



Synthesis of carboxylated chlorophyll derivatives and their activities in dye-sensitized solar cells

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ABSTRACT

Chlorophyll-*a* derivatives possessing a carboxy group in the substituent at the 3-position were prepared by chemical modification of methyl pyropheophorbide-*d* bearing the 3-formyl group via a Wittig, Barbier-type, or Knoevenagel reaction. The synthetic carboxylated chlorophyll pigments were employed as dye sensitizers for solar cells and their performances were compared in a conventional device based on a mesoporous titanium dioxide electrode and a liquid electrolyte. The solar power conversion efficiency was suppressed with an increase in the length of the oligomethylene moiety between the chlorin π -system and the carboxy group, while a corresponding π -linked ethylene spacer enhanced the efficiency.

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1. Introduction

Dye-sensitized solar cells (DSSCs) have been extensively investigated over the last three decades, largely owing to their readily fabrication [1,2]. In conventional DSSCs, liquid electrolytes are required but recently solid electrolytes were often examined due to their more practical usage [3]. A variety of dye molecules have been employed as their sensitizers and organic sensitizers are particularly attractive from the fact that their properties can be finely tuned in terms of redox potential, light-harvesting ability, and so on. Such sensitizers usually possess an anchoring moiety to attach a working electrode and a carboxy group is effective for adsorbing their molecules on the surface of mesoporous titanium dioxide [4]. The solar power conversion efficiency (η) has gradually increased since the first report (about 7%) [1] and lately reached to 13% [5] and over 14% [6].

Among organic dye sensitizers, chlorophylls possessing a cyclic tetrapyrrole π -skeleton have attracted much attention from their

availability from natural phototrophs, easy modification, low cost, environmental friendliness, efficient absorption of sunlight, etc [7–9]. We have previously reported that a conventional TiO₂-based DSSC using chlorophyll-*a* derivative **2** bearing a carboxy group at the 3-position (Fig. 1, right, $n = 0$) showed an η -value of 3.6%, which increased to 6.5% upon insertion of an ethenyl group between the carboxy group and the 3-position of the chlorin π -skeleton as in **1** (Fig. 1, left) [10]. Furthermore, the η -value was improved by substitution of the methyl group of the 17-propionate residue in **1** with longer alkyl chains: 6.5% (methyl ester for **1**) → 7.0% (hexyl ester) → 8.0% (dodecyl ester) [11]. Such an acrylate residue directly conjugated with a chlorin chromophore promotes the performance of chlorophyll-based DSSCs. The 3-(2-carboxyethenyl) group was previously introduced by Wittig reactions of the 3-formyl-chlorin with Ph₃P = CHCOOR and the successive hydrolysis of the resulting ester [10,12]. Here we report on new synthetic routes to access **1** via Barbier-type and Knoevenagel reactions as well as another Wittig reaction, to obtain more cost-effective and simpler procedures. The DSSC performances using the other carboxylated chlorophyll-*a* derivatives **3** and **4** prepared in the present work are compared with those of **1** and **2**.

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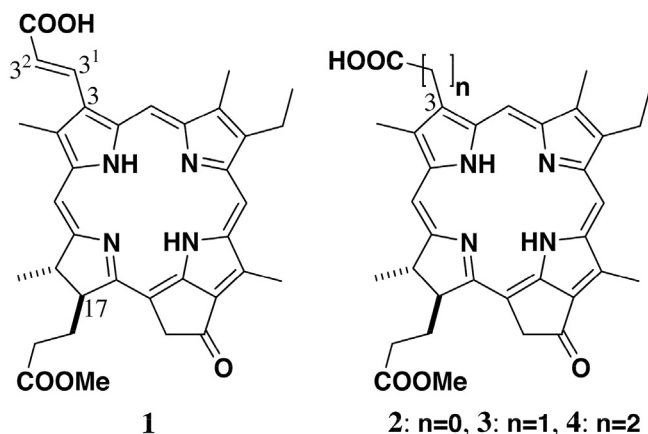


Fig. 1. Molecular structures of chlorophyll-*a* derivatives **1–4** bearing a carboxy group in the 3-substituent.

2. Results and discussion

2.1. Synthesis of chlorophyll-*a* derivative with an acrylate residue at the 3-position

Methyl (*E*)-3²-carboxy-pyropheophorbide-*a* (**1**) was already prepared according to the following procedures [10]. Methyl pyropheophorbide-*d* (**5H₂**) possessing a formyl group at the 3-position was reacted with *tert*-butyl (triphenylphosphoranylidene)acetate in refluxing toluene [step (i) in Scheme 1, R = CMe₃]. The olefinic adduct **6aH₂** was treated with trifluoroacetic acid (TFA) [step (ii), R = CMe₃] to give the desired compound **1** in 89% yield for the two steps.

