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Citation
Organic and Biomolecular Chemistry, 8(6): 1344-1350

Issue date
2010-03-21

Type
Journal Article

URL
http://hdl.handle.net/2298/18351

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Versatile chiroptics of peptide-induced assemblies of metalloporphyrins†

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Received (in XXX, XXX) Xth XXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X
First published on the web Xth XXXXXXXXX 200X
DOI: 10.1039/b000000x

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Zinc porphyrin functionalized with double long-chain alkylated L-glutamide (GTPP-Zn) was synthesized for the first time, and its self-assembling behaviour was investigated in nonpolar organic solvents. The uniqueness of this functionalized porphyrin is characterized by its drastic colour change from dark green to purple via the formation of chirally stacked structures through selective axial coordination on zinc with pyridine derivatives. In this paper, we report the versatility of the GTPP-Zn assembly process as a stimuli-responsive chiroptical switching system and describe the remarkable ligand-specific induction of secondary chirality accompanied by aggregation morphological change.

Introduction

Chiroptics is important for the investigation of chiral substances in nature. These optical techniques can be used to create complicated nanostructures from chiral molecules such as amino acids and sugars. Recently, chiroptical materials have come to be used in diverse fields such as analytical chemistry, photochemistry, and materials chemistry. Thus, nanofabrication with chiral molecules holds significant promise as a method to realize molecular devices with possible applications such as chiroptical switches, films, and molecular motors. Furthermore, molecular organogel systems have been widely investigated as unique organic media in which gelation occurs through the formation of a three-dimensional nanofibrillar network of self-assembling low-molecular-weight compounds such as peptide-, sugar- and cholesterol-based lipophilic compounds. The fibrillar aggregates are often chirally ordered and show secondary chirality with strong CD signals in organic media. Successfully synthesized examples include pyrene-, perylene-, isoquinoline-, triazine- and porphyrin-containing organogel systems. Therefore, a molecular organogel system is an attractive candidate for chiroptical materials.

On the basis of these viewpoints, we focus on chiroptical porphyrin derivatives with the aim of creating stimuli-responsive soft materials. Herein, we introduce a novel chiroptical molecule (GTPP-Zn) containing a zinc porphyrin unit that is functionalized with a double long-chain alkylated L-glutamide derivative as a promoter for chiral assembly (Scheme 1). It is expected that chiral stacking of porphyrin units can not only be induced through intermolecular hydrogen bonding between the L-glutamide units but also be tuned by axial coordination on zinc.

In this paper, we report the versatility of the GTPP-Zn self-assembling system as a stimuli-responsive chiroptical switch, exhibiting a remarkable ligand-specific spectral shift, induction of secondary chirality, and dynamic morphological change.

![Scheme 1](image_url)

Scheme 1 L-Glutamide-derivatives functionalized tetraphenylporphyrin.

Results and Discussion

Solubility change of the porphyrin derivative by zinc-insertion

The free-base tetraphenylporphyrin (TPP) derivative functionalized with L-glutamide-derived lipid (GTPP) showed almost no solubility in nonpolar organic solvents such as diethyl ether, cyclohexane and n-hexane. However, we observed that this limited solubility promotes gelation in organic media through nanofibrillar aggregation when solvent polarity is adjusted with polar solvents such as THF and DMF. This phenomenon is a form of low-molecular-mass organogelation.

Interestingly, zinc insertion into GTPP resulted in remarkably improved solubility in nonpolar organic solvents while the gelation ability almost disappeared. Good solubility is a significant advantage in the manufacture of soft materials. Reduction of the solvent absorption, especially in the UV region, is also important. As shown in Fig. 1a, a deep pink-coloured clear solution (0.25 mM) was obtained without any gelation at 20 °C when zinc-containing GTPP (GTPP-Zn) was dissolved in cyclohexane. The λmax of the glutamide-unit-free TPP moiety was located at 430 nm as a single peak,
which was longer by 13 nm than that in zinc-containing TPP (Figure 1a). This indicates aggregation of GTPP-Zn in cyclohexane. To address this observation, the following were examined: (1) $\lambda_{max}$ of GTPP-Zn shifted from 430 nm to 417 nm by high dilution such as to 1 µM. The spectral pattern with $\lambda_{max}$ of 417 nm is similar to that in the Soret band of TPP-Zn.† (2) At 10 µM, a reversible $\lambda_{max}$ shift between 430 nm and 417 nm was observed in the temperature range between 10 °C and 60 °C.† (3) The CD spectra of GTPP-Zn showed large Cotton effects ($[\theta]_{417} = 8 \times 10^5$ deg cm$^2$ dmol$^{-1}$ at 0.25 mM at 20 °C) around the Soret band (Figure 1b), indicating chiral ordering of a porphyrin moiety while almost no CD was observed at 10 µM at 60 °C or in a highly diluted solution such as 1 µM at 10 °C. These results indicate that GTPP-Zn in cyclohexane can disperse as certain aggregates through the amide bonds and also undergoes both lyotropic and thermotropic aggregate–monomer phase transitions.

