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Photophysical properties of synthetic monomer, dimer, trimer, and tetramer of chlorophyll derivatives and their application to organic solar cells

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ABSTRACT

Pyropheophorbides, chlorophyll-*a* derivatives, were quadruply esterified at the 17-propionate residue with a tetraol to give the covalently-linked tetramers. The synthetic tetramers were mixed with a C₇₀ fullerene derivative for utilization as the active layer in bulk heterojunction organic solar cells. Their photovoltaic performances were comparable to those of the corresponding monomeric pigments. The similar power conversion efficiencies would be ascribable to the increase of carrier mobility in the tetramers and the partial suppression of photoexcited state of the chlorin π -systems by intramolecular quenching. Photophysical properties of synthetic covalently-linked mesopyropheophorbide-*a* dimer, trimer, and tetramer as well as its monomer in a solution supported the intramolecular interaction of chlorin moieties to quench their singlet excited states, which was especially observed in the trimer and tetramer.

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1. Introduction

A variety of porphyrinoid oligomers were prepared and utilized for many scientific fields including material, biological, and medical sciences [1]. Chlorophylls (Chls) are natural occurring pigments and one of the important classes of porphyrinoids [2]. Supramolecular assemblies of Chls are observed in some apparatus of photosynthesis and play roles in light-harvesting, energy-transferring, and charge-separating processes [3]. In the photo-synthetic apparatus, most Chls (see the left drawing of Fig. 1) are specifically bound with peptides through coordination of the central magnesium with peptidyl residue including the imidazolyl group of histidine, hydrogen bonding of the peripheral carbonyl group with the hydroxy group in peptides, and so on [4]. Exceptionally, self-aggregates of Chls are available in the main light-harvesting antenna systems of green photosynthetic bacteria [5]. All the Chl molecules non-covalently interacted with any species including peptides, water, and Chls to form supramolecules in natural systems.

Oligomeric Chls are often observed in photosynthetic antennas and reaction centers and show specific optical and electrochemical properties different from the monomeric states. To mimic such natural Chl oligomers, numerous Chl self-assemblies have been reported as their synthetic models (see Ref. [6] as a recent article). Especially, Chl derivatives were covalently linked with any spacers to give Chl dimers, trimers, higher oligomers, and polymers. Many synthetic covalently-linked Chl dimers have already been reported (see Ref. [7] and cited therein), but Chl trimers, tetramers, oligomers, and polymers are limited in the papers reported by a few groups: a trimeric pyropheophorbide-*a* (one of the Chl-*a* derivatives, see the right drawing of Fig. 1) ester [8], trimeric and tetrameric (meso)pyropheophorbide-*a* with a C-3 or C-20 linkage [9–14], higher oligomeric (pyro)pheophorbide-*a* amides (esters) [15–33], and polymeric (pyro)pheophorbides [34–42].

We have reported that Chls are useful for photosensitizers of solar cells [43–47]. In organic solar cells (OSCs) dynamically based on the photoinduced electron transfer from Chls to fullerenes, the carrier mobility of Chl molecules in their active layer is important to determine the power conversion efficiency (PCE). To increase the carrier mobility, tetramers of Chl-*a* derivatives are here prepared by quadruple esterification at the 17-propionate residues and their performances in solution-processed bulk heterojunction (BHJ) OSCs are investigated in comparison with those of monomer-

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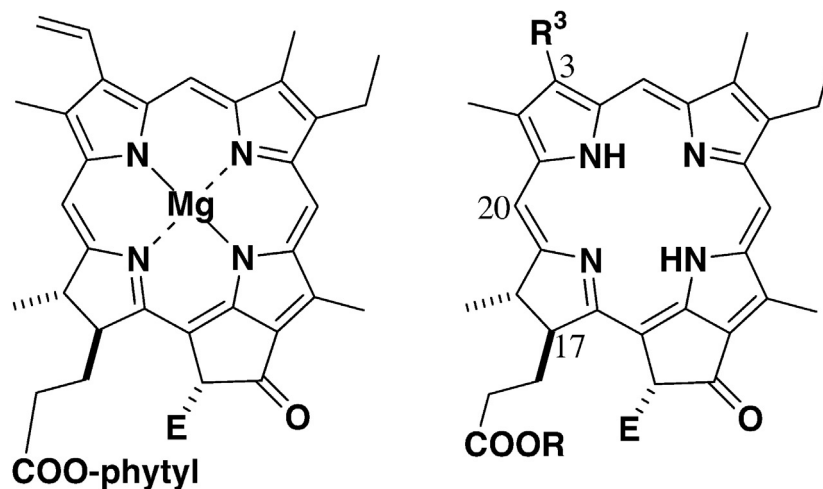


Fig. 1. Molecular structures of chlorophyll-*a* (left, E = COOMe) and its derivatives (right): R³ = vinyl, E = COOMe for pheophorbides-*a*, R³ = vinyl, E = H for pyropheophorbides-*a*, and R³ = Et, E = COOMe for mesopyropheophorbides-*a*.

based systems. Furthermore, photophysical properties of synthetic Chl monomer, dimer, trimer, and tetramer are measured in a solution and intramolecular interaction in the Chl π -systems is discussed.

