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Synthesis and optical properties of chlorin monomer, dimer and trimer on an amino nitrogen atom

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ABSTRACT

Naturally occurring chlorophyll-*a* was chemically modified to methyl 3-aminomethyl-pyropheophorbides-*a* including primary, secondary, and tertiary amines. Reductive amination of methyl pyropheophorbide-*d* possessing the 3-formyl group with ammonia efficiently gave a chlorin dimer covalently linked with CH_2NHCH_2 at the 3-position, which was transformed into a trimer through the substitution at the amino group. Conformational analyses by ^{1}H NMR spectroscopic observation and molecular modeling estimation indicated that the dimer and trimer were apt to form closely packed structures. Chlorin chromophores in the dimer and trimer were weakly interacted in dichloromethane to shift their Qy absorption bands to longer wavelengths by 4–6 nm than the maxima of the corresponding monomer. In the red-shifted Qy region, the trimer gave an S-shaped circular dichroism band by exciton coupling of composite chlorin units. All the semi-synthetic chlorophyll derivatives were highly fluorescent and no intramolecular quenching was observed even in the trimer. The behaviors would be ascribable to the formation of compact conformers and suppression of intramolecular motion, which are important to construct light-harvesting antenna complexes in phototrophs and their model systems.

1. Introduction

Light-harvesting antennas are one of the important apparatuses in phototrophs, and efficiently absorb sunlight and rapidly migrate the excited energy.[1] They contain a large amount of π-conjugated pigments due to the effective absorption of visible and near-infrared light from the Sun whose energy density is low in the Earth. The pigments are chlorophylls (cyclic tetrapyrroles, see left drawing of Fig. 1), bilins (linear tetrapyrroles), and carotenoids (polyenes), usually interacting with peptides to form various supramolecules in photosynthetic antennas.[2] The specific interaction includes both the covalent and noncovalent bondings: for example, addition of a mercapto group in cysteinyl residue to the ethylidene group of bilins and axial coordination of an imidazolyl nitrogen atom of histidyl residue to the central magnesium of chlorophylls. Only in major antenna systems of green photosynthetic bacteria (called chlorosomes),[3] no peptide is necessary for the construction and special chlorophyll molecules self-aggregate using coordination, hydrogen-bonding, and π–π interaction to provide a core part of chlorosomes.[4]

Inside the antenna systems, pigments are densely packed but directional migration of singlet excitation energy is performed with a high efficiency.[5] This is in sharp contrast with a concentrated solution of pigments where the photoexcited energy is quickly quenched through intermolecular interaction.[6] Therefore, the preparation of functional antenna models is challenging but must be successful for the realization of artificial photosynthesis. Although such model systems have been reported using semi-synthetic chlorophyll molecules,[7–13] limited models are functionally effective including self-aggregates of zinc chlorophyll derivatives (see central drawing of Fig. 1).[14,15] Here we report on the synthesis of chlorophyll monomer **1**, dimer **2**, and trimer **3** (see right drawing of Fig. 1) by modifying natural chlorophyll-*a* and their photophysical properties in a solution. While the covalent linker of 3-CH_2NCH_2 was assumed to be flexible in the semi-synthetic chlorophyll dyad and triad, no intramolecular quenching of the photoexcited chlorin chromophore was observed, showing that their conformation would be restricted to give highly fluorescent species.

Abbreviations: APCI, atmospheric pressure chemical ionization; CD, circular dichroism; FCC, flash column chromatography; HRMS, high resolution mass spectra; MALDI, matrix-assisted laser desorption/ionization.

