $ArOCH_2$), 4.94 (d, $J = 11.3$ Hz, 2H; olefinic H), 5.00 (d, $J = 18.6$ Hz, 2H; olefinic H), 5.74–5.89 (m, 2H; olefinic H), 7.25 ppm (s, 2H; ArH); IR (NaCl): $\tilde{\nu} = 3076$, 2925, 2854, 1722 (C=O), 1640, 1587, 1500, 1465, 1432, 1387, 1336, 1219, 1118, 1014, 909, 863, 766, 724 cm^{-1}; FAB-MS (NBA): *m/z*: 572 [M^+]; HR-FAB-MS (NBA): *m/z*: calcd for $C_{36}H_{60}O_5$ [M^+]: 572.4441; found: 572.4446.

3,4,5-Tris(oct-7-enyloxy)benzoic acid (4e): Compound **2e** (340 mg, 0.66 mmol) was added to a solution of potassium hydroxide (110 mg, 1.98 mmol) in ethanol (1 mL) and water (1 mL). After the mixture was heated to reflux for 1 h, it was poured into water (5 mL), acidified to pH 4 by addition of 1 N hydrochloric acid, and extracted with dichloromethane (2 mL × 2). The organic layer was washed with water (4 mL), dried over anhydrous magnesium sulfate, and evaporated in vacuo to give **4e** in 97% yield (320 mg, 0.64 mmol) as a colorless oil. Without further purification, **4e** was used for the next reaction. ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 1.29$–1.59 (m, 18H; CH_2), 1.63–1.90 (m, 6H; $ArOCH_2CH_2CH_2$), 1.93–2.16 (m, 6H; $ArOCH_2CH_2$), 4.02 (t, $J = 6.5$ Hz, 6H; $ArOCH_2$), 4.94 (d, $J = 11.3$ Hz, 3H; olefinic H), 4.99 (d, $J = 18.6$ Hz; 3H, olefinic H), 5.74–5.89 (m, 3H; olefinic H), 7.32 ppm (s, 2H; ArH); IR (NaCl): $\tilde{\nu} = 3076$, 2928, 2856, 2638, 1686 (C=O), 1640, 1586, 1502, 1433, 1386, 1330, 1270, 1228, 1119, 994, 909, 865, 768, 728 cm^{-1}.

3,5-Bis(oct-7-enyloxy)-4-dodecyloxybenzoic acid (4f): Compound **2f** (712 mg, 1.24 mmol) was added to a solution of potassium hydroxide (350 mg, 6.2 mmol) in ethanol (10 mL) and water (10 mL). After the reaction mixture was heated to reflux for 30 min, it was poured into water (50 mL), acidified to pH 4 by addition of 1 N hydrochloric acid, and extracted with dichloromethane (20 mL × 2). The organic layer was washed with water (20 mL × 2), dried over anhydrous magnesium sulfate, and evaporated to give **4f** in 97% yield (637.1 mg, 1.20 mmol) as colorless oil. Without further purification, **4f** was used for the next reaction. ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 0.88$ (t, $J = 6.6$ Hz; 3H; CH_3), 1.21–1.36 (m, 24H; CH_2), 1.37–1.54 (m, 6H; $ArOCH_2CH_2CH_2$), 1.69–1.87 (m, 6H; $ArOCH_2CH_2$), 2.06 (q, $J = 6.5$ Hz, 4H; CH_2=$CHCH_2$), 4.03 (t, $J = 6.3$ Hz, 6H; $ArOCH_2$), 4.94 (d, $J = 11.3$ Hz, 2H; olefinic H), 5.00 (d, $J = 18.6$ Hz, 2H; olefinic H), 5.74–5.89 (m, 2H; olefinic H), 7.32 ppm (s, 2H; ArH); IR (NaCl): $\tilde{\nu} = 3077$, 2924, 2852, 1685 (C=O), 1642, 1587, 1504, 1467, 1432, 1384, 1333, 1227, 1125, 990, 907, 863, 768, 723 cm^{-1}.

