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Oligoamylose-entwined porphyrin: excited-state induced-fit for chirality induction†

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An oligoamylose-strapped porphyrin displayed circularly polarized luminescence (CPL) in the S_1 state despite being silent in circular dichroism (CD) in the ground state, suggesting chirality induction in the photoexcited porphyrin moiety from the oligoamylose-strap in the photoexcited state.

Chromophores that show circularly polarized luminescence (CPL) are an attractive class of optical materials.[1] CPL originates from chiral dispersive interaction in the photoexcited state, as approximated by the quotient of the electronic dipole moment divided by the magnetic dipole moment.[2] Therefore, CPL is an alternative application of electromagnetic properties of light in Maxwell's equation. A photoexcited chiral chromophore can generate CPL even when no chiroptical properties are observed in the ground state.[3] However, organic chromophores that exhibit large differential luminescence of left- or right-handed CPL have been primarily limited to chiral chromophore aggregates.[1a–c] Otherwise, the structurally rigid π-framework including helicenes,[4] biaryls,[5] and sophisticatedly designed molecules[6] has been indispensable to suppress racemisation both in the ground state and the excited state. In this context, exploration of non-aggregated and non-polymeric CPL-active chromophores is a significant challenge.[1d,7] Given that there is a trade-off between the electronic dipole moment and the magnetic dipole moment, a conformational change of a chromophore in the photoexcited state could be a potential strategy to impart chiral nature to the photophysical properties of the chromophore.

In contrast to the conventional approaches, we investigated whether an induced-fit system[8] could be adaptable to induce chirality in an intrinsically achiral chromophore in the photoexcited state in a chiral environment. In this context, a spiral channel of a chiral biological entity may be appropriate to transfer chirality to the intrinsically achiral chromophore. This report describes a comprehensive proof-of-concept study to tackle challenges in developing a new class of CPL materials.

A spiral channel can be created by length-mismatched chain clamping between each terminal of a rigid rotatable axle, which leads to the axle moiety self-encapsulating in the channel. For example, clipping the side-groups of the oligomeric π-systems has been explored to provide helical π-systems, which have been coined as "geländer oligomers" by Vögtle and coworkers.[9] Gladysz and co-workers also reported a similar strategy to form spiral structures entwining a stiff axle.[10] Such a vine-twining analogy is also intriguing to tune the electronic properties by twisting the axle of the chromophore.[11] Here we present a biological entity as a chiral adaptable channel that includes an achiral chromophore.

Amylose is a polysaccharide composed of a D-glucose backbone connected *via* α(1 → 4)-glycoside linkages, adopting a 6_1 left-handed helix (6 glucopyranose units in one turn).[12] This is of particular interest because the formation of the amylose–iodine inclusion complex, which is known as a "starch blue reaction", is one of the most representative examples of an induced-fit host–guest binding of a helical polymer.[13] The interior channel of the folded amylose encapsulates versatile lipophilic guest molecules, such as chromophores and polymers.[14,15] The most representative examples are cyclic analogues of oligoamylose (cyclodextrins), which have been key elements in host–guest chemistry,[16] and some of which can exhibit CPL.[17]

Herein, we design an oligoamylose-strapped porphyrin **1** (Scheme 1), with which an achiral porphyrin axle is self-folded by a helically twisted polysaccharide. A flexible oligoamylose-strap (per-*O*-methylated maltoheptaose) was tethered to the rigid porphyrin, wherein an interaction between the oligoamylose and porphyrin moiety occurred based on the fact that cyclodextrin derivatives were able to form exceptionally stable inclusion