Fig. 1 UV-visible (a) and CD spectra (b) of TPP-Zn (red line) and GTPP-Zn (blue line) in cyclohexane (0.25 mM) at 20 °C.

Chiroptical response to pyridine doping on GTPP-Zn

Addition of pyridine as a ligand to GTPP-Zn induced an amazing colour change from deep pink to dark green while TPP-Zn showed only a slight change from deep pink to purple, and almost no colour change was observed in free-base GTPP. The typical results of the colour changes are summarized in Figure 2. Hu et al. reported that tetra(4-pyridyl)porphyrin formed greenish nanocrystals (rod-like nanocrystals) with assistance from cetyltrimethylammonium bromide as a cationic micellar compound, but there are few similar findings in reports of other synthetic porphyrin systems. Therefore, these observations suggest that pyridine promotes a change in aggregation morphology of GTPP-Zn into strongly stacked structures such as nanocrystals. A detailed discussion appears in the next section.

Fig. 2 Library of colour changes of the porphyrin derivatives (0.5 mM) in cyclohexane at 20 °C. (a) GTPP-Zn, (b) GTPP-Zn with pyridine (10 equiv), (c) GTPP-Zn with pyridine (2000 equiv), (d) GTPP-Zn in chloroform, (e) GTPP-Zn with pyridine (10 equiv) in chloroform, (f) TPP-Zn, and (g) TPP-Zn with pyridine (10 equiv).

Fig. 3 UV-visible (a) and CD (b) spectra of GTPP-Zn (0.25 mM) in cyclohexane at 20 °C without pyridine (red broken line), with 10 equiv (blue line) and 2000 equiv (black line) of pyridine.

The colour change of GTPP-Zn with 10 equiv of pyridine was accompanied by complicated splitting of the Soret band in the UV–visible spectrum. As shown in Figure 3a, four peak maximums are observed at 400, 427, 435 and 459 nm. Here, we initially focus on the peak maximum at 427 nm because TPP-Zn shows a simple $\lambda_{max}$ shift from 417 nm to 427 nm by addition of an equimolar amount of pyridine (Figure 2g). This can be explained by formation of a typical one-to-one complex via a nitrogen–zinc coordination. A similar $\lambda_{max}$ of 427 nm was also observed in GTPP-Zn in the presence of a large excess (2000 equiv) of pyridine (Figures 2c and 3a). This indicates that pyridine can be an effective solvent for GTPP-Zn as well as a ligand for coordination. In support of this, when pyridine-$d_5$ was used as a solvent in NMR spectroscopy, a peak-broadening phenomenon was observed, indicating complete disaggregation of an l-glutamide derivative. This is probably due to inhibition by pyridine of intermolecular interaction such as hydrogen bonding.
Therefore, we conclude that a peak maximum at 427 nm can be attributed to axial coordination of pyridine on GTPP-Zn without any aggregation.

The detailed concentration dependency of pyridine is shown in Figure 4. Neither significant colour nor spectral changes were observed in the presence of 0–4 equiv of pyridine. It seems that the colour change to dark green (Figure 2b) is specifically induced in the presence of 5–100 equiv of pyridine with an increase in the absorbance at 459 nm (Abs$_{459}$). Further addition of pyridine changes the colour to purple (Figure 2c) with a decrease in Abs$_{459}$. However, we found that a greenish colour was observed even in a one-to-one mixture of GTPP-Zn and an equimolar amount of pyridine. This was obtained by the following special procedure: when the one-to-one mixture was aged at 60°C for 10 min and then allowed to stand at 25°C for two days. Therefore, it is estimated that a one-to-one complex can be produced but is delayed due to the aggregation.

