

# Supramolecular light-harvesting antenna system by co-aggregates of zinc (bacterio)chlorophyll-*a* derivatives with biomimetic chlorosomal self-assemblies



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## ARTICLE INFO

**Keywords:**  
Chlorophyll  
Co-aggregates  
Energy transfer

## ABSTRACT

Light-harvesting (LH) antennas are one of the most important apparatuses for photosynthetic organisms to utilize solar energy. The main LH apparatuses in photosynthetic green bacteria are chlorosomes containing baseplate proteins. A chlorosome possesses a large number of bacteriochlorophyll(BChl)-*c-f* molecules. These BChls are chemically programmed pigments for *J*-aggregation, which self-assemble in a hydrophobic environment. The BChl-*c-f* self-assemblies in a chlorosome are primary energy donors, which absorb sunlight, migrate the excitation energy, and transfer it to energy acceptor BChl-*a* pigments in a baseplate protein. To develop such chlorosomal LH antenna in artificial systems, self-assemblies of synthetic BChl-*d* analogs and BChl-*a* derivatives have been used for the energy donors and acceptors, respectively. In this study, we report the co-aggregation of zinc chlorophyll derivatives with chlorosomal self-assemblies. The present system showed singlet excitation energy transfer from energetically donating chlorosomal self-assemblies to energetically accepting zinc chlorophyll derivatives in the solution and solid states.

## 1. Introduction

Photosynthesis is an important energy conversion system to utilize sunlight in nature. The initial stage of natural photosynthesis is performed by light-harvesting (LH) antennas, which absorb sunlight and migrate/transfer the excitation energy to give it finally to a charge separating system called reaction center (RC). Various LH antennas and RC complexes have been found in natural phototrophs, which have been analyzed by spectroscopy, microscopy and X-ray crystallography [1–4]. These apparatuses contain several pigments, such as bacteriochlorophyll (BChl), chlorophyll (Chl), carotenoid, and bilin molecules, which assemble in highly ordered supramolecular structures binding with or without the peptides [5–7]. BChl and Chl pigments are one of the most important porphyrinoids for natural photosynthesis and play key roles in the above photo-functions, including sunlight absorption, excitation energy migration/transfer, and electron transfer [8–12].

Major LH antennas in photosynthetic green bacteria are called chlorosomes, which consist of BChl-*c*, *d*, *e*, and *f* pigments (Fig. 1, upper left) enveloped by lipid monolayer [13–16]. These BChl pigments, whose molecular structures are magnesium complexes of 3<sup>1</sup>-hydroxy-13<sup>1</sup>-oxo-chlorins, are chemically programmed pigments which self-

assemble to be *J*-aggregates in a chlorosome without binding to any peptides [17–25]. The central magnesium atom as well as the peripheral hydroxy and keto groups are necessary for the chlorosomal self-assembly which is based on three intermolecular interactions: as coordination bonding (Mg...OH), hydrogen bonding (OH...O=C), and  $\pi$ - $\pi$  stacking of chlorin skeletons. In the primary photosynthetic process of green bacteria, the self-assemblies of BChls-*c-f* in the core part of chlorosomes absorb photons from the sun and transfer the excitation energy to acceptor molecules [26–28], such as BChl-*a* pigments (Fig. 1, upper right) in the baseplate proteins located at the chlorosome surface [29,30]. The excitation energy harvested by the extramembranous chlorosome is finally transferred to the BChl-*a* special dimer of the intrinsic RC proteins via BChl-*a* pigments of Fenna–Mathews–Olson protein and/or core LH antennas in the membranes [31].

