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Multi-chiro-informative System Created by a Porphyrin-functionalized Chiral Molecular Assembly

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We introduce multi-chiroptically active organic systems that exhibit circular dichroism, fluorescence and circularly polarized luminescence through chiral molecular orientation of a non-chiral porphyrin moiety. The spectra of these unique systems are distinctly sensitive to external conditions, including an enantiomeric factor.

Keywords: Circularly polarized luminescence |
Chiral self-assembly | Supramolecular gel

Chirality and chiroptical properties are essential phenomena in nature because most biomolecules contain asymmetric centers. Circularly polarized luminescence (CPL) is an interesting chiroptical phenomenon that contains more information than natural (unpolarized) or linearly polarized light; consequently, some animals and plants use CPL as a communication tool.¹ The simplest way to generate CPL involves subjecting normal light to a linear polarizer with a quarter-wave plate, although this method is accompanied by a serious reduction in light energy. To overcome this problem, CPL-generation systems have recently been developed that use chiral luminescent compounds that are totally organic,²⁻⁵ and the organic CPL generation systems are roughly classified into single-component² and molecular assembling systems.³⁻⁵ The former approach is based on precise molecular design and skillful organic synthesis. On the other hand, molecular-assembling systems are somewhat advantageous compared to single-component systems because both CPL intensity and wavelength can easily be tuned by selecting an appropriate luminescent moiety and by adjusting molecular ordering.

In this study, we focus on a stimuli-responsive chiral assembling system that provides multi-chiroptical signals based on circular dichroism (CD), fluorescence (FL) and CPL. For this purpose, we selected the molecular assembling approach for CPL generation by using the porphyrin-functionalized chiral system (**G-Por**) for the first time shown in Figures 1 and S1a to generate CPL because the **G**-moiety⁴⁻⁷ derived from glutamic acid, as a chiral source, promotes chiral ordering, generates secondary chirality and enhances CD intensity, while the zinc inserted in the porphyrin moiety exhibits unique axial coordination behaviors.^{5,7}

We prepared **G-Por** by coupling synthesized *N*²,*N*³-didodecyl-L-glutamide (**G**) with 5-(4-carboxyphenyl)-10,15,20-triphenyl-21*H*,23*H*-porphine and subsequent insertion of zinc according to previously reported methods.^{6,7}

Figure 1. Confocal microscopic images of the **G-Por** cyclohexane solution (b) before and after addition of one equivomolar of (a) pyridine and (c) MeIm. Figures 1e and 1f show the estimated structures of the assembled **G-Por** (e) before and (f) after addition of 1-methylimidazole (MeIm). The scale bars indicate 10 μ m.

Confocal microscopy showed that a solution of **G-Por** in cyclohexane contains globular images, as revealed through the fluorescence of the porphyrin moiety (Figure 1b). The globular aggregation morphology is unusual given that **G**-derivatives often produce fibrils.⁴⁻⁶ Fibrous aggregation is likely to be promoted by intermolecular chiral hydrogen bonding involving the three amide bonds in the **G** moiety, while zinc-carbonyl interactions dominate over amide-amide interaction in the zinc-inserted **G-Por**, as schematically illustrated in Figure 1e. These interactions are discussed later.

CD spectroscopy provides evidence for the aggregation of **G-Por**; Figure 2 reveals a distinct Cotton effect at around 430 nm for the **G-Por** (0.25 mM) solution in cyclohexane. The absorption band corresponds to the Soret band⁸ of a porphyrin moiety in which the porphyrin moiety itself is not chiral. In addition, the porphyrin moiety is not close to the chiral center of **G**; hence, we conclude that the Cotton effect exhibited by **G-Por** is due to the secondary chirality of chiral aggregates induced by the **G**-moiety. In support of this estimation, no CD was observed in the porphyrin derivative devoid of **G** (i.e., Por-COOMe, Figure S1b).

The addition of 1-methylimidazole (MeIm) to the solution of **G-Por** in cyclohexane resulted in a dramatic change in aggregation morphology (Figure 1c). On the other hand, no significant morphological change was observed when pyridine

Figure 2. Visible absorption (broken line) and CD (solid line) spectra of **G-Por** in cyclohexane; [**G-Por**] = 0.25 mM, temperature: 20 °C, pathlength: 0.1 cm.

Figure 3. (a) Visible absorption spectra and (b) the concentration dependencies of guest molecules on $\varepsilon_\alpha/\varepsilon_\beta$ of the **G-Por** cyclohexane solution. Guest molecules: none (black line), pyridine (blue line) and MeIm (red line). [**G-Por**] = 0.25 mM. (a) [Pyridine] and [MeIm] = 0.25 mM. (b) [Pyridine] and [MeIm] = 0–0.25 mM. Temperature: 20 °C, and pathlength: 0.2 cm. The original spectra for (b) are available in Figure S2.

was added instead of MeIm (Figure 1a). Figure 3, which shows visible absorption spectra around the Q bands of the porphyrin moiety, provides further evidence in support of this difference. The α and β band absorption ratio ($\varepsilon_\alpha/\varepsilon_\beta$) usually reflects the stability of the axially coordinated porphyrin-bound metal ion.⁹ In the case of MeIm, the absorption maximums of both the α and β bands were observed to red shift and the $\varepsilon_\alpha/\varepsilon_\beta$ value was also observed to distinctly increase with increasing amounts of added MeIm (Figures 3b and S2).

