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Synthesis, optical properties and protonation of chlorophyll derivatives appending a pyridyl group in the C3-substituent

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ABSTRACT

Chlorophyll(Chl)-*a* derivatives possessing a 2-(2/3/4-pyridyl)ethenyl group at the C3 position were synthesized by Wittig reaction of the 3-formyl group in methyl pyropheophorbide-*d*. The catalytic hydrogenation of the resulting 3-C=C double bond afforded the corresponding regioisomers of Chls bearing the 3-(2-pyridylethyl) group. Comparing their visible absorption spectra in dichloromethane, the longest wavelength (Qy) maxima were shifted bathochromically in the following order: C–C < C=C as the linker between the chlorin and pyridyl moieties. The red shifts are ascribable to their intramolecular π-conjugation through the 3-vinylene moiety. All the Chl derivatives in a diluted solution gave an intense fluorescence emission band at the red-side region of Qy band and their fluorescence quantum yields were about 20%. The synthetic Chl–pyridine conjugates were titrated with trifluoroacetic acid in chloroform. Their visible spectral changes indicated that the appended pyridyl group was first protonated, followed by protonation of the chlorin π-system at the inner nitrogen atoms in a molecule.

1. Introduction

Chlorophylls (Chls) are known to play important roles in light absorption and energy/electron transfer in natural photosynthesis [1]. Due to their excellent photofunctional abilities, various Chl derivatives have been prepared and their photophysical properties have been reported [2]. For about two decades, our group has focused on the development of Chl derivatives substituted with several kinds of functional groups at any peripheral positions including the C3, C7, C8, C13, C17 and C20 positions (see recent investigation in Ref. [3] and cited therein as well as Ref. [4]). We have already succeeded in the synthesis of Chl derivatives bearing various substituents at the C3 position by modification of the 3-vinyl group in methyl pyropheophorbide-*a* [5]. Among them, a Chl derivative possessing an ethynyl group at the C3 position has been used as a precursor for the preparation of novel Chls bearing π-extended moieties by replacement of the terminal ethynyl hydrogen atom to aromatics (Sonogashira coupling) and alkynes (Glaser reaction) [3,6]. Recently, we reported the synthesis and photophysical properties of Chl–(oligo)pyridine conjugates with the 3-ethynylene linker [3]. Here, we report the synthesis of Chls possessing a 2-(2/3/4-pyridyl)ethenyl group at the C3 position by Wittig reaction of methyl pyropheophorbide-*d* bearing the 3-formyl group, and the catalytic hydrogenation of the resulting 3-ethenyl group to afford the corresponding regioisomers of Chl–pyridine conjugates linked with the 3-ethylene spacer (Fig. 1). We discuss their optical properties in a solution and also the protonation of the 3^2-pyridyl group and chlorin ring by titration of trifluoroacetic acid (TFA).

2. Experimental

2.1. General

Visible absorption and fluorescence emission spectra were measured on Hitachi U-3500 and F-4500 spectrometers, respectively. Fluorescence quantum yields were measured at room temperature using a Hamamatsu Photonics absolute PL quantum yield measurement system C9920-03G. All melting points were measured with a Yanagimoto micro melting apparatus and were uncorrected. ^{1}H NMR spectra including COSY and NOESY were recorded on a JEOL JNM-AL-400 spectrometer in $CDCl_3$. Their chemical shifts (δs) are reported relative to the residual solvent peak: $\delta = 7.26$ ppm ($CHCl_3$). FTIR spectra in CH_2Cl_2 were measured with a Shimadzu IRAffinity-1 spectrophotometer. High resolution mass spectra (HRMS) were recorded on a Bruker micrOTOF II spectrometer: atmospheric pressure chemical ionization (APCI)