Blending different photo-functional organic molecules is important for the development of artificial LH antenna systems [32,33]. Various supramolecular light harvesting antennas using porphyrinoids have been reported [34]. To mimic the supramolecular structures and functions of natural chlorosomal BChl-*c-f* self-assemblies, their model compounds have been synthesized from naturally occurring Chl-*a* [35–39], and energy transferring systems were developed using such

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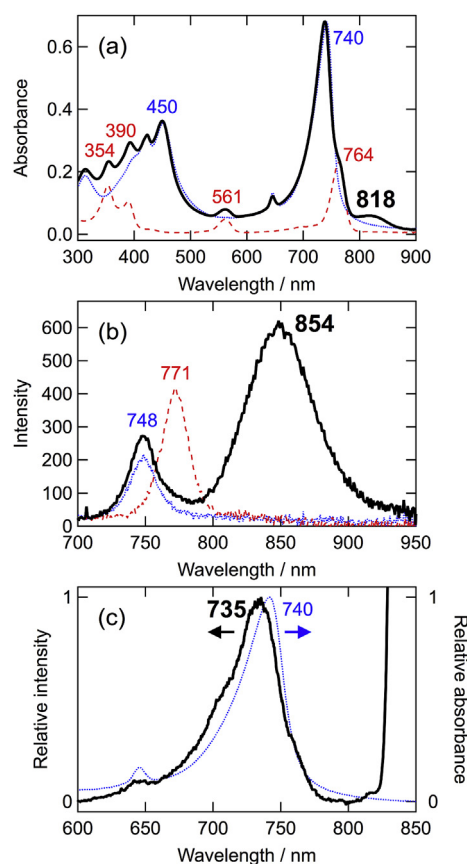
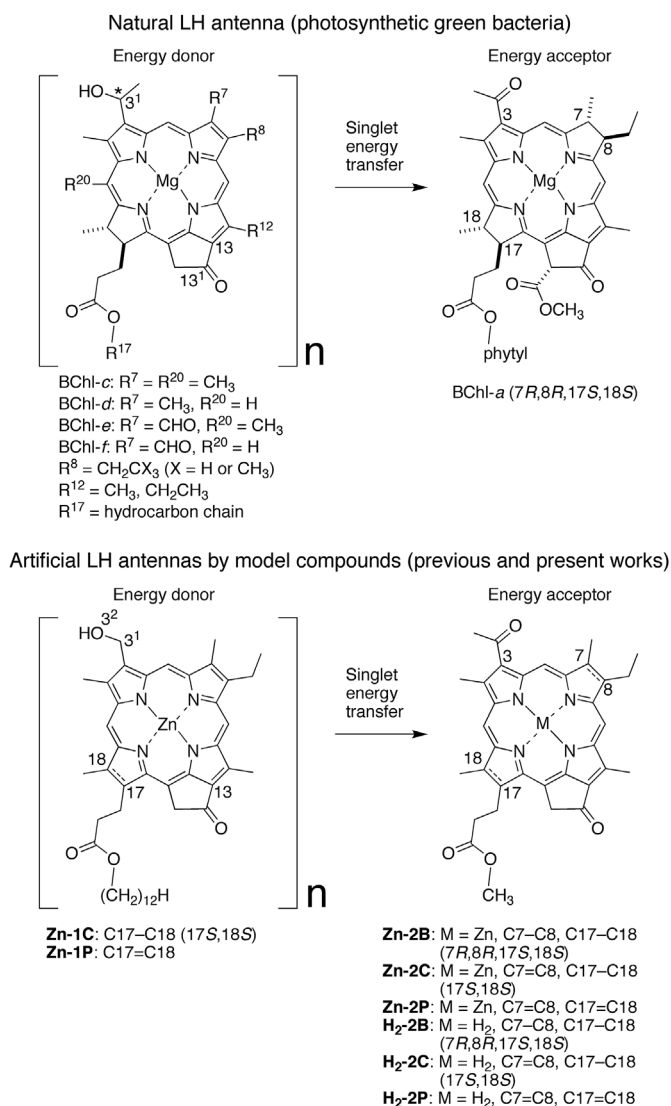
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<https://doi.org/10.1016/j.dyepig.2018.08.026>

Received 18 April 2018; Received in revised form 11 June 2018; Accepted 19 August 2018

Available online 21 August 2018

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**Fig. 2.** UV-Vis-NIR absorption (a), fluorescence emission (b, excitation at 450 nm), and fluorescence excitation spectra (c, emission at 850 nm) of **Zn-1C** self-assembly (blue dot), **Zn-2B** (red dashed), and co-aggregates of **Zn-2B** with **Zn-1C** self-assembly (black). In panel (c), Vis-NIR absorption spectrum of the **Zn-1C** self-assembly (blue dotted) is shown. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

