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# Syntheses of Chalcone-Type Chlorophyll Derivatives Possessing a Bacteriochlorin, Chlorin, or Porphyrin $\pi$ -System and Their Optical Properties

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## ABSTRACT

C3-(*Trans*-arylethenyl)carbonylated chlorophyll derivatives possessing a bacteriochlorin or chlorin  $\pi$ -system were synthesized by cross-aldol (Claisen-Schmidt) condensation of methyl pyrobacteriopheophorbide-*a* or 3-acetyl-3-devinyl-pyropheophorbide-*a* bearing the C3-acetyl group with *p*-(un)substituted benzaldehydes under basic conditions. The corresponding porphyrin-type chlorophyll derivatives were prepared by the oxidation (17,18-didehydrogenation) of the chlorin-type. Their Q<sub>y</sub> absorption and fluorescence emission maxima in dichloromethane correlated well with Hammett substituent constants of the

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*p*-substituents. Several electron-withdrawing *p*-substituents suppressed the emission due to photoinduced electron transfer quenching in a molecule. The substitution sensitivities for their maxima and fluorescence quantum yields decreased in the order of bacteriochlorin-, chlorin-, and porphyrin-type derivatives.

## INTRODUCTION

Photosynthesis is one of the most efficient energy conversion systems in nature.

(Bacterio)chlorophylls [(B)Chls] play significant roles such as light absorption, energy transfer, and charge separation in the initial stage of the photosynthetic processes (1,2).

Naturally occurring (B)Chls are cyclic tetrapyrrole pigments (3,4). They have various substituents at their peripheral positions and different fundamental  $\pi$ -systems, which largely affect their optical properties in the monomeric forms (5). In fact, Chls-*a/b* occurred in green plants and prochlorophytes possess a chlorin  $\pi$ -system (*trans*-17,18-dihydroporphyrin), while they have CH<sub>3</sub>/CHO groups at the C7-position (R<sup>7</sup> in Fig. 1 left). The C7-substituents impact their singlet excited energy levels known as site energies, which causes an efficient excitation energy transfer from Chl-*b* to Chl-*a* in the photosynthetic light-harvesting antennas (6).

Furthermore, Chl-*c*<sub>1</sub>/*c*<sub>2</sub> observed in chromophytes have a porphyrin  $\pi$ -skeleton (Fig. 1 middle).

They are utilized as accessory pigments like carotenoids in their photosynthetic light-harvesting antennas, and transfer excitation energy to Chl-*a* (6). BChl-*a* found in purple and green photosynthetic bacteria is a bacteriochlorin (*trans*-7,8-dihydrochlorin) with an electron-withdrawing acetyl group at the C3-position (Fig. 1 right), which yields a largely red-shifted Q<sub>y</sub> maximum at 771 nm in diethyl ether compared with Chl-*a* (661 nm). Therefore, BChl-*a* is able to absorb light at a near-infrared region (7). As mentioned above, (an)oxygenic phototrophs utilize three types of (B)Chl pigments depending on the illuminated light in their cultivation environments.

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Investigating the correlation between chemical structures of natural (B)Chl pigments and their optical properties is of considerable interest in the field of photobiological chemistry.

Several functional groups are available for peripheral substituents of natural (B)Chls (3,8): 3-acetyl, 3-vinyl, 7-formyl, 8-vinyl, 13-carbonyl, 17-acrylate groups, and so on. A lot of (B)Chl derivatives possessing a variety of substituents at their peripheral positions have been synthesized by the chemical modification of natural (B)Chls to understand the substitution effects on their optical properties based on several factors (5,9,10): the modification position,  $\pi$ -conjugation expansion, and electronic/steric effects. However, a limited number of reports are available for the substitution effects on (B)Chl derivatives possessing different fundamental  $\pi$ -systems (bacteriochlorin, chlorin, and porphyrin) (5,11–14).

Here, we prepared C3-(*trans*-2-arylethenyl)carbonylated (B)Chl derivatives possessing a bacteriochlorin **1a–f**, chlorin **2a–f**, or porphyrin  $\pi$ -system **3a–f** via cross-aldol (Claisen-Schmidt) condensation (Scheme 1). We compare optical properties between chlorin-type Chl derivatives **2a–f** and their structural isomers **4a–f**, and the substitution effect on three types of synthetic chalcone-(B)Chls **1/2/3a–f**.

