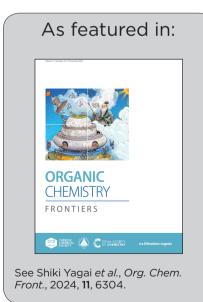


Showcasing research from Professor Shiki Yagai's laboratory, Division of Advanced Science and Engineering, Graduate School of Engineering, Chiba University, Chiba, Japan.

Dendron-mediated control over self-assembly of chlorophyll rosettes into columnar vs. discrete aggregates

By controlling the π - π stacking of chlorophyll supramolecular rosettes through steric hindrance of alkyl dendrons, it becomes possible to create chlorophyll tubes and discrete rings that resemble natural chlorophyll assemblies.









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Dendron-mediated control over self-assembly of chlorophyll rosettes into columnar vs. discrete aggregates†

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Photosynthetic bacteria have evolved highly efficient light-harvesting systems by organizing chlorophyll (Chl) pigments into circular and tubular supramolecular arrays. To construct these surapmoelcular Chl arrays from the same molecular design, we synthesized two hydrogen-bonding chlorins using natural Chl-a as the starting material: free-base chlorin functionalized with hydrogen-bonding barbituric acid and second- or third-generation alkyl dendrons (G2 and G3, respectively). The barbituric acid moiety promotes the formation of a hydrogen-bonded cyclic hexamer known as rosette. In chloroform, both the synthetic Chl-a derivatives formed rosettes; however, in methylcyclohexane as a low-polarity solvent, the G2-dendron chlorin formed columnar structures by stacking rosettes, while the G3-dendron chlorin formed disc-shaped particles. AFM revealed the formation of extended helical fibers for the former and homogeneous nanoparticles, possibly single rosettes, for the latter. These results suggest that the thirdgeneration of the dendron can inhibit the stacking of rosettes, leading to the formation of two distinct types of chlorin aggregates: circular and tubular.

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Introduction

Light-harvesting (LH) antenna systems used in bacterial photosynthesis are characterized by highly organized arrays of chlorophyll (Chl) pigments. In purple photosynthetic bacteria, circular organization of Chl pigments is achieved through supercomplexation with intrinsic membrane proteins. 1-18 In green photosynthetic bacteria, on the other hand, the selfassembly of specifically evolved self-aggregative Chls ("chlorosomal" Chls) enables the construction of tubular mesoscale structures without the need for protein scaffolding in extramembranous LH apparatuses. The self-assembly is driven by the concerted action of a variety of noncovalent interactions. Mimicking these highly organized arrays of naturallyoccurring pigments through synthetic supramolecular dye chemistry not only provides insights into structure-property correlations but also paves the way for using these naturallyabundant π-conjugated molecules as active materials in optoelectronic devices.25-27

In synthetic systems, self-assembly of metallochlorins designed based on the structures of chlorosomal Chls has been investigated in both organic solvents and aqueous solutions.28-41 These chlorins formed nanotubes through the concerted action of hydrogen bonds, coordination bonds, π - π stacking and van der Waals interactions. Although nanotubes are formed through non-hierarchical processes, from a topolo-

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gical perspective, slicing these nanotubes yields ring structures. 42 Conversely, from the viewpoint of hierarchical selfassembly, stacking rings results in the formation of nanotubes. Therefore, by designing circular supramolecular assembly and controlling their hierarchical stacking, both ring and tube structures can be created.

We herein report the construction of circular and tubular assemblies of synthetic Chl-a derivatives by hierarchical assembly control of the similar supramolecular motif. We have previously demonstrated that by modifying π -conjugated molecules with barbituric acid and a tri(dodecyloxy)phenyl (minidendron) units, 43 supramolecular polymers can be constructed through the formation of hydrogen-bonded cyclic hexamers (rosettes) and their hierarchical stacking. 44-49 In order to obtain discrete and stackable rosettes of Chl-a derivatives, we synthesized a series of barbituric-acid-functionalized chlorins ChG2 and ChG3, modified with Percec-type dendrons⁴³ of different bulkiness: second- (G2) and third-generation (G3) dendrons (Fig. 1). ChG2 formed supramolecular nanofibers of stacked rosettes, while ChG3 only assembled to rosette level.