**Fig. 1.** Energy transferring systems in natural (upper) and artificial LH antennas (lower) by BChl-*c-f* self-assemblies (upper left) and BChl-*a* (upper right) and by semi-synthetic **Zn-1C/P** (lower left) and **M-2B/C/P** (lower right), respectively.

models as the energy donors and synthetic Chl-*a* or BChl-*a* derivatives as the energy acceptors in a non-polar organic solvent or an aqueous micelle solution to construct artificial LH antennas (Fig. 1, lower) [40–44]. In this study, we report that co-aggregation of a zinc BChl-*a* or Chl-*a* derivative with biomimetic chlorosomal self-assemblies of synthetic BChl-*d* analogs, which showed singlet energy transfer from the latter chlorosomal self-assemblies to the former acceptor in the solution and solid states.

## 2. Results and discussion

BChl-*d* analogs, **Zn-1C/P** (Fig. 1, lower left), were prepared according to the reported procedures, which functioned as good model compounds for chlorosomal assemblies [37,44]. (B)Chl-*a* derivatives possessing different  $\pi$ -systems, **M-2B/C/P** (M = Zn or H<sub>2</sub>; Fig. 1, lower right), were synthesized according to the reported procedures [45,46]. **Zn-1C/P** self-assemblies and **M-2B/C/P** were examined as energy donors and acceptors, respectively. UV-Vis-NIR absorption spectrum of **Zn-1C** in 1% (v/v) THF-hexane (10  $\mu$ M) showed Qy/Soret bands at 740/450 nm (Fig. 2a, blue dotted line), which corresponds to the formation of its large oligomer by chlorosomal *J*-aggregation [37,39]. **Zn-**

**2B** in 1% (v/v) THF-hexane (2  $\mu$ M) showed monomeric absorption peaks:  $\lambda_{\max}$  (Qy) = 764,  $\lambda_{\max}$  (Qx) = 561, and  $\lambda_{\max}$  (Soret) = 390 and 354 nm (Fig. 2a, red dashed line). A 5:1 mixture of **Zn-1C** and **Zn-2B** in THF was added to 99-fold hexane ([**Zn-1C**] = 10  $\mu$ M and [**Zn-2B**] = 2  $\mu$ M), showing an 818-nm peak in addition to the original absorption bands of the **Zn-1C** self-assembly and **Zn-2B** (Fig. 2a, black line). Emission spectra of a 100:1 mixture of **Zn-1C** and **Zn-2B** in 1% (v/v) THF-hexane ([**Zn-1C**] = 10  $\mu$ M and [**Zn-2B**] = 0.1  $\mu$ M) were measured by excitation at the Soret maximum of the **Zn-1C** self-assembly where **Zn-2B** scarcely absorbs the light, and the resulting spectra showed emission bands at 748 and 854 nm (Fig. 2b, black line). The emission peak at 748 nm was identical to the fluorescence of **Zn-1C** self-assembly (Fig. 2b, blue dotted line), but the broad band at 854 nm was different from the **Zn-2B** emission peak at 771 nm (Fig. 2b, red dashed line) as well as that of the **Zn-1C** assembly. These spectroscopic analyses indicated that the newly appearing NIR absorption and emission over 800 nm were produced by co-aggregates of **Zn-2B** with chlorosomal self-assembly of **Zn-1C**. The excitation spectrum at 850 nm of the above mixture showed a 735-nm peak similar to the Qy absorption of the **Zn-1C** self-assembly (Fig. 2c). Thus, the present system showed downhill energy transfer from the chlorosomal assembly of **Zn-1C** to **Zn-2B** co-aggregated with (**Zn-1C**)<sub>n</sub>.

Similar experiments were performed for **Zn-1C** and metal-free **H<sub>2</sub>-2B** to examine their co-aggregation. UV-Vis-NIR absorption spectra showed that a mixture of **Zn-1C** and **H<sub>2</sub>-2B** in 1% (v/v) THF-hexane consisted of oligomeric **Zn-1C** and monomeric **H<sub>2</sub>-2B** independently (Fig. S1a). The emission spectrum of the mixture solely showed the

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