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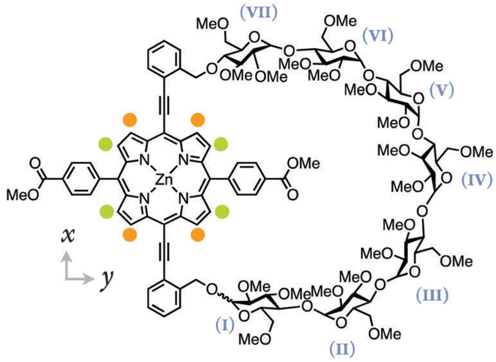
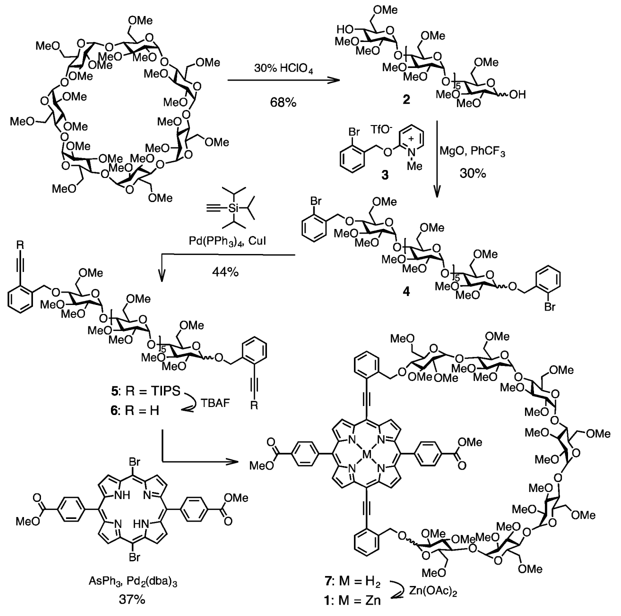


Scheme 1 Chemical structure of oligoamylose-strapped porphyrin **1**.

complexes with aqueous porphyrinoid.[18,19] With the aim of creating an induced-fit system through intramolecular host–guest interactions, the rotatable ethynylene linkages may be effective in inducing helicity around the porphyrin plane. Moreover, achiral porphyrin macrocycle is a privileged substrate to induce chirality.[20] At the same time, such a macrocyclic cavity composed of a porphyrin–cyclodextrin hybrid is also intriguing as a novel structural unit, the so-called "element-block",[21] in host–guest systems.[22]

The synthetic route is outlined in Scheme 2. Single scission of the glycoside linkage opened the ring of per-*O*-methylated β-cyclodextrin,[23] and both the $1^{(I)}$-hemiacetal and $4^{(VII)}$-hydroxy terminal of the methylated maltoheptaose **2** was simultaneously subjected to the Dudley's benzyl-transfer protocol[24] with **3**, and **4** was obtained in 30% yield. Then silylated acetylene was introduced to each bromine-terminal of **4** by the Sonogashira–Hagihara coupling reaction to give **5**, which was then desilylated. The linear oligoamylose **6** was re-cyclized with the corresponding porphyrin. The oligoamylose-strapped porphyrin **7** was metallated with zinc ion. The products were satisfactory to identification by NMR and MALDI-TOF MS spectra, as described in the ESI.†[25]



Scheme 2 Synthetic route of oligoamylose-strapped porphyrin **1**.

Self-folded conformations were rationally simulated by the computational energy-minimized model study (B97D). In the folded conformation of **1** (Fig. 1A), the distance between the 5-oxygen atom of the glucose-(III) ring and the zinc atom is 2.3 Å, suggesting the presence of a coordination bond. The presence of multiple CH–π interactions between the glucose and porphyrin plane was also predicted. The folded conformation gave rise to the structural strain of the oligoamylose-strap, leading to a "chair"-to-"boat" conformational change of the glucose-(III) ring.

The folded conformation of **1** was verified by NMR spectroscopy in toluene-d_8. The aromatic resonances of the porphyrin ring were heterogeneously multiplied due to the asymmetric environment of the oligoamylose strap (Fig. 1A). Similarly, some of the methyl protons of the oligoamylose-strap shifted upfield due to shielding in the vicinity of the porphyrin moiety. The computational structure was also supported by unambiguous nuclear Overhauser effect (NOE) correlations between the protons of the oligoamylose-strap and the aromatic resonances of porphyrin-β and *meso*-aryl groups (Fig. S1, ESI†).[25] Therefore, **1** formed a self-inclusion complex at ambient temperature in toluene.

The addition of pyridine-d_5 as a competitively coordinating axial ligand ($K_a = 2.6 \times 10^4\ M^{-1}$) disturbed the glucose-to-zinc axial coordination (Fig. 1B). Then, **1**·Py showed no substantial NOE correlation between the aromatic resonances of the porphyrin ring and the oligoamylose strap, unlike the results observed in toluene-d_8. The glucose C1-protons (5.2–4.0 ppm) mostly shifted downfield upon addition of pyridine-d_5, suggesting that the protons of