## MATERIALS AND METHODS

*Apparatus.* Electronic absorption spectra were measured with a Hitachi U-3500 spectrophotometer. Fluorescence emission spectra and quantum yields were obtained with a Hamamatsu Photonics C9920-03G spectrometer.  $^1\text{H-NMR}$  and  $^{19}\text{F-NMR}$  spectra were measured with a JEOL AL-400 (400 and 376 MHz) spectrometer; chemical shifts ( $\delta\text{s}$ ) are expressed in parts per million relative to the residual  $\text{CHCl}_3$  ( $\delta_{\text{H}} = 7.26$  ppm) or  $\text{CDHCl}_2$  ( $\delta_{\text{H}} = 5.32$  ppm) as an internal reference, and  $\text{C}_6\text{F}_6$  ( $\delta_{\text{F}} = -164.90$  ppm) as an external reference. High resolution mass spectra (HRMS) were recorded on a Bruker micrOTOF II spectrometer: a

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time-of-flight analyzer, atmospheric pressure chemical ionization (APCI), and positive mode in an acetonitrile solution.

*Materials.* Commercially available organic solvents and reagents were used without further purification. Acetonitrile, dichloromethane, *N,N*-dimethylformamide (DMF), tetrahydrofuran (THF), and toluene were purchased from Nacalai Tesque (spectroscopy grade). Thin layer chromatography (TLC) and flash column chromatography (FCC) were performed with silica gel (Kieselgel 60, 40–63  $\mu\text{m}$ , 230–400 mesh).

Methyl pyrobacteriopheophorbide-*a* (**1g**) (12), methyl 3-acetyl-3-devinyl-pyropheophorbide-*a* (**2g**) (9,13), methyl 3-acetyl-3-devinyl-protophyropheophorbide-*a* (**3g**) (12), and methyl pyropheophorbide-*a* (**4g**) (9,15) were prepared according to reported procedures.

Synthetic procedures of chalcone-bacteriochlorins/chlorins/porphyrins are described below, and their spectral data are available in the Supporting Information file. All the reactions were done under  $\text{N}_2$  in the dark and monitored by TLC and visible (Vis) absorption spectroscopy.

*Cross-aldol (Claisen-Schmidt) condensation for the synthesis of 1a–c and 2a–c.*

3-Acetyl-bacteriochlorin/chlorin **1/2g** (10.2/10.9 mg, 18/19  $\mu\text{mol}$ ) and benz-, *p*-anis-, or *p*-tolualdehyde (12/10 mmol) were dissolved in a 1:1 mixture of methanol and chloroform (16 ml), to which 28% sodium methoxide in methanol (1/0.5 ml, 5/3 mmol) was added. The reaction mixture was refluxed for 1 h. After cooling down to room temperature, the reaction mixture was diluted with  $\text{CH}_2\text{Cl}_2$ , washed with aq. 2% HCl, aq. sat.  $\text{NaHCO}_3$ , and distilled water, dried over  $\text{Na}_2\text{SO}_4$ , and filtered. All the solvents were evaporated and the residue was purified by FCC (6–9%  $\text{Et}_2\text{O}-\text{CH}_2\text{Cl}_2$ ) and recrystallization ( $\text{CH}_2\text{Cl}_2$ –hexane) to give the corresponding 3-[*trans*-2-(phenyl, *p*-anisyl, or

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*p*-tolyl)ethenyl]carbonyl-bacteriochlorin/chlorin **1/2a**, **1/2b**, or **1/2c**. Isolated yields were 66/30% for **1/2a** (R = H), 53/59% for **1/2b** (R = OCH<sub>3</sub>), and 47/33% for **1/2c** (R = CH<sub>3</sub>).