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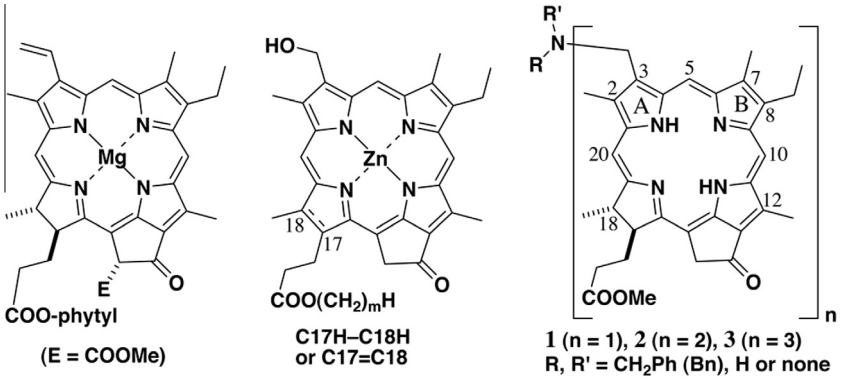
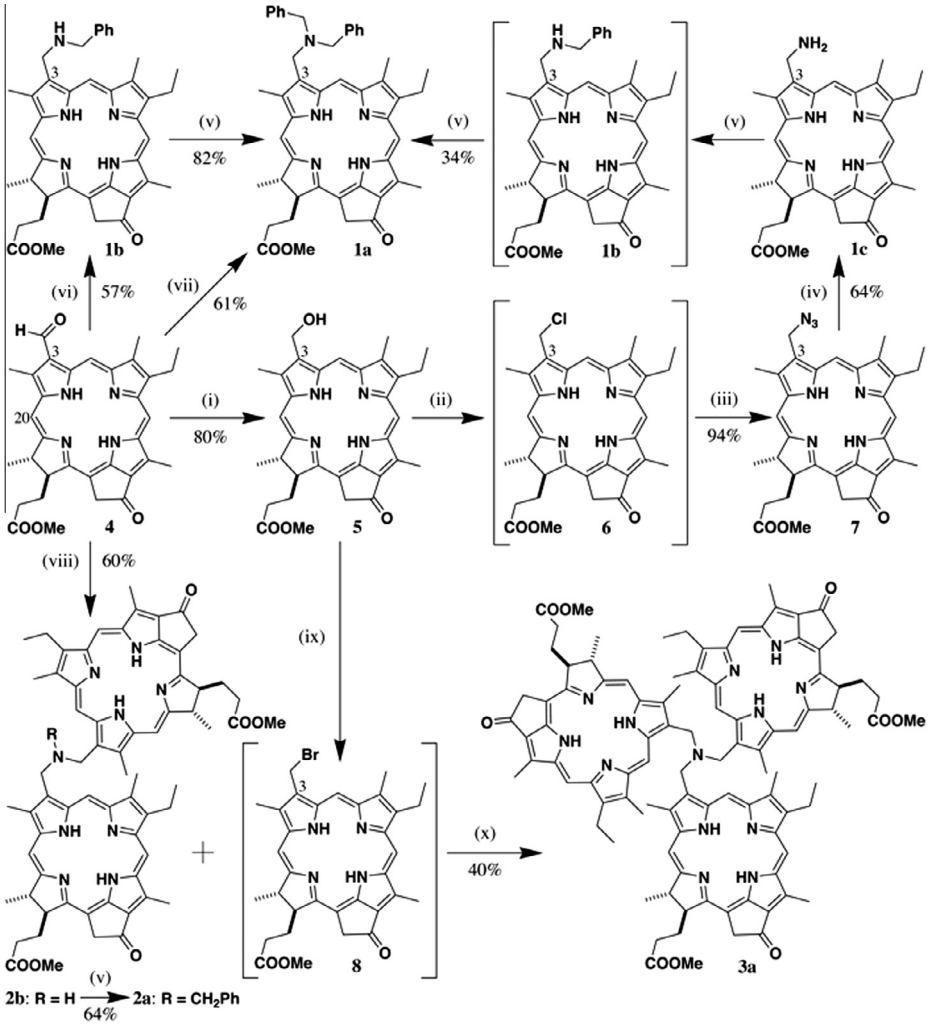


Figure 1. Molecular structures of natural chlorophyll-*a* (left), semi-synthetic zinc chlorophyll derivatives (center), and methyl pyropheophorbide monomer **1**, dimer **2** and trimer **3** reported here (right).

2. Results and discussion

2.1. Synthesis of monomer, dimer and trimer of chlorophyll derivatives

Methyl pyropheophorbide-*d* (**4**, see Scheme 1) possessing a formyl group at the 3-position was prepared by oxidation of the 3-vinyl group of methyl pyropheophorbide-*a*, one of the chlorophyll-*a* derivatives.[16,17] According to reported procedures,[18] the 3-formyl group was transformed to the 3-aminomethyl group in **1c** through selective reduction of 3-C=O in **4** by a complex of borane with *tert*-butylamine, chlorination of the 3-CH_2OH in **5** with thionyl chloride, azidation of the 3-CH_2Cl in **6** with sodium azide, and Staudinger reduction of 3-CH_2N_3 in **7**. Benzylation of



Scheme 1. Synthesis of methyl 3-aminomethyl-pyropheophorbide-*a* monomers **1**, dimers **2** and trimer **3** by modifying methyl pyropheophorbide-*d* (**4**): (i) *t*$BuNH_2{\cdot}BH_3$/CH_2Cl_2, rt; (ii) $SOCl_2/CH_2Cl_2$, 0 °C; (iii) NaN_3/MeCN, THF, H_2O, reflux; (iv) PPh_3/THF, H_2O, 50 °C; (v) $PhCH_2Br$, K_2CO_3/Me_2CO, reflux; (vi) $PhCH_2NH_2$, AcOH, $NaBH_3CN/CH_2Cl_2$, rt; (vii) $(PhCH_2)_2NH$, AcOH, $NaBH_3CN/CH_2Cl_2$, rt; (viii) $AcONH_4$, $NaBH_3CN/CH_2Cl_2$, rt; (ix) PBr_3/CH_2Cl_2, rt; (x) K_2CO_3/Me_2CO, reflux.

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