On the other hand, no similar changes were observed for addition of equimolar pyridine, while the $\varepsilon_\alpha/\varepsilon_\beta$ value increased to 0.87 with addition of 10 equiv. pyridine (Figure S3). FT-IR spectra of **G-Por** in cyclohexane (Figure S4) proved that the absorption of amide I of **G-Por** was shifted to lower wavenumber with equimolar MeIm but no change was observed with equimolar pyridine, indicating that the coordination of MeIm on Zn core affected the chiral orientation of **G-Por** aggregates. The difference is probably caused by the basicity of those small molecules. These results indicate that the **G-Por** aggregates are very sensitive to the axially coordinated small molecule which can trigger dramatic changes in aggregation morphology.

Figure 4. (a) CD, (c) FL and (e) CPL spectra, and the concentration dependencies of guest molecules on (b) molar ellipticity at 451 nm, (d) and (f) FL and CPL intensities at the peak emission wavelengths of the **G-Por** cyclohexane solution. Guest molecules: none (black line), pyridine (blue line) and MeIm (red line). [**G-Por**] = 0.25 mM. (a), (c), and (e) [Pyridine] and [MeIm] = 0.25 mM. (b), (d), and (f) [Pyridine] and [MeIm] = 0–0.25 mM. Temperature: 20 °C. Path lengths: 0.01 cm for (a) and (b), 0.2 cm for (c) and (d), and 1.0 cm for (e) and (f). Excitation: at 580 nm for (c)–(f). The original spectra for (b), (d) and (f) are available in Figures S5, S6 and S7, respectively.

The axial coordination of MeIm to **G-Por** affects the FL and CD spectra. Figure 4c shows FL spectra of solutions of **G-Por** in cyclohexane containing equimolar amounts of MeIm or pyridine, which were acquired by excitation of the Q band ($\lambda_{\text{ex}} = 580$ nm) because the FL intensity from Soret-band excitation is very small compared with that from Q-band excitation.¹⁰ The FL intensity decreased with increasing MeIm concentration, and the FL bands were observed to red shift, although small change was observed in the case of pyridine. The concentration dependencies shown in Figure 4d also reveal high sensitivity toward MeIm.

Figure 4a shows the effect of the addition of equimolar MeIm or pyridine on the CD spectrum. The complicated change of the CD pattern was observed in MeIm with appearance of new Cotton effects around 451 nm. Furthermore, Figure 4b

showed that the concentration dependency on the newly-appeared Cotton effects was specific with MeIm but not with pyridine, and therefore this difference can be explained by the preferential axial coordination of MeIm to the zinc atom, which leads to the changes of chirally-orientated structures suggested in Figures 1e and f. According to our previous NMR investigation, the addition of 10 molar equivalents of pyridine promotes the axial coordination of pyridine to Zn, which leads to reduced carbonyl-Zn interactions, with larger excesses (i.e., 1000×) of pyridine completely suppressing hydrogen bonding interactions around the **G**-amide bonds. On the other hand, it is clear that even the addition of equimolar MeIm completely changes the intermolecularly interacting structures.

Figure 4e shows the first example of CPL generated from a porphyrin derivative. Regardless of the guest molecule, **G**-Por exhibited distinct CPL in cyclohexane solution. No CPL was observed in chloroform (as a good solvent) nor did the non-**G** porphyrin (Por-COOMe) exhibit CPL in cyclohexane. Therefore, we conclude that the CPL generated by **G**-Por is due to secondary chirality induced by chiral orientations among porphyrin moieties rather than by its inherent molecular chirality. CPL was also influenced by the guest molecule; the concentration dependency shown in Figure 4f also demonstrates that CPL intensity is sensitive to the nature of the small molecule.

We also examined the enantioselective responses of the chiroptical properties of **G**-Por. Figure 5 shows CD, FL, and CPL spectra in the presence of benzyloxycarbonyl L- or D-histidines as model enantiomers. While significant changes in the CD spectra were observed, they were not in FL and CPL spectra as clear as those observed for MeIm. These results indicate that the **G**-Por aggregates recognize the steric structure of histidine enantiomers through the coordination with Zn core.

In conclusion, we developed a multi-chiroptically active organic system and examined it by FL, CD, and CPL spectroscopies.

Figure 5. (a) CD, (c) FL and (d) CPL spectra and (b) the concentration dependencies of enantiomeric guest molecules on molar ellipticity at 429 nm of the **G**-Por cyclohexane solution. Guest molecules: none (black line), *N*-benzyloxycarbonyl L- (orange line) and D-histidine (green line). [**G**-Por] = 0.25 mM. [*N*-Benzyloxycarbonyl histidine] = (a), (c), and (d) 0.20 mM and (b) 0–0.25 mM. Temperature: 20 °C. Pathlength: 0.01 cm for (a) and (b), 0.2 cm for (c), and 1.0 cm for (d). The original spectra for (b) are available in Figure S8.

copies. Our system is advantageous because the observed chiroptical signals are absolutely enhanced by secondary chirality induced through chiral molecular assembly. In this study, we used porphyrin as a sensitive supramolecular tool. The less-limiting molecular design of our system provides a general and sensitive molecular tool that can be broadly applied.

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Supporting Information is available on <https://doi.org/10.1246/cl.200018>.

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