*Cross-aldol (Claisen-Schmidt) condensation for 1d–f and 2d–f.*

3-Acetyl-bacteriochlorin/chlorin **1/2g** (10.9/10.7 mg, 19 μmol) and *p*-trifluoromethyl-, *p*-cyano-, or *p*-nitrobenzaldehyde (3/6 mmol) were dissolved in a 1:1 mixture of methanol and chloroform (16 ml), to which 28% sodium methoxide in methanol (1/0.5 ml, 5/3 mmol) was added. The reaction mixture was stirred in an ice bath for 1 h. The same work-up as mentioned above afforded the corresponding 3-[*trans*-2-(*p*-trifluoromethyl-, *p*-cyano-, or *p*-nitro)phenylethenyl]carbonyl-bacteriochlorin/chlorin **1/2d**, **1/2e**, or **1/2f**. Isolated yields were 14/27% for **1/2d** (R = CF<sub>3</sub>), 11/10% for **1/2e** (R = CN), and 25/13% for **1/2f** (R = NO<sub>2</sub>).

*DDQ oxidation of chlorins 2a–f to porphyrins 3a–f.* According to reported procedures (12), zinc metallation of chlorins **2a–f**, 17,18-oxidation by 1.2 equivalent of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in dry acetone for a few minutes, and demetallation by treatment with 10% (v/v) sulfuric acid in methanol gave the corresponding porphyrins **3a–f**.

## RESULTS AND DISCUSSION

### Synthesis of chalcone-type bacteriochlorins/chlorins/porphyrins 1/2/3a–f

Methyl pyrobacteriopheophorbide-*a* (**1g**) bearing an acetyl group at the C3-position and a bacteriochlorin  $\pi$ -skeleton was semi-synthesized by modifying natural BChl-*a* extracted from *Rhodobacter sphaeroides* as previously reported [steps (i) and (ii) in Scheme 1] (12).

3-Acetyl-bacteriochlorin **1g** was treated with benzaldehyde in a 1:1 mixture of methanol and chloroform in the presence of 28% sodium methoxide in methanol under reflux for 1 h (16) to

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give 3-(*trans*-styryl)carbonyl-bacteriochlorin **1a** as the product of cross-aldol (Claisen-Schmidt) condensation (17) in 66% isolated yield [step (iii)]. Under the above refluxing conditions, ketone **1g** reacted with *p*-anisaldehyde or *p*-tolualdehyde to give 3<sup>3</sup>-arylated 3-acryloyl-bacteriochlorin **1b** (53%) or **1c** (47%), respectively. In contrast, the reaction of **1g** with benzaldehyde substituted with an electron-withdrawing group at the *p*-position, *p*-trifluoromethyl-, *p*-cyano-, or *p*-nitrobenzaldehyde, under refluxing conditions gave no chalcone-bacteriochlorins **1d/e/f** as products. Under milder conditions in an ice bath, the desired products **1d/e/f** were successfully obtained in 14/11/25% isolated yields, respectively. Thus, the introduction of an electron-withdrawing group to the *p*-position of benzaldehyde accelerated the reaction due to an increase of the electrophilicity of the formyl group, and would lead to undesired over-reactions (not determined) at the refluxing temperature. These observations are consistent with the previous results for Claisen-Schmidt condensation of *p*-(un)substituted acetophenone with a 3-formyl-chlorin (16).

We then prepared 3-acetyl-chlorin **2g** from natural Chl-*a* extracted from *spirulina* as previously reported [steps (iv), (v), and (vi) in Scheme 1] (9). The reactions of **2g** with *p*-(un)substituted benzaldehydes afforded chalcone-chlorins **2a-f** (10–59% isolated yields) [step (iii)] in a similar manner for the synthesis of **1a-f**.

To obtain chalcone-porphyrins **3a-f** bearing a porphyrin  $\pi$ -system, the following pathways were examined. The chlorin ring of **2g** was oxidized through zinc metallation, DDQ oxidation, and acidic demetallation, to give 3-acetyl-porphyrin **3g** [step (vii) in Scheme 1] (12). Cross-aldol condensation of 3-acetyl-porphyrin **3g** with benzaldehyde was performed in a similar manner for the synthesis of **1/2a** [step (iii)]. Unfortunately, the isolation of **3a** from the reaction mixture by silica gel chromatography was very difficult due to its broadening on the gel. Chalcone-porphyrins **3a-f** were successfully synthesized by the oxidation of chalcone-chlorins **2a-f** as mentioned above [step (vii)]. All the synthetic compounds **1/2/3a-f**

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were fully characterized by their Vis,  $^1\text{H-NMR}$ , HRMS spectra (see Supporting Information). The coupling constant  $^3J(3^2\text{H}-3^3\text{H})$  of 16 Hz in the olefin moiety at the C3-position indicates that the products were *trans*-isomers.

