

Double Helices of a Pyridine-Appended Zinc Chlorophyll Derivative

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Supporting Information

ABSTRACT: Self-assembled structures formed from a pyridine-appended zinc chlorophyll derivative are reported. While the zinc complex forms cyclic oligomers in chloroform solution, as indicated by ¹H NMR studies (including diffusion-ordered spectroscopy), vapor pressure osmometry, and cold-spray ionization mass spectrometry, it forms double-stranded helical coordination polymers in the solid state, as revealed by single-crystal X-ray analysis.

Supramolecular assemblies of porphyrin analogues have drawn considerable attention not only for the understanding of natural photosynthetic function but also for the development of synthetic architectures for the absorption of light and manipulation of excitation energy in materials science.^{1,2} Nature uses (bacterio)chlorophyll-based assemblies as light-harvesting antennae and electron relays in photosynthetic bacteria and chloroplasts in plants.³ One type of light-harvesting antenna consists of chlorophyll–protein complexes, such as LH1 and LH2 in purple photosynthetic bacteria as well as light-harvesting complexes found in plants.⁴ Chlorosomes found in green photosynthetic bacteria belong to another type of antenna.⁵ They consist of agglomerates of bacteriochlorophyll molecules called rod elements that are constructed only through pigment–pigment interactions without a protein scaffold.

A number of model compounds to mimic the structure and function of chlorosomes have been prepared.^{6–12} Most of the synthetic analogues prepared to date closely follow their natural counterparts and retain the functional groups believed to be crucial for the formation of higher-order structures, including the 3¹-hydroxy group. In the meantime, less attention has been paid to the design of structurally diverse chlorophyll derivatives that could also form novel, highly ordered assemblies. We have examined the zinc complex of a chlorophyll derivative bearing a pyridine moiety as a much less explored coordination site in comparison with hydroxide groups, which may provide more robust platforms for artificial antenna systems.^{13–16} Here we report on the self-assembly of the pyridine-appended zinc chlorophyll derivative **2** (see Figure 2 for the structure) in

solution and in the solid state. Zinc complex **2** forms cyclic oligomers in chloroform, as indicated by extensive ¹H NMR studies, including diffusion-ordered spectroscopy (DOSY); vapor pressure osmometry (VPO); and cold-spray ionization mass spectrometry (CSI-MS).¹⁷ Single-crystal X-ray diffraction (XRD) analysis revealed that **2** forms double-stranded helical coordination polymers in the solid state. This is the first double-stranded helical crystal structure formed by a porphyrin analogue. This is also the first crystal structure of a pyridine-coordinated assembly of a chlorophyll-derived compound, although the crystal structures of pyridine complexes of synthetic chlorin derivatives have been reported.^{18,19}

In the ¹H NMR spectrum of the free base **1** in CDCl₃, the signals for the α and β protons of the pyridine moiety appeared at 8.81 and 7.68 ppm, respectively (Figure 1). Although these

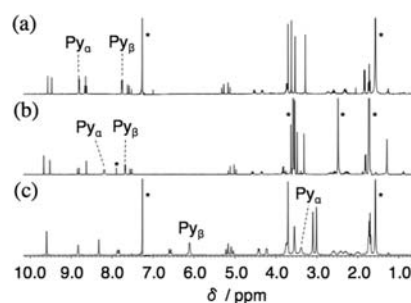


Figure 1. ¹H NMR spectrum of (a) free base **1** in CDCl₃ and (b, c) zinc complex **2** in (b) THF-*d*₈ and (c) CDCl₃. Asterisks indicate solvent and water peaks.

protons in **2** appeared in a similar region in tetrahydrofuran-*d*₈ (THF-*d*₈), they underwent marked upfield shifts to 3.40 and 6.11 ppm, respectively, in CDCl₃. Signals corresponding to other protons were also upfield-shifted by successively smaller amounts as the distance between the protons and the pyridyl group increased (Figure 2). The magnitudes of the upfield shifts for the pyridine protons and the trend observed for the

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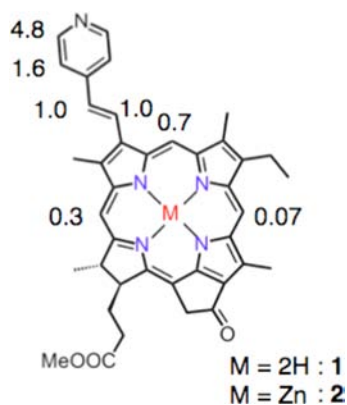


Figure 2. Chemical shift differences ($\delta_{\text{THF-d}_6} - \delta_{\text{CDCl}_3}$) for zinc complex **2**.

other protons in CDCl_3 are consistent with a self-assembled structure in which the pyridine moiety of a molecule of **2** coordinates to the zinc center of another molecule of **2**. These upfield chemical shifts, including those for the α and β protons of the pyridine moiety, showed little change over a temperature range of 223–348 K [Figure S8 in the Supporting Information (SI)]. Furthermore, these values were also almost independent of concentration over a range of 0.1–10 mM (Figure S9). The insensitivity of the chemical shifts to changes in temperature and concentration over wide ranges, combined with the appearance of a single set of proton signals for the molecular structure, is inconsistent with the formation of linear oligomeric structures in solution but instead points to the assembly of a stable, well-defined discrete cyclic oligomer (or different-membered cyclic oligomers) held together through pyridine–zinc axial coordination.