3,4,5-Tris(oct-7-enyloxy)benzoyl chloride (5e): Thionyl chloride (300 mg, 0.17 mL, 2.48 mmol) was added to a solution of **4e** (310 mg, 0.62 mmol) in dichloromethane (2 mL) at room temperature under an argon atmosphere. After the reaction mixture was stirred for 30 min at room temperature, the solvent and excess thionyl chloride were removed by distillation to give **5e** in 99% yield (320 mg, 0.62 mmol) as a colorless oil. Without further purification, **5e** was treated with **7**. ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 1.29$–1.59 (m, 18H; CH_2), 1.63–1.90 (m, 6H; $ArOCH_2CH_2CH_2$), 1.93–2.16 (m, 6H; $ArOCH_2CH_2$), 4.02 (t, $J = 6.5$ Hz; 6H, $ArOCH_2$), 4.94 (d, $J = 11.3$ Hz, 3H; olefinic H), 4.99 (d, $J = 18.6$ Hz, 3H; olefinic H), 5.74–5.89 (m, 3H; olefinic H), 7.31 ppm (s, 2H; ArH); IR (NaCl): $\tilde{\nu} = 3076$, 2929, 2856, 1751 (C=O), 1640, 1585, 1496, 1466, 1428, 1388, 1329, 1235, 1144, 1119, 994, 909, 851, 771, 692 cm^{-1}.

3,5-Bis(oct-7-enyloxy)-4-dodecyloxybenzoyl chloride (5f): Thionyl chloride (500 mg, 0.28 mL, 4.16 mmol) was added to a solution of **4f** (600 mg, 1.07 mmol) in dichloromethane (4 mL) at room temperature under an argon atmosphere. After the reaction mixture was stirred for 30 min at room temperature under an argon atmosphere, the solvent and excess thionyl chloride were removed by distillation to give **5f** in 100% yield (617 mg, 1.07 mmol) as colorless oil. Without further purification, **5f** was treated with **7**. ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 0.88$ (t, $J = 6.6$ Hz, 3H; CH_3), 1.21–1.36 (m, 24H; CH_2), 1.37–1.54 (m, 6H; $ArOCH_2CH_2CH_2$), 1.69–1.87 (m, 6H; $ArOCH_2CH_2$), 2.06 (q, $J = 6.5$ Hz, 4H; CH_2=$CHCH_2$), 4.03 (t, $J = 6.3$ Hz, 6H; $ArOCH_2$), 4.94 (d, $J = 11.3$ Hz, 2H; olefinic H), 5.00 (d, $J = 18.6$ Hz, 2H; olefinic H), 5.74–5.89 (m, 2H; olefinic H), 7.33 ppm (s, 2H; ArH); IR (NaCl): $\tilde{\nu} = 3075$, 2925, 2854, 1752 (C=O), 1641, 1585, 1496, 1467, 1428, 1385, 1328, 1235, 1144, 1119, 994, 909, 851, 770 cm^{-1}.

2,4,6-Tris(4-aminophenyl)-1,3,5-triazine (7): A solution of P(tBu)$_3$ in hexane (0.05 M, 700 μL, 0.35 mmol) was added to a solution of [Pd(dba)$_2$] (201 mg, 0.35 mmol; dba = *trans*,*trans*-dibenzylideneacetone) in dry toluene (17.5 mL) at room temperature under an argon atmosphere and allowed to stand for 10 min. 2,4,6-Tri(4-bromophenyl)-1,3,5-triazine (**6**, 1.91 g, 3.5 mmol) and a solution of lithium bis(trimethylsilyl)amide in hexane (1.06 M 10.9 mL, 11.55 mmol) were added to the mixture, which was heated at 80 °C for 39 h (dark violet solution to dark greenish brown suspension). After the reaction mixture (brown suspension) was cooled to room temperature, it was quenched by addition of aqueous 1.2 N hydrochloric acid solution (7 mL) and diluted with water (10 mL) and diethyl ether (10 mL). The suspension was filtered and washed with aqueous 1.2 N hydrochloric acid solution (40 mL), water (110 mL), and diethyl ether (100 mL). The combined filtrate was transferred to a separating funnel. The separated water phase was washed with diethyl ether (50 mL × 2) and treated with cold aqueous 1 N sodium hydroxide solution (15 mL). The obtained white precipitate was collected by filtration and washed with water (150 mL), methanol (30 mL), and dichloromethane (20 mL) to give **7** in 34% yield (417 mg, 1.18 mmol) as a pale yellow solid: m.p. 415–420 °C (decomp); ^{1}H NMR (395 MHz, $(CD_3)_2SO$): $\delta =$ 5.90 (s, D_2O exchange, 6H; NH_2), 6.68, 8.34 ppm (d, $J = 8.6$ Hz, each 6H; ArH); IR (KBr): $\tilde{\nu} = 3461$ (NH), 3378 (NH), 3323 (NH), 3211 (NH), 3030, 1633, 1606, 1578, 1497, 1433, 1366, 1294, 1179, 1147, 1129, 813 cm^{-1}; EI-MS (70 eV): *m/z*: 354 [M^+]; elemental analysis calcd (%) for $C_{21}H_{18}N_6 \cdot 0.5\,H_2O$ (354.4): C 69.40; H 5.30; N 23.23; found: C 69.12; H 5.06; N 22.62.