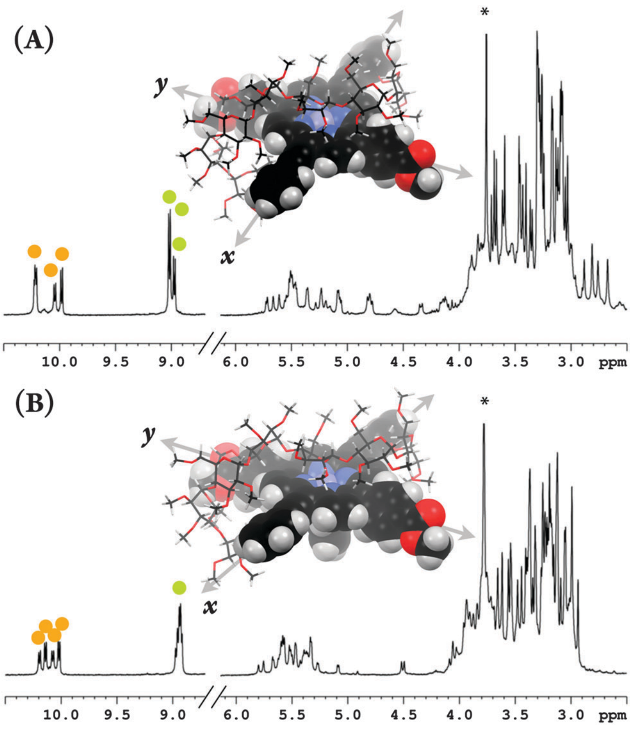


Fig. 1 ^1H NMR spectra and computer-optimized structures of folded **1** in toluene-d_8 (A) and semifolded **1**·Py in the presence of 5% of pyridine-d_5 (B) at 298 K. Orange and green circles indicate the β-protons as indicated in Scheme 1.

the oligoamylose strap were less shielded by the porphyrin ring (Fig. 1B). At the same time, the methyl protons at 3.0–2.5 ppm shifted downfield. These results suggest that the folded conformation of **1** was disturbed in the presence of pyridine. Nevertheless, the oligoamylose-strap retained helical conformation. Actually, the β-protons at 10.3–9.9 ppm indicated an increase in dissymmetrisation along the x direction following the addition of pyridine. The optimized structure suggested that the porphyrin moiety remained in the self-included structure even after pyridine bound the axial position. These experiments prove that there are intramolecular interactions between the oligoamylose-strap and the porphyrin moiety. It is known that dipole interactions play a crucial role in the host–guest interaction of the polar cavity of cyclodextrin[26] in aqueous media[18a,27] and in nonpolar solvents.[28] Eventually, in the presence of pyridine, **1** adopted the semifolded conformation.

The chiroptical properties of **1** in the ground state were verified by circular dichroism (CD) (Fig. 2B). An intense positive sign of induced CD (ICD) emerged at the Soret band (S_2 state at 452 nm) of the achiral porphyrin moiety. It is known that glucose alone is not sufficient to induce a CD signal on the Soret band.[29] Instead, assuming that **1** was amenable to the ICD rule for an encapsulated molecule in a cyclodextrin cavity,[30] the positive CD signal suggested that the orientation of the porphyrin moiety was laid along the axis of the helical channel of the oligoamylose-strap, where the Soret transition along the y direction is predominant in electronic transition based on the time-dependent (TD)-DFT calculation.[25,31] The helically twisted conformation of the *meso*-aryl groups along the y direction may contribute to chiroptical properties to some extent. The absorption dissymmetry factor, $g_{\mathrm{abs}} = \Delta\varepsilon/\varepsilon = 2(\varepsilon_{\mathrm{left}} - \varepsilon_{\mathrm{right}})/(\varepsilon_{\mathrm{left}} + \varepsilon_{\mathrm{right}})$, was $+4.5 \times 10^{-4}$ at 452 nm for folded **1** and $+6.0 \times 10^{-4}$ at 454 nm for semifolded **1**·Py. In contrast, the CD signal was only faint at the Q band (S_1 state approximately 650 nm; $g_{\mathrm{abs}} < \sim 10^{-5}$ for **1** and **1**·Py). In these cases, the Q_x transition is predominantly based on the TD-DFT calculation.[25,32] Such diagonal orientations of the Q_x transition dipole could account for the contrasting chiroptical properties of the Q band in the CD spectra.