### UV-Vis absorption spectra of chalcone-chlorins **2a–f** and their structural isomers **4a–f** in dichloromethane

UV-Vis absorption spectra of 3-styrylcarbonyl-chlorin **2a** and its *p*-substituents **2b–f** were measured in dichloromethane to investigate the substitution effects on their Qy absorption maxima, and compared with those of their structural isomers **4a–f** bearing the 3-benzoylphenyl group with(out) *p*-substituents (Fig. 2) (16).

A diluted dichloromethane solution of **2a** gave the intense Qy(0,0) band at 678 nm (green line in Fig. 3). The Qy(0,0) maximum of **2a** (3-COCH=CHPh-*trans*) in dichloromethane was blue-shifted by 5 nm than that of **2g** (3-COMe) as shown in Fig. 3. This hypsochromic shift could be explained by considering the following two factors. (i) The 3<sup>1</sup>-vinyl group of **2a** is able to be  $\pi$ -conjugated with the 3<sup>3</sup>-phenyl ring and is more electronegative than a methyl group (18), resulting in a red-shifted Qy(0,0) maximum. (ii) The larger 3-acyl group of **2a** than the 3-acetyl group of **2g** induced its larger steric repulsion with the neighboring C2-CH<sub>3</sub>/C5-H and the rotation around the C3–C3<sup>1</sup> bond to give a less  $\pi$ -conjugated conformer between the C3-substituent and the chlorin  $\pi$ -system, which resulted in a blue-shifted Qy(0,0) maximum. The factor (ii) would be superior to the factor (i), which caused such a hypsochromic shift for **2g**  $\rightarrow$  **2a**. Molecular modeling calculations (19) also supported the above conformations (Supporting Information, Fig. S1). The dihedral angle between the 3<sup>1</sup>-CH=CH and 3<sup>3</sup>-phenyl ring in **2a** was estimated to be 2° and the styryl group was almost planar, while that between the 3-CO and 3<sup>1</sup>-CH=CH was 24°, giving a partial  $\pi$ -conjugation between the carbonyl and styryl

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groups. In addition, the dihedral angles of C2–C3–C3<sup>1</sup>–O and C4–C3–C3<sup>1</sup>–O were 14° in **2a** and larger than 1–2° in **2g**. The 3-acryloyl group in **2a** was rotated from the chlorin  $\pi$ -plane, but the 3-acetyl group in **2g** was almost coplanar to the chlorin  $\pi$ -skeleton. The blue shift of the Q<sub>y</sub>(0,0) maximum is consistent with our previous works for 3-acyl-chlorins (20): 683 (3-COMe, **2g**) > 679 (3-COCH=CH<sub>2</sub>) > 675 nm (3-COCH=CHMe-*trans*).

UV-Vis absorption spectra of chalcone-chlorins **2a–f** in dichloromethane were compared with those of isomeric reverse chalcone-chlorins **4a–f**. The Q<sub>y</sub>(0,0) maximum of **2a** (3-COCH=CHPh-*trans*, green line in Fig. 3) was blue-shifted by 12 nm than that of the corresponding isomer **4a** (3-CH=CHCOPh-*trans*, pink line in Fig. 3). The blue shifts shown in Table 1 could be caused by a steric factor. The 3-substituents of **2a–f** interacted with their neighboring C2-CH<sub>3</sub>/C5-H more largely than those of **4a–f**, so the former should give less  $\pi$ -conjugated conformers with a chlorin  $\pi$ -system than the latter, resulting in the hypsochromic shifts. The steric factor is more effective than the electronic factor that the more electron-withdrawing C3-carbonyl group of **2a–f** than the C3-vinyl group of **4a–f** moves a Q<sub>y</sub>(0,0) maximum to a longer wavelength: 668 (3-CH=CH<sub>2</sub>, **4g**) < 683 nm (3-COMe, **2g**). The observed blue shifts are consistent with our previous works (16,20): 675 (3-COCH=CHMe-*trans*) < 685 nm (3-CH=CHCOMe-*trans*). The estimated dihedral angles of the 3-C=O with the chlorin moiety and the 3<sup>1</sup>-CH=CH in **2a** were 14° and 24°, respectively, and larger than those of the 3-CH=CH with chlorin and 3<sup>2</sup>-C=O which were 7° and 12°, respectively. Based on the calculations, the  $\pi$ -conjugation of chalcone-chlorin **2a** would extend along the molecular y-axis less than that of reverse chalcone-chlorin **4a**, supporting the observed blue shifts.