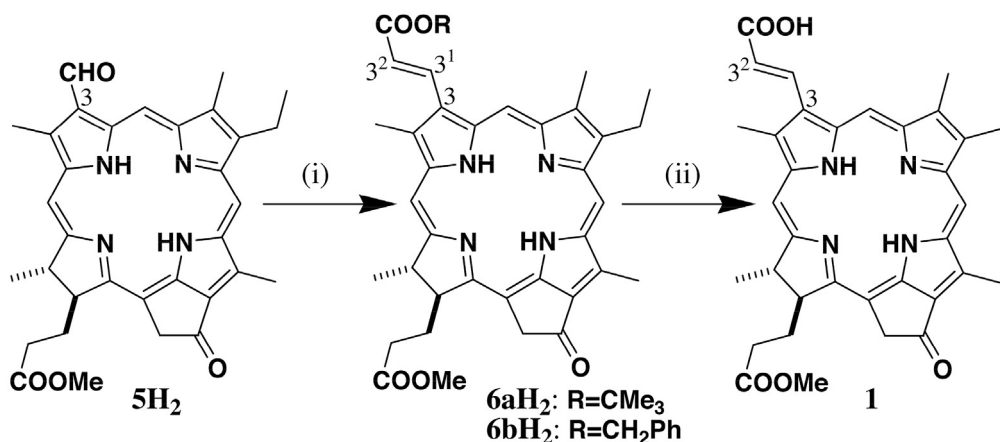
A similar Wittig reaction of aldehyde **5H₂** with the benzyl ester reagent in refluxing chloroform afforded the corresponding adduct **6bH₂** in 96% isolated yield [step (i) in Scheme 1, R = CH₂Ph]. The product was a sole (*E*)-isomer at the 1,2-disubstituted olefin in the 3-acrylate residue from the ¹H NMR analysis: ³*J* (C3¹H–C3²H) = 16 Hz. When the resulting adduct **6bH₂** in tetrahydrofuran (THF) containing acetone was treated with hydrogen gas in the presence of palladium on activated carbon, a mixture of products including the 3-CH₂CH₂- and/or 3²-COOH moieties were obtained, indicating that reduction of the olefin and cleavage of the

benzyl ester in the 3-acrylate residue proceeded. Such catalytic hydrogenation showed no site-selectivity and the desired cleavage of the benzyl ester did not occur predominantly. In contrast, the benzyl ester **6bH₂** was smoothly cleaved by trifluoromethanesulfonic acid (TFMSA) in TFA [13] to give **1** nearly quantitatively [step (ii), R = CH₂Ph]. The present synthetic route using the benzyl ester as a Wittig reagent is more cost-effective than the previous one via *tert*-butyl ester.

Next, bromoacetates, precursors of the above Wittig reagents, were utilized as the reagents for the addition toward **5Zn**, the zinc complex of free base **5H₂**. In the presence of indium powder and sodium iodide [14], **5Zn** was treated with *tert*-butyl bromoacetate [step (iii) in Scheme 2, R = CMe₃ and R' = H]. After sonication at 60 °C for a few days, adduct **7a** was obtained in 48% isolated yield by purification with flash column chromatography (FCC) and recrystallization. Adduct **7a** was a 1:1 epimeric mixture at the chiral 3¹-position. In the present Barbier-type reaction, zinc complex **5Zn** was used to avoid the undesired metalation of indium at the central position of **5H₂**. The resulting secondary alcohol **7a** was dehydrated by heating in a benzene and THF solution of *p*-toluenesulfonic acid (pTSA) [15] to afford **6aZn** (73%) as the (*E*)-isomer [step (iv) in Scheme 2]. During the acidic procedure, neither zinc-demetalation nor cleavage of the *tert*-butyl ester was observed. The product **6aZn** was dissolved in TFA, the solution was stirred at room temperature [step (ii) in Scheme 3, R = CMe₃], the reaction was quenched by pouring into water [step (v)], and then **6aZn** was converted to **1**. Acidic cleavage of the *tert*-butyl ester to free carboxylic acid and demetalation of zinc complex to free base proceeded smoothly. The synthetic pathway proceeded with a lower overall yield (ca. 35% for **5H₂** → **5Zn** → **7a** → **6aZn** → **1**) than the aforementioned yield (89% for **5H₂** → **6aH₂** → **1**).

Benzyl bromoacetate was suitable for the substrate of the above Barbier-type reaction (Scheme 2, R = CH₂Ph and R' = H). Indium-treated reaction of **5Zn** with benzyl bromoacetate (49%) [step (iii) in Scheme 2] and acidic dehydration of **7b** (87%) [step (iv) in Scheme 2], followed by double deprotection of **6bZn** in TFMSA/TFA gave **1** [steps (ii) and (v) in Scheme 3]. It is noted that selective hydrogenation of the benzyl ester in **6bZn** could not be performed, similarly as in the case of the free base **6bH₂** (vide supra).

Methyl bromoacetate was effective for the preparation of chlorin bearing the 3-acrylate residue (Scheme 2, R = Me and R' = H). Its Barbier-type reaction with **5Zn** (60%) followed by dehydration of **7c** (70%) afforded **6cZn**. Additionally, methyl 2-



Scheme 1. Synthesis of methyl (*E*)-3²-carboxy-pyropheophorbide-*a* (**1**) from methyl pyropheophorbide-*d* (**5H₂**) via Wittig reaction: (i) Ph₃P = CHCOOCMe₃, PhMe, reflux (for **6aH₂**) or Ph₃P = CHCOOCH₂Ph, CHCl₃, reflux (for **6bH₂**); (ii) CF₃COOH, rt (for R = CMe₃) or CF₃SO₃H, CF₃COOH, rt (for R = CH₂Ph).

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