2,4,6-Tris{4-[3,4,5-tris(propyloxyphenyl)carbonylamino]phenyl}-1,3,5-triazine (8a): Compound **5a** (315 mg, 1.0 mmol) in dry THF (2 mL) was added dropwise to a solution of **7** (106 mg, 0.3 mmol) and triethylamine (0.17 mL, 1.2 mmol) in dry THF (8 mL) at 0 °C under an argon atmosphere. The mixture was stirred at room temperature for 3 h. The reaction mixture was filtered to remove triethylamine hydrochloride and the filtrate was evaporated in vacuo to dryness. The residue was suspended in diethyl ether (10 mL), collected by filtration, and washed with diethyl ether (20 mL). The solid was purified by column chromatography on silica gel (KANTO 60N) with chloroform/methanol (200/1) as eluant to give **8a** in 53% yield (190 mg, 0.16 mmol) as a white powder: m.p. 306–307 °C; ^{1}H NMR (395 MHz, $CDCl_3$): $\delta = 0.97$ (t, $J = 7.3$ Hz, 9H; CH_3), 1.07 (t, $J = 7.3$ Hz, 18H; CH_3), 1.69–1.84 (m, 18H; OCH_2CH_2), 3.90 (t, $J = 5.9$ Hz, 12H; OCH_2), 4.00 (t, $J = 6.4$ Hz, 6H; OCH_2), 7.23 (s, 6H; ArH), 7.38 (brs, 6H; ArH), 8.01 (brs, 6H; ArH), 8.83 ppm (brs, 3H; NH); IR (KBr): $\tilde{\nu} = 3317$ (NH), 2964, 2876, 1653 (C=O), 1591, 1489, 1427, 1405, 1370, 1332, 1237, 1205, 1178, 1119 cm^{-1}; FAB-MS (NBA): *m/z*: 1190 [$(M+1)^+$]; elemental analysis calcd (%) for $C_{69}H_{84}N_6O_{12} \cdot H_2O$ (1189.4): C 68.64; H 7.18; N 6.96; found: C 68.81; H 7.09; N 6.99.

2,4,6-Tris{4-[3,4,5-tris(octyloxyphenyl)carbonylamino]phenyl}-1,3,5-triazine (8b): Compound **5b** (525 mg, 1.0 mmol) in dry THF (2 mL) was added dropwise to a solution of **7** (106 mg, 0.3 mmol) and triethylamine (0.14 mL, 1.0 mmol) in dry THF (8 mL) at 0 °C under an argon atmosphere. The mixture was stirred at room temperature for 1 h. The reaction mixture was filtered to remove triethylamine hydrochloride and the filtrate was evaporated in vacuo to dryness. The residue was purified by column chromatography on silica gel (KANTO 60N) with chloroform/methanol (300/1 v/v) as eluant to give **8b** in 59% yield (321 mg, 1.76 mmol) as a white solid: m.p. 269–273 °C; ^{1}H NMR (395 MHz, $CDCl_3$): $\delta = 0.88$ (t, $J = 6.3$ Hz, 27H; CH_3), 1.23–1.38 (m, 72H; $OCH_2CH_2CH_2(CH_2)_4$), 1.43–1.53 (m, 18H; $OCH_2CH_2CH_2$), 1.72–1.86 (m, 18H; OCH_2CH_2), 3.99 (t, $J = 6.6$ Hz 12H; CH_2), 4.02 (t, $J = 6.6$ Hz, 6H; OCH_2), 7.21 (s, 6H; ArH), 7.77 (d, $J = 8.6$ Hz, 6H; ArH), 8.18 (s, 3H; NH), 8.63 ppm (d, $J = 8.6$ Hz, 6H; ArH); IR (KBr) $\tilde{\nu} = 3317$ (NH), 2925, 2855, 1649 (C=O), 1584, 1490, 1427, 1406, 1372, 1335, 1239, 1177, 1114, 805, 760 cm^{-1}; FAB-MS (NBA): *m/z*: 1821 [$(M+1)^+$]; elemental analysis calcd (%) for $C_{114}H_{174}N_6O_{12}$ (1820.6): C 75.21; H 9.63; N 4.62; found: C 75.58 ; H 9.59; N 4.66.