**Table 1.** Qy(0,0) absorption maxima  $\lambda_{\text{abs}}[\text{Qy}(0,0)]$  (nm) of **2/4a-f** in  $\text{CH}_2\text{Cl}_2$ .

R	<b>2</b> [3-COCH=CHPh( <i>p</i> -R)]	<b>4</b> [3-CH=CHCOPh( <i>p</i> -R)]
H ( <b>a</b> )	678 ( <b>2a</b> )	690 ( <b>4a</b> )
OCH <sub>3</sub> ( <b>b</b> )	676 ( <b>2b</b> )	688 ( <b>4b</b> )
CH <sub>3</sub> ( <b>c</b> )	677 ( <b>2c</b> )	689 ( <b>4c</b> )
CF <sub>3</sub> ( <b>d</b> )	681 ( <b>2d</b> )	693 ( <b>4d</b> )
CN ( <b>e</b> )	682 ( <b>2e</b> )	696 ( <b>4e</b> )
NO <sub>2</sub> ( <b>f</b> )	683 ( <b>2f</b> )	697 ( <b>4f</b> )

We have previously reported that there was a good correlation (correlation coefficient  $r^2 = 0.959$ ) between the Qy(0,0) maxima of **4a-f** and Hammett substituent constants ( $\sigma$ ) of the *p*-substituents (R) (16). Similarly, the relationship between the Qy(0,0) maxima of **2a-f** and the  $\sigma$ -values (21) was investigated (Fig. 4). As expected, these two parameters showed a good correlation ( $r^2 = 0.995$ ). The estimated slope (6.3) for **2a-f** was smaller than the reported 8.1 for **4a-f**. This result indicates that the electronic effect of the *p*-substituents on the C3<sup>3</sup>-phenyl ring on Qy(0,0) maxima of **2a-f** is less than those of **4a-f**, which would be due to less  $\pi$ -conjugation of **2a-f** along the molecular *y*-axis than that of **4a-f** (vide supra).

## Electronic absorption spectra of chalcone-bacteriochlorins/chlorins/porphyrins **1/2/3a-f** in dichloromethane

Diluted dichloromethane solutions of **1/2/3a** showed totally different electronic absorption spectra due to their different fundamental  $\pi$ -systems, to give Q<sub>y</sub>(0,0) maxima at 749/678/644 nm, respectively (Fig. 5).

The effects of the *p*-substituents in the C3<sup>3</sup>-phenyl ring on the Q<sub>y</sub>(0,0) maxima were compared among **1/2/3a-f** (Supporting Information, Table S1). Similarly as in **2a-f**, good correlations between the Q<sub>y</sub>(0,0) maxima and the  $\sigma$ -values in **1/3a-f** were observed with  $r^2 = 0.993/0.941$  (Figs. 6-7). The slopes for the estimated lines decreased in the following order: 10.9 (**1a-f**) > 6.3 (**2a-f**) > 3.5 (**3a-f**). This tendency should be considered as follows. The  $\pi$ -electrons of a bacteriochlorin ring are more localized along the molecular *y*-axis than those of a chlorin, and those of a porphyrin ring are delocalized over the  $\pi$ -skeleton, which may suppress the sensitivity to the substitution effects in the above order.

## Fluorescence emission data of chalcone-bacteriochlorins/chlorins/porphyrins **1/2/3a-f** in dichloromethane

Upon the excitation of **1/2/3a** in dichloromethane at the intense Soret maxima (354/411/423 nm), their main emission peaks  $\lambda_{em}$  were observed at 768/693/652 nm, respectively (Table 2 and Fig. S2). The Stokes shifts  $\Delta$  of **1/2/3a** were calculated to be 330/320/190 cm<sup>-1</sup>, respectively (Table S2). The effects of the *p*-substituents in the C3<sup>3</sup>-phenyl ring on the  $\lambda_{em}$ -values were also examined among **1/2/3a**. Except for the nitro-substituents **1/2f**, there were good correlations between  $\lambda_{em}$  and the  $\sigma$ -values (Figs. S3-S5): the reason of the deviation is currently being investigated.