Diffusion coefficients (D) of $(6.37 \pm 0.20) \times 10^{-10}$ and $(3.43 \pm 0.05) \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ were obtained for free base **1** and zinc complex **2**, respectively, in CDCl_3 (10 mM, 298 K) by means of DOSY experiments (Figure S10). The hydrodynamic radii (r) were then estimated using the Stokes–Einstein equation (eq 1),²⁰

$$r = \frac{k_B T}{6\pi\eta D} \quad (1)$$

where k_B , T , and η are the Boltzmann constant, absolute temperature, and viscosity of the medium, respectively. The r values obtained for **1** and **2** were 6.32 and 11.8 Å, respectively. The radius for **1** is consistent with the dimensions of the monomeric species (Figure 3), whereas the radius for **2** is about twice that for **1**, which is more or less in accord with the dimensions of the cyclic tetramer.

The VPO data for **1** ($M = 612 \text{ Da}$) and **2** ($M = 689 \text{ Da}$) in CHCl_3 at 37 °C indicated the molar masses of the species in

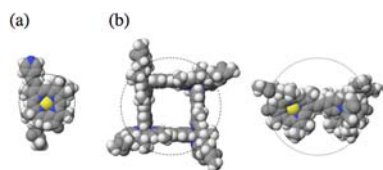


Figure 3. Molecular models of the (a) monomer and (b) cyclic tetramer of zinc complex **2**. The circles indicate the hydrodynamic radii estimated from the DOSY measurements.

solution to be 828 ± 67 and $2600 \pm 190 \text{ g mol}^{-1}$, respectively, the latter being in good agreement with the value for the tetramer of **2** ($M = 2756 \text{ Da}$) (Figure S11). CSI-MS detected ions from the monomer up to the pentamer (Figures S12–S14). From all of the evidence combined, we concluded that **2** exists as stable, cyclic oligomers in solution, with the tetramer being the predominant species.

Preliminary time-resolved measurements were performed to probe the excited-state dynamics of the assembly. Excitation of **2** leads to the formation of the singlet excited state, as demonstrated by the transient absorption (TA) spectra (Figure S15), which were taken in toluene as the materials decomposed in CHCl_3 under our TA measurement conditions. The fluorescence of **2** ($41 \mu\text{M}$) in CHCl_3 decayed biexponentially with a major lifetime of 3.3 ns (92%) and a minor, fast component of 0.47 ns (8%) (Figure S16). In pyridine, the fast component was drastically different: a fast rising component appeared (0.19 ns, 10%), while the long component was slightly affected (3.6 ns, 90%). The rise was also observed in CHCl_3 in the presence of a small amount of pyridine (1–2%), which would disrupt the assembly. Thus, the difference in the dynamics of the excited states in CHCl_3 and pyridine is not an effect of the medium but may be ascribed to the cyclic organization of the assembly. Further study will be needed to clarify the nature of the rising component and the effects of the assembly upon it.

Quite interestingly, XRD analysis of a single crystal obtained from a mixture of CHCl_3 and CH_3CN using a liquid–liquid diffusion method revealed that the zinc complex **2** forms double-stranded coordination helices in the solid state (Figure 4; crystallographic data are summarized in Table S2 in the SI). Two nonequivalent chlorophyll molecules are contained in the unit cell (Figure S17). The coordination geometry of the zinc ion of each molecule is square-pyramidal. The pattern of the lengths of the bonds between the zinc ion and the inner nitrogen atoms, among which that between the zinc ion and the reduced pyrrole nitrogen is the longest, is in accord with that for a reported zinc tetraphenylchlorin–pyridine complex [$\text{ZnTPC}(\text{Py})$].¹⁸ The displacements of the zinc ion out of the plane of the central nitrogens are 0.26 and 0.30 Å, which are somewhat less than that in $\text{ZnTPC}(\text{Py})$ (0.33 Å) (Table S3).¹⁸

Each of the nonequivalent chlorophyll molecules forms a double helix, resulting in two nonequivalent double helices, one of which is shown in bluish colors in Figure 4a,b. Both of the double helices have similar gross features as follows. The pyridine group in one molecule coordinates axially to the zinc ion in the next molecule. The array of coordination makes a right-handed helical structure with a pitch consisting of three molecules of **2**. Two such helices wrap around one another, forming a double-helical structure. The two chains within the same double helix run in the same direction, that is, the pyridine→Zn bonds are oriented in the same direction, as indicated by the two arrows in Figure 4a. On the other hand, the other nonequivalent double helix (shown in reddish colors in Figure 4c,d) runs in the opposite direction. The chlorophyll molecules in one double helix make π – π stacking interactions with molecules in the other oppositely running double helix, with an intermacrocycle separation of $\sim 3.6 \text{ Å}$, apparently mutually stabilizing the helices.