2,4,6-Tris{4-[3,4,5-(trisdodecyloxyphenyl)carbonylamino]phenyl}-1,3,5-triazine (8c): Compound **5c** (694 mg, 1.0 mmol) in dry THF (2 mL) was

added dropwise to a solution of **7** (106 mg, 0.3 mmol) and triethylamine (0.14 mL, 1.0 mmol) in dry THF (8 mL) at 0 °C under an argon atmosphere. The mixture was stirred at room temperature for 1 h. The reaction mixture was filtered to remove triethylamine hydrochloride and the filtrate was evaporated in vacuo to dryness. The residue was purified by column chromatography on silica gel (KANTO 60N) with chloroform/methanol (400/1) as eluant and recrystallized from chloroform/acetone (2/1, 20 mL) to give **8c** in 57 % yield (391 mg, 0.17 mmol) as a white solid: m.p. 256–260 °C; ^{1}H NMR (395 MHz, $CDCl_3$): $\delta = 0.88$ (t, $J =$ 6.4 Hz, 27 H; CH_3), 1.23–1.38 (m, 48 H; $OCH_2CH_2CH_2(CH_2)_8$), 1.45–1.53 (m, 18 H; $OCH_2CH_2CH_2$), 1.74–1.87 (m, 18 H; OCH_2CH_2), 4.01–4.07 (m, 18 H; OCH_2), 7.14 (s, 6 H; ArH), 7.78 (d, $J = 8.9$ Hz, 6 H; ArH), 8.13 (br s, 3 H; NH), 8.65 ppm (d, $J = 8.9$ Hz, 6 H; ArH); IR (KBr): $\tilde{\nu} = 3317$ (NH), 2924, 2853, 1646 (C=O), 1582, 1490, 1426, 1406, 1374, 1336, 1239, 1205, 1177, 1115, 803, 764 cm^{-1}; MALDI-TOF-MS (CHCA): *m/z*: calcd for $C_{150}H_{246}N_6O_{12}$ [M^+]: 2324.89; found: 2324.81; elemental analysis calcd (%) for $C_{150}H_{246}N_6O_{12}$ (2325.6): C 77.47; H 10.66; N 3.61; found: C 77.50; H 10.65; N 3.64.

2,4,6-Tris{4-[(3,4,5-tris((*S*)-3,7-dimethyloctyloxyphenyl)carbonylamino]-phenyl}-1,3,5-triazine (8d): Compound **5d** (402 mg, 0.66 mmol) in dry THF (1.5 mL) was added dropwise to a solution of **7** (71 mg, 0.2 mmol) and triethylamine (0.10 mL, 0.72 mmol) in dry THF (6 mL) at 0 °C under an argon atmosphere. The mixture was stirred at room temperature for 2 h. The reaction mixture was filtered to remove triethylamine hydrochloride and the filtrate was evaporated in vacuo to dryness. The residue was purified by column chromatography on silica gel (KANTO 60N) with chloroform/methanol (400/1) as eluant and recrystallized from acetone (30 mL) to give **8d** in 60 % yield (247 mg, 0.12 mmol) as a white solid: m.p. 289–294 °C; ^{1}H NMR (395 MHz, $CDCl_3$): $\delta = 0.87$ (d, $J =$ 6.6 Hz, 54 H; CH_3), 0.94 (d, $J = 6.6$ Hz, 27 H; CH_3), 1.12–1.90 (m, 90 H; CH_2), 4.01–4.08 (m, 18 H; OCH_2), 7.14 (s, 6 H; ArH), 7.84 (d, $J = 8.7$ Hz, 6 H; ArH), 8.02 (s, 3 H; NH), 8.75 ppm (d, $J = 8.7$ Hz, 6 H; ArH); IR (KBr): $\tilde{\nu} = 3317$ (NH), 2954, 2926, 2853, 1649 (C=O), 1583, 1492, 1427, 1406, 1374, 1334, 1240, 1177, 1114, 803, 761 cm^{-1}; MALDI-TOF-MS (CHCA): *m/z*: calcd for $C_{132}H_{210}N_6O_{12}$ [M^+]: 2072.60; found: 2072.44; elemental analysis calcd (%) for $C_{132}H_{210}N_6O_{12}$ (2073.1): C 76.47; H 10.21; N 4.05; found: C 76.16; H 10.13; N 3.99.