Aggregation structure of the greenish complex

The greenish complex with $\lambda_{\text{max}}$ of 459 nm should be furthermore discussed in detail because it is expected to be a model system for a natural chlorophyll system. As shown in Figure 3b, the complexation with pyridine was accompanied by an extreme enhancement of CD intensity around 459 nm. The largest value can be detected in the concentration range of 5–100 equiv of pyridine and exceeds $1 \times 10^5$ deg cm$^{-1}$ dmol$^{-1}$ in [θ]$_{362}$ (Figure 3b), which was 20 times larger than that of the original GTPP-Zn aggregates. On the other hand, a decrease of CD intensity was observed in free-base GTPP (15 to $0.08 \times 10^3$ deg cm$^{-1}$ dmol$^{-1}$). Therefore, it is considered that the axial coordination of pyridine on GTPP-Zn promotes a drastic change of chirally ordered structures as well as strong stacking among the porphyrin moieties.

On the other hand, the Q band absorptions are also helpful to understand the molecular aggregation of G$_9$TPP-Zn. It is known that an absorption spectrum of normal metalloporphyrin shows the other two absorption maximums called the Q or $\alpha$ and $\beta$ bands, which are found between 500 and 650 nm. As shown in Figure 3a, the complexation with pyridine induced a relative intensity change of the $\alpha$ and $\beta$ bands ($\varepsilon_\alpha/\varepsilon_\beta$) as well as a $\lambda_{\text{max}}$ shift. Generally, the value of $\varepsilon_\alpha/\varepsilon_\beta$ and the red shift of $\alpha$ and $\beta$ bands are qualitatively correlated with the strength of a coordination bonding of zinc–ligand bond and stability of the complex. Table 1 summarizes the observed $\alpha$ and $\beta$ bands under various conditions. It is clear that the complexation with pyridine increases $\varepsilon_\alpha/\varepsilon_\beta$ but the most remarkable $\lambda_{\text{max}}$ shifts and enhancement of the $\varepsilon_\alpha/\varepsilon_\beta$ value were observed in the GTPP-Zn–pyridine complex. These results indicate that the molecular stacking results in a remarkable increase of the stability of the complex.

Table 1 Absorption spectral date of TPP-Zn and GTPP-Zn

<table>
<thead>
<tr>
<th>porphyrin$^*$</th>
<th>guest molecule</th>
<th>solvent</th>
<th>$\beta$ (nm)</th>
<th>$\alpha$ (n.m)</th>
<th>$\varepsilon_\alpha/\varepsilon_\beta$</th>
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</thead>
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<td>CHCl$_3$</td>
<td>551</td>
<td>594</td>
<td>0.16</td>
</tr>
<tr>
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<td>pyridine (10)</td>
<td>CHCl$_3$</td>
<td>562</td>
<td>602</td>
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<tr>
<td></td>
<td></td>
<td>cyclohexane</td>
<td>545</td>
<td>585</td>
<td>0.09</td>
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<tr>
<td></td>
<td>pyridine (10)</td>
<td>cyclohexane</td>
<td>560</td>
<td>599</td>
<td>0.34</td>
</tr>
<tr>
<td></td>
<td></td>
<td>toluene</td>
<td>549</td>
<td>588</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
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<td>toluene</td>
<td>562</td>
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<td>0.43</td>
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<tr>
<td>GTPP-Zn</td>
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<td>CHCl$_3$</td>
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<td>597</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>pyridine (10)</td>
<td>CHCl$_3$</td>
<td>562</td>
<td>603</td>
<td>0.46</td>
</tr>
<tr>
<td></td>
<td></td>
<td>cyclohexane</td>
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<td>598</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>pyridine (10)</td>
<td>cyclohexane</td>
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<td>0.89</td>
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<td>pyridine (200)</td>
<td>cyclohexane</td>
<td>561</td>
<td>601</td>
<td>0.41</td>
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</table>