Porphyrin **1** showed fluorescence with absolute quantum yield (Φ) = 0.12 and 0.13 in the absence and presence of pyridine, respectively (Table 1). Upon excitation of the Soret band (450 nm), fluorescence was obtained from the Q band through internal conversion. The time-resolved fluorescence spectroscopy exhibited biexponential decay components regardless of the absence or presence of pyridine, suggesting structural relaxation in the excited state,[25] *i.e.*, the induced-fit conformational change in the photoexcited state. Considering the fact that the photoexcited porphyrin plane is ruffled,[33] the porphyrin plane could be reorganized into a helical fashion at the photoexcited state. Moreover, it was recently reported that the vibrational mode is coupled with the photoexcited Q_y transition.[30] Together with the above TD-DFT results, we hypothesize that the electronic transition anisotropy is diagonally reorganized from the Q_x to Q_y transition at the photoexcited state. Under these conditions, **1** could display CPL.

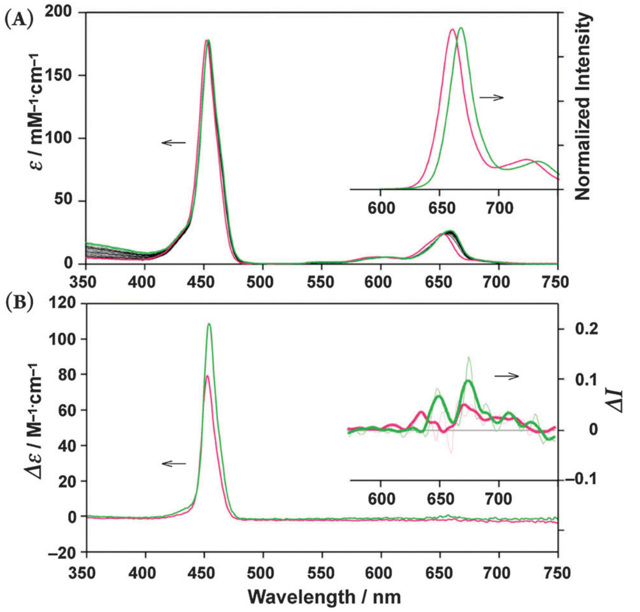


Fig. 2 (A) Absorption spectra of **1** (1×10^{-6} M) in the course of addition of pyridine (up to 3750 equiv.; red to green) in toluene at 298 °C. The inset shows normalized fluorescence spectra (λ_{ex} = 450 nm). (B) CD spectra of folded **1** (red) and semifolded **1**·Py (green) in toluene. The inset shows CPL spectra (λ_{ex} = 450 nm) with fitted curves (thick line).

Indeed, the emission from the S_1 state of **1** was circularly polarized (Fig. 2B). The luminescence with an anisotropy factor, g_{lum}, of $+2 \times 10^{-4}$ at 664 nm and $+4 \times 10^{-4}$ at 674 nm was observed as folded **1** and semifolded **1**·Py, respectively. These values maintained similar magnitudes of the g_{abs} values at the Soret band. These results are in sharp contrast to the Q band that is substantially silent in the CD spectra in the ground state. From these results, we conclude that the conformational change caused by photoexcitation induced chirality in the intrinsically achiral S_1 state of the porphyrin moiety of **1**. Moreover, the somewhat enhanced g_{lum} value resulting from the addition of pyridine suggests that the more adaptable the induced-fit system the more effective the induction of chirality.

In conclusion, we demonstrated chirality induction based on the excited state induced-fit mechanism. A spiral channel created by a flexible oligoamylose-strap definitely had a chiral impact on the photoexcited conformational change of the achiral porphyrin axle to exhibit explicit CPL, although the g_{lum} magnitude of **1** still ranged at a moderate level for a non-aggregated chromophore. Excited-state induced-fit mechanisms for chirality induction have highlighted a new potential approach to develop CPL-active chromophores. A further study of host–guest

Table 1 Photophysical properties of the S_1 state of **1** upon excitation at 450 nm

	λ_{max}/nm Φ[a]	τ (α)[b]	g_{lum}[c]
1	659 (0.12)	0.51 (19%), 1.98 (81%)	$+2 \times 10^{-4}$ (664 nm)
1·Py	666 (0.13)	0.44 (21%), 1.68 (79%)	$+4 \times 10^{-4}$ (674 nm)

[a] Emission maxima (λ_{max}) and absolute quantum yield (Φ). [b] Fluorescence lifetime (τ) and the normalized amplitude (α) determined from the fluorescence decay profiles. [c] Luminescence anisotropy factor, $g_{\mathrm{lum}} = \Delta I/I = 2(I_{\mathrm{left}} - I_{\mathrm{right}})/(I_{\mathrm{left}} + I_{\mathrm{right}})$.

systems featuring **1** as an element block is also now under active investigation.

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