2,4,6-Tris{4-{[3,4,5-tris(oct-7-enyloxy)phenyl]carbonylamino}phenyl}-1,3,5-triazine (8e): Compound **5e** (310 mg, 0.60 mmol) in dry THF (2 mL) was added dropwise to a solution of **7** (64 mg, 0.18 mmol) and triethylamine (70 mg, 0.10 mL, 0.69 mmol) in dry THF (3 mL) at 0 °C under an argon atmosphere. After the reaction mixture was stirred at room temperature for 3 h, it was filtered to remove triethylamine hydrochloride and evaporated in vacuo to dryness. The residue was purified by column chromatography on silica gel (KANTO 60N) with chloroform/hexane (1/1) as eluant and recrystallized from acetone/methanol (1/1) to give **8e** in 52 % yield (168 mg, 0.094 mmol) as a white powder; m.p. 250–253 °C; ^{1}H NMR (395 MHz, $CDCl_3$): $\delta = 1.29$–1.59 (m, 54 H; CH_2), 1.63–1.90 (m, 18 H; $ArOCH_2CH_2$), 1.93–2.16 (m, 18 H; CH_2=$CHCH_2$), 4.04 (t, $J = 6.5$ Hz, 18 H; $ArOCH_2$), 4.95 (d, $J = 11.1$ Hz, 9 H; olefinic H), 5.00 (d, $J = 18.9$ Hz, 9 H; olefinic H), 5.74–5.89 (m, 9 H; olefinic H), 7.16 (s, 6 H; ArH), 7.76 (d, $J = 8.6$ Hz, 6 H; ArH), 8.19 (s, 3 H; NH), 8.60 ppm (d, $J =$ 8.6 Hz, 6 H; ArH); IR (KBr): $\tilde{\nu} = 3302$ (*NH*), 3076, 2929, 2855, 1648 (C=O), 1584 (C=O), 1489, 1427, 1405, 1372, 1335, 1239, 1178, 1117, 993, 909, 818, 770 cm^{-1}; FAB-MS (NBA): *m/z*: 1802 [M^+]; elemental analysis calcd (%) for $C_{114}H_{156}N_6O_{12}$ (1802.5): C 75.96; H 8.72; N 4.66; found: C 75.92; H 8.69; N 4.66.

2,4,6-Tris{4-{[4-dodecyloxy-3,5-bis(oct-7-enyloxyl)phenyl]carbonylamino}-phenyl}-1,3,5-triazine (8f): Compound **5f** (610 mg, 1.06 mmol) in dry THF (2 mL) was added dropwise to a solution of **7** (114 mg, 0.32 mmol) and triethylamine (0.2 mL, 116 mg, 1.15 mmol) in dry THF (10 mL) at 0 °C under an argon atmosphere. After the reaction mixture was stirred at room temperature for 1 h, it was filtered to remove triethylamine hydrochloride and evaporated in vacuo to dryness. The residue was purified by column chromatography on silica gel (KANTO 60N) with chloroform/hexane (1/1) as eluant to give **8f** in 67 % yield (422 mg, 0.21 mmol) as a white solid; m.p. 253–255 °C; ^{1}H NMR (395 MHz, $CDCl_3$): $\delta = 0.88$ (t, $J =$ 6.6 Hz, 9 H; CH_3), 1.21–1.36 (m, 72 H; CH_2), 1.37–1.54 (m, 18 H; $ArOCH_2CH_2CH_2$), 1.69–1.87 (m, 18 H; $ArOCH_2CH_2$), 2.06 (q, $J = 6.5$ Hz, 12 H; CH_2=$CHCH_2$), 4.06 (t, $J = 6.3$ Hz, 18 H; $ArOCH_2$), 4.94 (d, $J =$ 11.3 Hz, 6 H; olefinic H), 5.00 (d, $J = 18.6$ Hz, 6 H; olefinic H), 5.74–5.89 (m, 6 H; olefinic H), 7.13 (s, 6 H; ArH), 7.81 (d, $J = 8.9$ Hz, 6 H; ArH), 8.05 (s, 3 H; NH), 8.73 ppm (d, $J = 8.91$ Hz, 6 H; ArH); IR (KBr): $\tilde{\nu} =$ 3302 (NH), 2925, 2854, 1645 (C=O), 1583 (C=O), 1490, 1427, 1406, 1373, 1335, 1239, 1177, 1117, 909, 804 cm^{-1}; FAB-MS (NBA): *m/z*: 1977 [M^+]; elemental analysis calcd (%) for $C_{126}H_{186}N_6O_{12}$ (1976.9): C 76.55; H 9.48; N 4.25; found: C 76.43; H 9.39; N 4.29.