$^*$ Concentration of porphyrin: 0.25 nM
$^*$ Date from reference 11

For $^1$H NMR spectroscopy, a sample of the GTPP-Zn–pyridine complex was obtained by recrystallization from a concentrated cyclohexane solution and successive washing with cyclohexane. Analysis was performed in a chloroform-d solution. The resultant $^1$H NMR spectrum shows large upfield shifts of the proton resonances of the pyridyl ring ($\Delta$H$_{\text{up}}$ = 5.24 ppm, $\Delta$H$_{\text{max}}$ = 1.48 ppm) caused by the shielding effect of the porphyrin. This result supports that the complexation of GTPP-Zn with pyridine is formed by axial coordination. In addition, the binding ratio of GTPP-Zn and pyridine was also estimated by the peak areas of a chiral carbon in an L-glutamate moiety and m-H in a coordinated pyridine, indicating a one-to-one complex of GTPP-Zn and pyridine.

The IR spectra showed informative absorption shifts on the amide bond. The typical absorptions of GTPP-Zn with pyridine in cyclohexane were located at 1632 cm$^{-1}$ and 1550 cm$^{-1}$ and were attributed to amides I and II, respectively, while nonbonding amide I and II bands measured in a chloroform solution were located at 1652 cm$^{-1}$ and 1525 cm$^{-1}$, respectively. These results indicate that a strong and ordered hydrogen bonding interaction derived from an L-glutamidate moiety is present for the aggregation of GTPP-Zn. A chirally stacked structure of the aggregates can be estimated from a CD spectral pattern. The greenish complex...
showed a typical splitting with a positive Cotton effect around 462 nm and a negative Cotton effect around 454 nm (Figure 3b). According to Huang’s definition, this pattern can be assigned to a typical R-chiral plane-to-plane ordering.

**Induction of morphological change**

As shown in Figure 5a, only globular-like structures having diameters of 300–500 nm were observed in the cast film prepared from a cyclohexane solution containing 0.25 mM GTPP-Zn. It should be noted that no staining reagent such as heavy metals was used in the sample preparation, and therefore the good contrast of the TEM image supports the existence of zinc ions in the aggregates. This explains that the good solubility of GTPP-Zn in nonpolar solvents is due to globular aggregation although free-base GTPP forms nanofibrillar aggregates to make a gel.

Figure 5b shows that the complexation with pyridine induces a drastic change of aggregation morphology from globular to needle-like structures. The dimensions of the newly detected morphology are a minimum diameter of several nanometers and a length of a couple of micrometers. This supports the spectral estimation that the greenish aggregates of a one-to-one complex of GTPP-Zn with pyridine would be based on nanocrystals. On the other hand, no similar aggregation was observed in the TPP-Zn–pyridine complex. Therefore, the 1-glutamide moiety provides an essential driving force for aggregation and ordering on the basis of intermolecular hydrogen bonding interaction.

**Selective chiroptical response on axial coordination**

UV–visible and CD spectral responses of GTPP-Zn (0.25 mM) were investigated for various pyridine derivatives such as monoalkyl- and dialkylpyridines. As shown in Figure 6, the obtained UV–visible and CD spectra were distinctly different from each other because of the chemical difference of pyridines such as (a) 4-methylpyridine, (b) 3,5-dimethylpyridine, (c) 4-tert-butylpyridine, and (d) 2,6-di-tert-butylpyridine, as typical examples. For example, strong CD signals were induced by 4-methylpyridine, but the chiral sense at around 450 nm was opposite that in pyridine. On the other hand, 2,6-di-tert-butylpyridine induced few CD signals. It is clear that the spectral patterns vary in \( \lambda_{\text{max}} \), sharpness, intensity, chiral sense, and splitting pattern. In addition, the spectral response was accompanied by a change of aggregation morphology. Typical examples are shown in Figure 7. Both 2,3- and 3,5-dimethylpyridine induced nanofibrillar aggregation (Figures 7b and 7c), but 2,6-dimethylpyridine did not induce fibrillar structure but rather globular-like structure (Figure 7d). As compared with Figure 5b, these morphological changes are clearly different from that in pyridine where needle-like aggregates were produced. As supporting this, the complexes with 2,3- and 3,5-dimethylpyridine showed a typical mass gelation behavior in 1 mM (Figure 7a), although the complexation with pyridine promotes the crystallization. These results indicate that the coordination structures influence to the macroscopic morphologies.
Fig. 7 (a) Photo image of the GTPP-Zn (1 mM) gel in cyclohexane at 15 °C with 2,3-dimethylpyridine (100 equiv). TEM images of the GTPP-Zn aggregates with (b) 2,3-dimethylpyridine (100 equiv), (c) 3,5-dimethylpyridine (10 equiv), and (d) 2,6-dimethylpyridine (10 equiv) in the cast film prepared by 0.25 mM cyclohexane solution. (b) and (c) were stained by 2.0 wt% ammonium molybdate.