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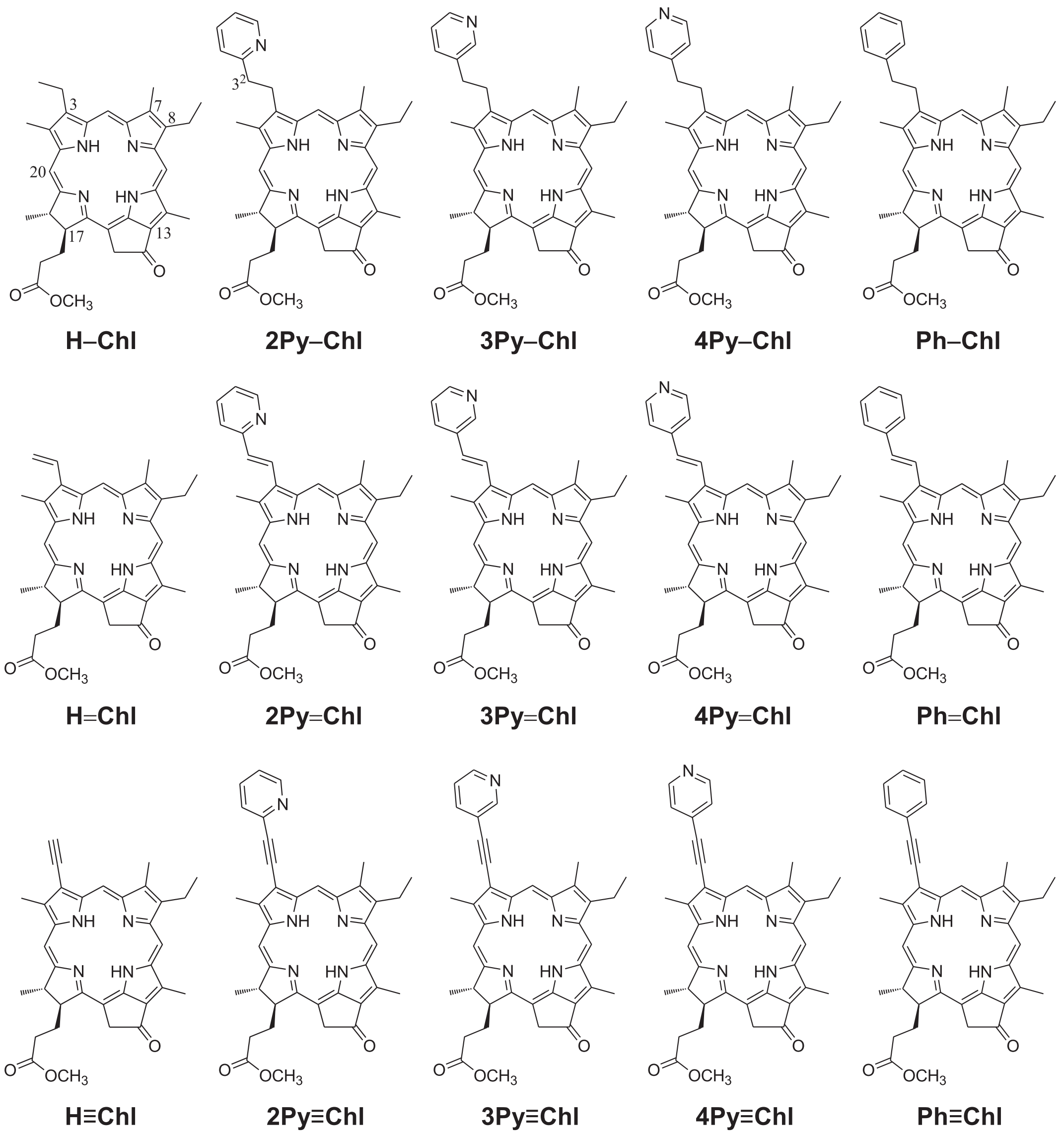

Fig. 1. Chlorophyll derivatives possessing (or lacking) a 2/3/4-pyridyl or phenyl group at the C3^2 position.

and positive mode in a methanol solution. Flash column chromatography (FCC) was performed with silica gel (Merck, Kieselgel 60).

Methyl pyropheophorbide-*a* (**H=Chl**) [4a,5a], methyl pyropheophorbide-*d* [4a,5a], methyl mesopyropheophorbide-*a* (**H–Chl**) [4a,5a], methyl *trans*-3^2-phenyl-pyropheophorbide-*a* (**Ph=Chl**) [5b], methyl 3-(2/3/4-pyridylethynyl)-pyropheophorbides-*a* (**2/3/4Py≡Chl**s) [3], methyl 3-devinyl-3-ethynyl-pyropheophorbide-*a* (**H≡Chl**) [6a], and methyl 3-devinyl-3-phenylethynyl- pyropheophorbide-*a* (**Ph≡Chl**) [6a], were prepared according to reported procedures. Commercially available THF (Nacalai Tesque) was passed through an alumina column before use. The other solvents and reagents were used as purchased without further purification. Solvents for optical spectroscopy were purchased from Nacalai Tesque as reagents prepared specially for spectroscopy and used without further purification.

2.2. Protonation experiments

A chloroform solution (2×10^{-3} to 2 M) of TFA (an appropriate volume) was added to a chloroform solution (2×10^{-5} M) of **2/3/4Py=Chl** or **H=Chl** (1 ml) and the mixed solution was diluted with chloroform until the final volume was 5 ml ([Chl] = 4.0×10^{-6} M). After stirring at room temperature, the solution was analysed by visible absorption spectroscopy. The association constants were determined by reported procedures [7] using changes of the absorbance of **2Py=Chl**, **3Py=Chl**, **4Py=Chl**, and **H=Chl** at 677/700, 673/700, and 680/700 nm, respectively. **H=Chl**: Vis ($CHCl_3$) λ_{max} 668 (ε, 44,000), 609 (8000), 539 (9000), 507 (10,000), 414 nm (101,000) and the corresponding spectral data of **2/3/4Py=Chl**s were described in the following sections.

2.3. Wittig reaction

A DMF solution (50 ml) of 2/3/4-(chloromethyl)pyridine hydrochloride (1.5 g, 9.2 mmol) and triphenylphosphine (2.4 g, 9.2 mmol) was refluxed for 1 h under N_2, and cooled down to room temperature. The resulting precipitates were filtered and recrystallized from EtOH and toluene to give the corresponding hydrochloride salt of 2/3/4-pyridylmethyl(triphenyl)phosphonium chloride (2.8 g, 6.5 mmol) [8] as a Wittig pre-reagent.