1,3,5-tris{4-[*N*-(*tert*-butoxycarbonylamino)]phenyl}benzene (9): 4-[*N*-(*tert*-Butoxycarbonyl)amino]phenylboronic acid (226 mg, 0.95 mmol) and aqueous 2 M sodium carbonate solution (5 mL) were added to a mixture of 1,3,5-tribromobenzene (50 mg, 0.16 mmol) and [$Pd(PPh_3)_4$] (37 mg, 0.032 mmol) in DME (10 mL) under an argon atmosphere. After the mixture was heated to reflux for 18 h, it was poured into water (50 mL) and extracted with dichloromethane (10 mL × 3). The organic layer was dried over anhydrous magnesium sulfate and evaporated in vacuo to dryness. The residue was passed though a short pad of silica gel (KANTO 60N) with chloroform as eluant to give a mixture of **9** and the corresponding mono- and disubstituted products. 4-[*N*-(*tert*-Butoxycarbonyl)amino]phenylboronic acid (226.0 mg, 0.95 mmol) and aqueous 2 M sodium carbonate solution (5 mL) were added to a mixture of crude **9** and [$Pd(PPh_3)_4$] (37.0 mg, 0.032 mmol) in DME (10 mL) under an argon atmosphere. After the mixture was heated to reflux for 18 h, it was poured into water and extracted with dichloromethane. The organic layer was dried over anhydrous magnesium sulfate and evaporated in vacuo to dryness. The residue was purified by column chromatography on silica gel (KANTO 60N) with chloroform as eluant to give **9** in 10 % yield (10.8 mg, 0.017 mmol) as a white powder; m.p. 149–150 °C; ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 1.54$ (s, 27 H; CH_3), 6.55 (s, 3 H; NH), 7.46 (d, $J =$ 8.4 Hz, 6 H; ArH), 7.55 (d, $J = 8.4$ Hz, 6 H; ArH), 7.67 ppm (s, 3 H; ArH); IR (KBr): $\tilde{\nu} = 3354$ (NH), 2978, 1698 (C=O), 1614, 1586 (C=O), 1521, 1437, 1392, 1368, 1314, 1235, 1162, 1055, 828 cm^{-1}; FAB-MS (NBA): *m/z*: 652 [$(M+1)^+$]; elemental analysis calcd (%) for $C_{39}H_{45}N_3O_6$ (651.8): C 71.87; H 6.96, N 6.45; found: C 71.96; H 7.14; N 6.30.

1,3,5-Tris(4-aminophenyl)benzene (10): trifluoroacetic acid (504.0 mg, 341 μL, 4.42 mmol) was added to a solution of **9** (40.0 mg, 0.06 mmol) in dichloromethane (2 mL) at 0 °C under an argon atmosphere. After the mixture was stirred at room temperature for 2 h, it was extracted with diethyl ether (30 mL) and washed with saturated aqueous sodium hydrogencarbonate solution (30 mL × 2). The organic layer was acidified with aqueous 1.2 N hydrochloric acid solution (5 mL) and extracted with water (10 mL × 2). The water layer was neutralized with aqueous 5 N sodium hydroxide solution (2 mL). The resulting precipitate was collected by filtration and washed with water (5 mL), cold methanol (1 mL), and dichloromethane (1 mL) to give **10** in 76 % yield (16.3 mg, 0.0464 mmol) as a brown powder. Without further purification, **10** was used for the next reaction. M.p. 161–165 °C; ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 5.53$ (s, 6 H; NH_2), 6.70 (d, $J = 8.1$ Hz, 6 H; ArH), 7.79 (d, $J = 8.1$ Hz, 6 H; ArH), 7.80 ppm (s, 3 H; ArH); IR (KBr): $\tilde{\nu} = 3377$ (NH), 1612, 1517, 1283, 1183, 1061, 823 cm^{-1}.