Results and discussion

Free base chlorins ChG2 and ChG3 were synthesized following Scheme S1 (in the ESI†). These compounds were characterized by ¹H and ¹³C NMR spectroscopies and ESI mass spectrometry. To study the rosette formation, we measured concentrationdependent ¹H NMR spectra of ChG2 and ChG3 (Fig. S1†). At submillimolar concentrations (e.g., 0.1 mM), two sharp signals

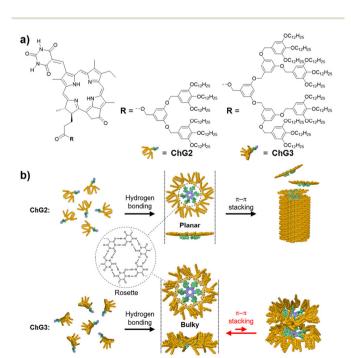


Fig. 1 (a) Molecular structures of ChG2 and ChG3. (b) Schematic representation showing the self-assembly of ChG2 and ChG3 into columnar and discrete aggregates.

corresponding to the N-H protons (H_{svn} and H_{anti}) of the barbituric acid unit appeared around 8.1 ppm for both the molecules. As the concentration increased to 20 mM, these two N-H signals gradually shifted downfield, indicating hydrogenbonding. The difference in downfield shifts, $\Delta(\delta_{syn} - \delta_{anti})$, between H_{syn} and H_{anti} reached 0.29 ppm for ChG2 and 0.27 ppm for ChG3 at 20 mM, respectively (Fig. S2†). This result is characteristic of rosette formation where the two N-H protons experience different deshielding environments. 49

Next, we studied self-assembly of ChG2 and ChG3 in methylcyclohexane (MCH), a nonpolar solvent, by using variable-temperature (VT) UV/Vis and circular dichroism (CD) spectroscopies (Fig. 2). The UV/Vis spectrum of ChG2 (c =10 μM) at 100 °C showed Soret and Oy absorption maxima at 386 and 713 nm, respectively (Fig. 2a, upper). Upon cooling to 20 °C at a rate of 1 °C min⁻¹, these peaks shifted hypsochromically to 362 and 698 nm. The spectral change indicates that the chlorin chromophore stacks in a face-to-face (H-type) arrangement. Plotting the UV/Vis absorption change at 386 nm against temperature revealed a non-sigmoidal aggregation curve (Fig. S3a,† blue line). Upon heating at a rate of 1 °C min⁻¹, the plot showed significant thermal hysteresis, suggesting that the cooling process is not under thermodynamic control. This was further supported by retardation of nucleation upon increasing cooling rate (Fig. S4†).50 These results indicated that ChG2 exhibits cooperative supramolecular polymerization involving nucleation followed by elongation processes.⁵¹ In the VT-CD measurements, the growth of a strong Cotton effect was observed in the Soret region upon cooling, while the Qy band showed a weak Cotton effect (Fig. 2a, lower). These CD signals are in good agreement with the face-to-face stacking of the entire chlorin chromophores, which is different from aggregation of chlorosomal Chls along to their Qy axes. In sharp contrast, UV/Vis and CD spectra of ChG3 displayed only marginal changes upon cooling even at a much higher concentration of 150 µM (Fig. 2b). Temperaturedependence of the absorption spectra are unlikely those recorded for aggregation and dissociation, and no significant thermal hysteresis was observed upon heating at a rate of 1 °C

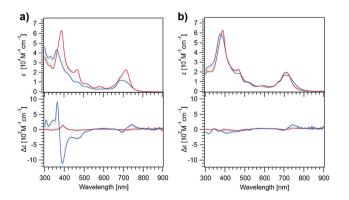


Fig. 2 UV/Vis (upper) and CD absorption spectra (lower) of ChG2 (a) and ChG3 (b) in MCH at 100 °C (red lines) and 20 °C (blue lines). (Concentration: ChG2 = 10 μ M, ChG3 = 150 μ M.)

min⁻¹ (Fig. S3b†). The entirely different temperature-dependence of ChG2 and ChG3 implies their distinct self-organization behaviors.