Only a very limited number of crystal structures of chlorophyll assemblies are known to date. Knapp and co-workers reported a coordination polymer of a 3¹-oxime derivative of zinc chlorophyll held together by axial

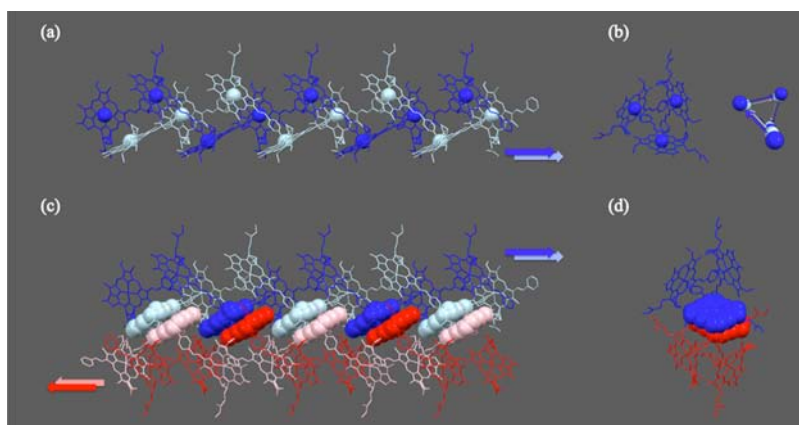


Figure 4. Double-stranded helical structure of zinc complex **2**. The colored arrows indicate the coordination direction (pyridine→Zn) of the correspondingly colored helices. H atoms and solvent molecules have been omitted for clarity. A 3D animation for the pair of double helices can be viewed in the SI. (a, b) One of the double helices. Zinc atoms are shown by space-filling models. (c, d) Two different helices packed with π – π stacking interactions. Stacked chlorin rings are shown by space-filling models. (a) and (c) are views perpendicular to the *c* axis, while (b) and (d) are views along the *c* axis.

coordination by the 13¹-carbonyl group.²¹ Very recently, Tamiaki and co-workers reported another coordination polymer of a zinc bacteriochlorophyll derivative held together by coordination of the 17-propionyl carbonyl group to the zinc ion.²² Both of them form staircaselike structures without any helical turns. It is interesting to note that a tetraphenylporphyrin derivative functionalized with a vinylpyridine moiety at the β -position also forms a staircase structure without any twist.²³ The chirality of zinc complex **2** must play an important role in the formation of the helical structure, but obviously chirality alone is not a sufficient condition for achieving the helical structure.

The double-stranded helical structure obtained in this work has some implications for the design of artificial antennae for efficient light harvesting. The axial coordination strategy via a coordination site coplanar with the chlorophyll plane as exemplified by **2** has an intrinsic weakness in the construction of light-harvesting antennae because the chromophores organized in this coordination mode are arranged in mutually perpendicular orientations. The perpendicular orientation is unfavorable for Förster-type energy transfer, which relies on dipole–dipole interactions.² Approximating the transition dipole moments as lying in the direction of the diagonal line connecting the nitrogen in pyrrole A bearing the pyridylvinyl group and the nitrogen in pyrrole C,²⁴ we calculated the factors κ^2/r^6 , where κ^2 is the orientation factor and *r* is the interchromophore center-to-center distance (Figure S18). These factors are expected to be proportional to the energy transfer rates among the chromophores in the double helices in the crystal. As expected, energy transfer along the *intrastrand* pathways is not efficient, with κ^2/r^6 values of $7\text{--}9 \times 10^{-9} \text{ \AA}^{-6}$ between the nearest neighbors in the same strand due to vanishingly small orientation factors ($\kappa^2 = 0.03\text{--}0.05$). However, the κ^2/r^6 factors are 2 orders of magnitude larger (225×10^{-9} and $162 \times 10^{-9} \text{ \AA}^{-6}$) between nearest neighbors residing in complementary strands. Even the κ^2/r^6 factors between next-nearest neighbors residing in complementary strands are large (166×10^{-9} and $157 \times 10^{-9} \text{ \AA}^{-6}$) because of favorable orientations ($\kappa^2 = 1.42$ and 1.51 , respectively). Thus, the double-helical architecture confers efficient, contiguous *interstrand* energy transfer pathways along which energy migrates among chromophores belonging to complementary

strands alternatively in the double helix, even in the case that *intrastrand* energy transfer is slow. This analysis demonstrates that the double helices have a functional significance as a light-harvesting antennae in addition to the aesthetic beauty. In this particular crystal structure, *inter-double-helix* pathways should be even more efficient because of the π – π overlap (Figure 4c,d) and parallel orientation.

For the double-helical structures reported herein, unlike other staircase structures, isolation of each double helix may be possible by peripheral modification of the molecular structure. Such assemblies hold promise as light-harvesting antennae.^{2,25} Our work is directed toward revealing the structural requirements for the formation of such structures as well as photophysical properties of these assemblies.

■ ASSOCIATED CONTENT

📄 Supporting Information

Preparation and characterization data for monomers and assemblies of **1** and **2**, crystallographic data (CIF), and a 3D animation for **2** (QT). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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