1,3,5-Tris{4-[3,4,5-tris((*S*)-3,7-dimethyloctyloxy)phenylcarbonylamino]-phenyl}benzene (11): Compound **5d** (43 mg, 0.070 mmol) in dry THF (2 mL) was added dropwise to a solution of **10** (7.5 mg, 0.021 mmol) and triethylamine (16.9 mg, 12.4 μL, 0.084 mmol) in dry THF (2 mL) at 0 °C under an argon atmosphere. After the mixture was stirred at room temperature for 3 h, it was filtered to remove triethylamine hydrochloride and evaporated in vacuo to dryness. The residue was purified by column chromatography on silica gel (KANTO 60N) with chloroform/methanol (100/1) as eluant to give **11** in 32 % yield (14 mg, 0.007 mmol) as a white powder; m.p. 136–137 °C; ^{1}H NMR (395 MHz, $CDCl_3$): $\delta = 0.83$–0.98 (m, 81 H; CH_3), 1.12–1.90 (m, 90 H; CH_2), 4.01–4.08 (m, 18 H; $ArOCH_2$), 7.10 (s, 6 H; ArH), 7.73 (d, $J = 8.6$ Hz, 6 H; ArH), 7.77 (s, 3 H; ArH), 7.78 (d, $J = 8.6$ Hz, 6 H; ArH), 7.88 ppm (s, 3 H; NH); IR (KBr): $\tilde{\nu} = 3435$ (NH), 2954, 2926, 2869, 1645 (C=O), 1584 (C=O), 1512, 1496, 1468, 1427, 1385, 1335, 1236, 1208, 1116 cm^{-1}; MALDI-TOF-MS (CHCA): *m/z*: calcd for $C_{135}H_{213}N_3O_{12}$ [M^+]: 2069.62; found: 2069.64; elemental analysis calcd

(%) for $C_{135}H_{213}N_3O_{12}$ (2070.1): C 78.33; H 10.37, N 2.03; found: C 78.14; H 10.35; N 2.19.

General procedure for ring-closing olefin metathesis: A stock solution of **8d** (0.83 mg, 0.0004 mmol) in octane (20 mL) was added to **8f** (78.3 mg, 0.0396 mmol) in dry hexane (4000 mL) under an argon atmosphere and stirred at room temperature. After the mixture had changed to a homogeneous solution, Grubbs catalyst (0.98 mg, 0.0012 mmol) in dry hexane (10 mL) was added at room temperature. After 5 min, the reaction mixture was quenched by bubbling oxygen and the solvent was removed by evaporation. The residue (71.3 mg) was suspended in chloroform (50 mL) and filtered to remove the insoluble material (21.3 mg). The filtrate was evaporated in vacuo to dryness. The residue (49.2 mg) was divided into five portions, which were subjected to SEC with chloroform as eluant to give poly-2 in 43% yield (32.1 mg, 0.017 mmol as monomer unit) and to recover **8d** quantitatively. The characterization of the poly-2 is described in the text.

Theoretical calculations: All calculations were performed at the Hartree–Fock 6-31G* level with the Spartan 04 package.

AFM: Atomic force microscopy (AFM) images were obtained on a SII SPA400 DFM (tapping mode). SI-DF20 type tips were used. Samples were prepared by drop casting from a 0.01 mM (as monomer unit) THF solution on cleaved highly oriented pyrolytic graphite (HOPG).

TEM: A JEM-2020 (JEOL) transmittance electron microscope was used for recording the TEM images. The accelerating voltage was 200 kV. TEM samples were prepared by placing a THF solution of poly-2 (0.01 mM as monomer unit) onto a carbon-coated copper grid (200 mesh) and then allowing the samples to dry overnight at room temperature under reduced pressure.

Acknowledgements

We thank Professor Dr. Shigeori Takenaka and Dr. Keiichi Otsuka (Kyushu University) for measurement of MALDI-TOF-MS. This work was partially supported by a Supporting Young Researchers with Fixed-term Appointments, Special Coordination Funds for Promoting Science and Technology of Japan.

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Received: June 23, 2005
Published online: October 13, 2005