2. Experimental

2.1. General

All melting points were measured with a Yanagimoto micro melting apparatus and were uncorrected. Visible absorption and circular dichroism (CD) spectra were measured with a Hitachi U-3500 spectrophotometer and a Jasco J-720W spectropolarimeter, respectively. Fluorescence emission spectra were obtained by a Hitachi F-4500 spectrophotometer. Fluorescence emission quantum yields and lifetimes were determined by a Hamamatsu Photonics C9920-03G spectrometer and C7990S system, respectively. ¹H-NMR spectra were recorded on a JEOL ECA-600 (600 MHz) spectrometer; CHCl₃ (δ = 7.26 ppm) was used as an internal reference. Standard mass data were obtained using direct laser desorption/ionization (LDI) or matrix-assisted LDI (MALDI) by a Shimadzu AXIMA-CFR plus spectrometer: 7,7,8-tetracyanoquinodimethane (TCNQ) was used as a matrix. High resolution mass spectra (HRMS) were recorded on a Bruker micrOTOF II spectrometer: electrospray ionization (ESI) or atomic pressure chemical ionization (APCI) and positive mode in an acetonitrile solution. TLC or flash column chromatography (FCC) was performed with silica gel (Merck, Kieselgel 60 F₂₅₄ or Kieselgel 60, 40–63 μ m, 230–400 mesh).

Methyl 13¹-deoxy-mesopyropheophorbide-*a* (**1a**), methyl 13¹-deoxy-3¹-oxo-mesopyropheophorbide-*a* (**1b**), methyl mesopyropheophorbide-*a* (**1c**), and methyl 3¹-oxo-mesopyropheophorbide-*a* (**1d**) were prepared according to reported procedures [48]. For esterification, chloroform (Nacalai Tesque) was treated with alumina and dry *N,N*-dimethylformamide (DMF) was purchased from Wako Pure Chemical Ind. as super dehydrated grade. Commercially available chloroform dichloromethane, diethyl ether, hexane, methanol, and tetrahydrofuran (Nacalai Tesque) were used as solvents for preparation of compounds. Other reagents were obtained from commercial suppliers and utilized as supplied. Dichloromethane for optical spectroscopy was purchased from Nacalai Tesque as reagent prepared specially for spectroscopy and used without further purification.

2.2. Synthesis of mesopyropheophorbide-*a* monomer, dimer, trimer, and tetramer

2.2.1. Synthetic procedures for esterification

An aqueous THF solution (1:1) of methyl mesopyropheophorbide-*a* (**1c**) or methyl 3¹-oxo-mesopyropheophorbide-*a* (**1d**) was treated with sulfuric acid at room temperature [49] to give mesopyropheophorbide-*a* (**1cH**) [50] or 3¹-oxo-mesopyropheophorbide-*a* (**1dH**) [42,51], respectively.

A solution of carboxylic acid **1cH/1dH** (0.1 mmol), alcohol, 4-(dimethylamino)pyridine (DMAP, 24 mg, 0.2 mmol), and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC·HCl, 77 mg, 0.4 mmol) in solvent (25 ml) was stirred at room temperature in the dark under argon for 1 day. The reaction mixture was diluted with chloroform, washed with aq. 2% HCl, aq. 4% NaHCO₃, and water, dried over Na₂SO₄, and filtered. After all the solvents were evaporated in vacuo, the residue was purified by FCC with CH₂Cl₂ and Et₂O or MeOH to give the desired ester. Recrystallization from CH₂Cl₂ and hexane afforded its analytically pure sample.

2.2.2. Synthesis of mesopyropheophorbide-*a* monomer (**1c'**)

Using 2,2-dimethyl-1-propanol (neopentyl alcohol, 18 mg, 0.2 mmol), CHCl₃, and 2–3% Et₂O as alcohol, reaction solvent, and additive solvent for FCC, respectively; 91% yield; dark purple solid; mp 99–100 °C; VIS (CH₂Cl₂) λ_{\max} 656 (relative intensity, 0.42), 600 (0.08), 534 (0.09), 503 (0.09), 409 (1.00), 394 (0.76), 317 nm (0.20); ¹H-NMR (CDCl₃) δ 9.46 (1H, s, 10-H), 9.20 (1H, s, 5-H), 8.46 (1H, s, 20-H), 5.24, 5.10 (each 1H, d, *J* = 19 Hz, 13¹-CH₂), 4.48 (1H, dq, *J* = 1, 7 Hz, 18-H), 4.29 (1H, dt, *J* = 8, 1 Hz, 17-H), 3.83 (2H, q, *J* = 8 Hz, 3-CH₂), 3.77, 3.72 (each 1H, d, *J* = 10 Hz, 17²-COOCH₂), 3.68 (2H, q, *J* = 8 Hz, 8-CH₂), 3.66 (3H, s, 12-CH₃), 3.29 (3H, s, 2-CH₃), 3.25 (3H, s, 7-CH₃), 2.74–2.67, 2.59–2.52, 2.38–2.26 (1H + 1H + 2H, m, 17-CH₂CH₂), 1.81 (3H, d, *J* = 7 Hz, 18-CH₃), 1.73 (3H, t, *J* = 8 Hz, 3¹-CH₃), 1.70 (3H, t, *J* = 8 Hz, 8¹-CH₃), 0.85 (9H, s, 17⁵-C(CH₃)₃), 0.63, –1.59 (each 1H, s, NH x 2); MS (LDI) found: *m/z* 607.0, calcd. for C₃₈H₄₇N₄O₃: MH⁺, 607.4; HRMS (ESI) found: *m/z* 607.3643, calcd. for C₃₈H₄₇N₄O₃: MH⁺, 607.3643.

2.2.3. Synthesis of mesopyropheophorbide-*a* dimer (**2c**)

Using 2,2-dimethyl-1,3-propanediol (neopentyl glycol, 2,2-bis(hydroxymethyl)propane, 2.1 mg, 0.02 mmol), dry DMF, and 0.6–0.7% MeOH; 37% yield; dark purple solid; mp 177–179 °C; VIS

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