The formation of extended fibrous structures by ChG2 and small species by ChG3 was demonstrated by small-angle X-ray and neutron scattering (SAXS/SANS) experiments in MCH- d_{14} (Fig. 3). Analysis of the combined datasets for each solution, using a model representing a core-shell cylinder with globally constrained assembly dimensions, was performed using SasView, 52 as detailed in the ESI.† The SAXS/SANS data for a solution of ChG2 is indicative of elongated fibers, with length, $L \ge 100$ nm, aromatic core radius, $R_{\rm core} = 2.6 \pm 0.1$ nm and *n*-alkyl shell thickness, $\delta_{\rm shell}$ = 1.2 ± 0.1 nm (Fig. 3a and c). This gives a fiber diameter of 7.6 \pm 0.2 nm, in line with the diameter of the ChG2 rosette estimated by molecular modelling calculations (Fig. S5†). There is good agreement between SAXS/SANS data and the model for much of the Q-range. However, maximum at $Q \sim 0.28 \text{ Å}^{-1}$ is visible in the SAXS that is not apparent in the SANS and unaccounted for in the analysis. While we are presently unable to definitively explain this phenomenon, its possible origin is suggested in the ESI.† The SAXS/SANS data for a solution of ChG3 is quite different to that for ChG2 (Fig. 3b and d). The SANS data exhibits a flat $I(Q) \sim Q^{\circ}$ region at low Q on the log-log plot and therefore indicates far less elongated assembly structures in solution. Combined SAXS/SANS analysis gave $R_{\rm core}$ = 3.1 \pm 0.1 nm, $\delta_{\rm shell}$ = 1.1 \pm 0.1 nm and L = 2.1 \pm 0.1 nm. This supports the existence of rosettes of ChG3 in solution but suggests that, unlike ChG2, they do not extensively stack—in line with the UV/Vis and CD findings. The upturn in I(Q) at low Q in the SAXS data for ChG3 may suggest some localised aggregation or limited stacking of a small number of rosettes, which may explain the slight differences before and after cooling noted in Fig. 2b.

Highly extended nanofibers were imaged for self-assembled ChG2 by atomic force microscopy (AFM) and transmission

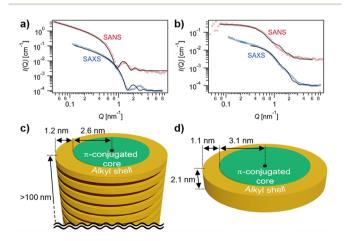


Fig. 3 (a and b) SANS (red circles) and SAXS (blue triangles) data of ChG2 (a) and ChG3 (b) in MCH-d₁₄ (c = 300 μ M). Black solid lines represent fits of the data. The scattered intensity, I(Q), is plotted as a function of the scattering vector, Q. (c and d) Schematic illustrations of assemblies of ChG2 (c) and ChG3 (d).

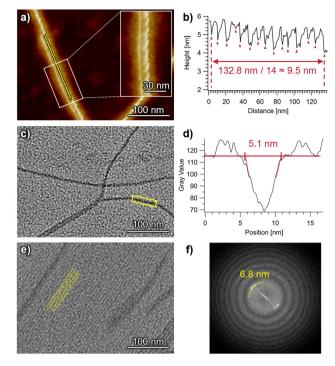


Fig. 4 (a) AFM image of aggregates spin-coated immediately after cooling an MCH solution of ChG2 (10 µM) from 100 °C to 20 °C at a rate of 1 $^{\circ}\text{C}$ min $^{-1}$. The inset image is magnified view. (b) AFM height analysis of a fiber formed by ChG2 (along the yellow line in a). (c and e) TEM images of ChG2 (30 μ M) drop-casted on an amorphous carbon film. (c) TEM image of an individual and bundled fibers. (d) Intensity profile of the selected area in c (yellow box). The horizontal line (red) corresponds to gray value of the image background. (e) TEM image of aligned fibers. Yellow dotted lines indicate fiber orientation and spacing. (f) Fast Fourier transform pattern corresponding to (e), showing the signal assignable to the interfiber spacing of 6.8 nm.