These results demonstrate the potential for applicability as a sensing system through axial coordination. In this regard, further detailed investigation was carried out by using 11 kinds of pyridine derivatives as guest molecules. As summarized in Table 2, the λmax shifts of the α and β bands, εα/εβ, and the CD intensity were apparently dependent on the guest molecules. Here, when the focus is on the value of εα/εβ and the relative CD intensity (Figure 8), we recognize that there are roughly two classifications in the response pattern: one is to show the results with a weak CD strength as well as a small εα/εβ.

Table 2 Observed α and β bands and the CD intensities of GTPP-Zn with various guest molecules in cyclohexane at 20 °C

<table>
<thead>
<tr>
<th>No.</th>
<th>guest molecule</th>
<th>β (nm)</th>
<th>α (nm)</th>
<th>εα/εβ</th>
<th>[α]max (10⁶ deg cm² dmol⁻¹)</th>
<th>[β]min (10⁶ deg cm² dmol⁻¹)</th>
<th>Δθ ([α]max - [β]min)</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>none</td>
<td>558</td>
<td>598</td>
<td>0.33</td>
<td>433 (0.8)</td>
<td>443 (0.7)</td>
<td>1.5</td>
</tr>
<tr>
<td>2</td>
<td>pyridine</td>
<td>573</td>
<td>613</td>
<td>0.89</td>
<td>462 (15.9)</td>
<td>454 (-13.2)</td>
<td>29.1</td>
</tr>
<tr>
<td>3</td>
<td>4-methylpyridine</td>
<td>566</td>
<td>603</td>
<td>0.64</td>
<td>444 (4.5)</td>
<td>448 (-8.3)</td>
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<tr>
<td>4</td>
<td>3-methylpyridine</td>
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<td>603</td>
<td>0.56</td>
<td>426 (3.3)</td>
<td>439 (-3.8)</td>
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<tr>
<td>5</td>
<td>3-ethylpyridine</td>
<td>565</td>
<td>604</td>
<td>0.59</td>
<td>426 (6.2)</td>
<td>440 (-4.9)</td>
<td>11.1</td>
</tr>
<tr>
<td>6</td>
<td>4-tert-butylpyridine</td>
<td>561</td>
<td>602</td>
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<td>424 (0.8)</td>
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<td>599</td>
<td>0.35</td>
<td>434 (0.6)</td>
<td>427 (-0.5)</td>
<td>1.1</td>
</tr>
</tbody>
</table>

Concentration of GTPP-Zn: 0.25 mM, guest molecule: 2.5 mM (10 equiv).

Fig. 8 Plot of εα/εβ versus Δθ values of GTPP-Zn (0.25 mM) with 10 equiv of various guest molecules in cyclohexane at 20°C. Numbers refer to complexes in Table 2.
These guest molecules are 2-alkyl and/or tert-butyl derivatives. This strongly indicates that GTPP-Zn is very sensitive to the steric bulk of the guest molecules. The other one is a category showing the increase of the CD intensity with the increase of the ε/ε₀ value although there is one exception in 3,5-dimethylpyridine. However, this exception is probably related to the steric factor derived from two methyl groups. The value of ε/ε₀ is an indicator of the complex stability, and therefore it is reasonable that the increase of ε/ε₀ is accompanied by an enhancement of chiral ordering, showing an increase of CD strength.