electron microscopy (TEM) (Fig. 4). In the AFM images acquired for spin-coated samples, right-handed helical structures with a helical pitch of 9.5 nm are observed (Fig. 4a, b and S6†). The right-handed helicity indicates clockwise rotation of the ChG2 rosette upon stacking. On the other hand, TEM imaging of drop-cast samples visualized both isolated individual nanofibers and also dense arrays of bundled nanofibers (Fig. 4c, e and S7†). This finding could be attributed to a concentration gradient during a slow drying process of solvent after drop casting, which was confirmed by concentration-dependent AFM images (Fig. S8†). For the isolated nanofibers, the visible width was measured to be approximately 5.1 nm (Fig. 4c and d). This value is very similar to the diameter of the π -conjugated core (2 $R_{core} = 5.2$ nm) indicated by SAXS/SANS analysis. For the bundled nanofibers, their longrange ordering with a periodicity of 6.8 nm was observed (Fig. 4e and f). This value is smaller than the diameter of solvated nanofibers (7.6 nm) shown by SAXS/SANS analysis, suggesting that the alkyl chains are tightly packed or interdigitated between nanofibers on the substrate.

In stark contrast, uniform small particles with heights of 2-3 nm and widths of 7-8 nm were imaged for ChG3 by AFM

(Fig. 5 and S9†), corresponding to the dimension of the height (2.1 nm) and diameter (8.4 nm) of the rosette indicated by SAXS/SANS analysis. Additionally, TEM imaging of the spin-coated samples revealed particles with a smallest width of approximately 6 nm (Fig. 5e and f), corresponding to the diameter of the π -conjugated core ($2R_{\rm core} = 6.2$ nm) as indicated

by SAXS/SANS. This dimension closely matches that of a single ChG3 rosette in TEM simulation (Fig. S10†). These analyses corroborate that ChG3 rosette indeed exists as discrete species, likely due to the bulky G3 dendrons inhibiting the stacking of chlorin moieties.

Conclusions

While Chl nanotubes have been the subject of numerous studies, there has been limited exploration into the cross-sectional counterpart, i.e., circular assemblies that can hierarchically assemble into nanotubes. Our present research focused on engineering circular assemblies of Chl pigments using the hydrogen-bonding capability of barbituric acid. These circular assemblies tend to stack into tubular structures; however, by altering the bulkiness of surrounding alkyl side chains, we have effectively distinguished between the formation of circular and tubular assemblies. This approach enables precise control over the hierarchical organization of molecular assemblies with similar motifs, allowing for an unbiased comparison of their structural and functional properties. Investigating the optical characteristics of these ring and tube structures may provide crucial insights into the evolutionary importance of Chl's light-harvesting mechanism in photosynthesis, and pave the way for future applications.

Author contributions

Conceptualization, R. K., S. Y.; resources, H. T., N. H.; investigation, data curation, formal analysis except for SAXS/SANS and TEM, R. K.; investigation of SANS, S. R.; investigation of SANS, data curation and formal analysis of SAXS/SANS, M. H., H. H.; investigation, data curation, formal analysis of TEM, B. M., K. H.; all authors prepared and edited the overall manuscript including figures; funding acquisition, H. T., S. Y.; supervision, S. Y. All authors have read and agreed to the final version of the manuscript.

Data availability

The data that support the findings of this work have been included in the main text and ESI.†

Conflicts of interest

Authors declare no conflicts of interest.

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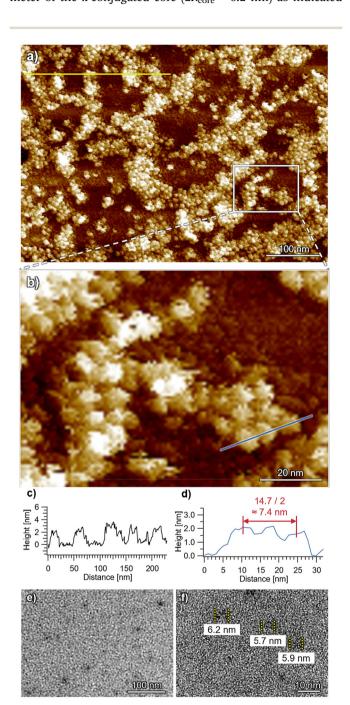


Fig. 5 (a and b) AFM images of aggregates spin-coated immediately after cooling an MCH solution of ChG3 (150 μ M) from 100 °C to 20 °C at a rate of 1 °C min $^{-1}$. (c and d) AFM cross-sectional analysis of particles formed by ChG3 along the yellow line in (a) and the blue line in (b), respectively. (e) TEM images of ChG3 particles on an amorphous carbon film. (f) High-magnification TEM image showing individual ChG3 particles.

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