Conclusions
In this paper, we have described the synthesis of a new zinc-inserted porphyrin lipid (GTPP-Zn) and the chiroptical response toward pyridine derivatives. The following findings can be summarized: (1) the solubility in a nonpolar solvent was fully modified by insertion of zinc into GTPP compared with free-base GTPP. TEM observations indicated that the solubility improvement was related to a change in aggregation morphology from fibrils to globules. (2) Axial coordination of pyridine on GTPP-Zn induced new chirality in the Soret band as well as a drastic visible spectral change. This is caused by induction of highly ordered chiral stacking among the porphyrin moieties. (3) By investigation of axial coordination with various pyridine derivatives, it was confirmed that the resultant spectral patterns varied in intensity, shift, and splitting. This indicates that GTPP-Zn has high potential applicability as a multiresponsive molecular switching device.

Experimental
Materials and instrumentations
5-(4-methoxycarbonylphenyl)-10, 15, 20-triphenyl-21H, 23H-porphine and 5, 10, 15, 20-tetraphenyl-21H, 23H-porphine were purchased from Tokyo Chemical Industry. Reagent grade solvents and Measurement grade solvent were used. N,N,N′,N′-diisopentyl-1-L-glutamate (G) was synthesized by the previously reported procedure with slight modification. 1H NMR (400 MHz) spectra were recorded in CDCl₃ with SiMe₄ as an internal standard with a JNM-EX400 (JEOL), FT-IR spectra were measured in a KBr method with FT/IR-4100 (JASCO). FT-IR spectra of solution were obtained from 1 mM cyclohexane or chloroform solutions. MALDI TOF-MS spectra was recorded on a Voyager RP (PerSeptiv Biosystem). UV-visible and CD spectra were measured with V-560 (JASCO) and J725 (JASCO), respectively. The solution was poured into a 1 mm, 1.0 mm and 10 mm quartz cell. TEM images were observed with JEM-2000EX (JEOL). The solution was cast in a carbon-coated copper grid and dried by a vacuum pump under reduced pressure. The accelerating voltage of the TEM was 80 kV and the beam current was 40 A.

Zinc inserted porphyrin-lipid (GTPP-Zn)
Zinc inserted porphyrin (GTPP-Zn) was prepared by mixing a solution of Zn(OAc)₂·2H₂O (0.17 g, 0.80 mmol) in methanol (10 mL) and a solution of GTPP (0.3 g, 0.25 mmol), which was obtained by the previously reported procedure in chloroform (100 mL). The mixture solution was stirred for 6 h at room temperature. The solution was concentrated in vacuo. The residue was dissolved with water and dried with sodium sulfate. The solution was dried in vacuo to give purple solids (196 mg, 72%). mp: 230.5-232.5 °C. (Found: C, 74.56; H, 7.28; N, 8.21. C₂₇H₅₃N₃O₂Zn requires C, 74.95; H, 7.22; N, 8.27%). nmax(KBr)/cm⁻¹ 3395 and 3310 (NH), 2925 and 2852 (CH), 1647 (CO), 1523 (NH), δ0 (400 MHz; CDCl₃; Me₂Si) 0.79-0.86 (6 H, t, -CH₃), 1.16-1.25 (40 H, br, -(CH₂)₃), 1.54 (2 H, br, -CH₂CO), 1.75-1.91 (2 H, br, -CH₂), 2.67-2.81 (4 H, m, -NHCH₂), 3.46 (1H, q, -CH₃), 5.56 (1 H, br, NH), 6.28 (1 H, br, NH), 7.45-7.51 (1 H, br, NH), 7.74-7.76 (9 H, m, ArH), 8.13-8.22 (10 H, m, ArH). MALDI TOF MS (2,5-dihydroxybenzoic acid matrix): Calcd for C₇₅H₆₆N₃O₇Zn 1183.60, m/z = 1184.45 (M⁺).

Acknowledgement
This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture of Japan.

Notes and references
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Graphical Abstract

Title: Versatile chiroptics of peptide-induced assemblies of metalloporphyrins

Author’s Names: Hirokuni Jintoku, Takashi Sagawa, Tsuyoshi Sawada, Makoto Takafuji and Hirotaka Ihara

Textual Information
Zinc porphyrin functionalized with L-glutamide has been newly synthesized and its unique responses such as ligand-specific induction of secondary chirality thorough the aggregation morphology change are reported.

Graphical Information