**Table 2.** Fluorescence emission maxima  $\lambda_{em}$  (nm) of **1/2/3a-f** in  $CH_2Cl_2$  (excitation at the intense Soret maxima).

R	<b>1</b>	<b>2</b>	<b>3</b>
H ( <b>a</b> )	768 ( <b>1a</b> )	693 ( <b>2a</b> )	652 ( <b>3a</b> )
OCH <sub>3</sub> ( <b>b</b> )	766 ( <b>1b</b> )	691 ( <b>2b</b> )	651 ( <b>3b</b> )
CH <sub>3</sub> ( <b>c</b> )	768 ( <b>1c</b> )	692 ( <b>2c</b> )	652 ( <b>3c</b> )
CF <sub>3</sub> ( <b>d</b> )	775 ( <b>1d</b> )	698 ( <b>2d</b> )	654 ( <b>3d</b> )
CN ( <b>e</b> )	775 ( <b>1e</b> )	700 ( <b>2e</b> )	655 ( <b>3e</b> )
NO <sub>2</sub> ( <b>f</b> )	769 ( <b>1f</b> )	697 ( <b>2f</b> )	655 ( <b>3f</b> )

Fluorescence emission quantum yields  $\Phi_{em}$  of **1/2/3a-f** were measured in dichloromethane by the absolute determination method. As shown in Table 3, the introduction of strongly electron-withdrawing groups (CN and/or NO<sub>2</sub>) on the C3<sup>3</sup>-phenyl ring reduced their  $\Phi_{em}$ -values. Especially, the  $\Phi_{em}$  of bacteriochlorin **1** was largely suppressed by the substitution with cyano and nitro groups as in **1e** and **1f** (14%  $\rightarrow$  4% and 0%). The introduction of a nitro group as in chlorin **2a**  $\rightarrow$  **2f** similarly reduced the  $\Phi_{em}$ -value (22%  $\rightarrow$  1%). A slight decrease was caused by the substitution with a nitro group of porphyrin **3a** to **3f**:  $\Phi_{em} = 3\% \rightarrow 2\%$ . The sensitivity for  $\Phi_{em}$  is obeyed in the order of **1** > **2** > **3**, which is consistent with the above observation in the Qy(0,0) maxima.

**Table 3.** Fluorescence emission quantum yields  $\Phi_{em}$  (%) of **1/2/3a–f** in  $\text{CH}_2\text{Cl}_2$  (excitation at the intense Soret maxima).

R	<b>1</b>	<b>2</b>	<b>3</b>	
H ( <b>a</b> )	14 ( <b>1a</b> )	22 ( <b>2a</b> )	3 ( <b>3a</b> )	F
OCH <sub>3</sub> ( <b>b</b> )	14 ( <b>1b</b> )	24 ( <b>2b</b> )	3 ( <b>3b</b> )	or
CH <sub>3</sub> ( <b>c</b> )	13 ( <b>1c</b> )	22 ( <b>2c</b> )	3 ( <b>3c</b> )	the
CF <sub>3</sub> ( <b>d</b> )	11 ( <b>1d</b> )	19 ( <b>2d</b> )	3 ( <b>3d</b> )	further
CN ( <b>e</b> )	4 ( <b>1e</b> )	18 ( <b>2e</b> )	3 ( <b>3e</b> )	er
NO <sub>2</sub> ( <b>f</b> )	0 ( <b>1f</b> )	1 ( <b>2f</b> )	2 ( <b>3f</b> )	investigation

of the decrease in the  $\Phi_{em}$ -values of **1/2/3** by the substitution with strongly electron-withdrawing groups, the  $\Phi_{em}$  of **1/2/3a** as well as those of their trifluoromethyl- **1/2/3d**, cyano- **1/2/3e**, and nitro-substituents **1/2/3f** were measured in various solvents (Table 4). Their  $\Phi_{em}$ -values of bacteriochlorins, chlorins, and porphyrins in toluene which is a less polar solvent than dichloromethane were relatively close for their substituents, 13–16%, 23–27%, and 4–5%, respectively. As the dielectric constant ( $\epsilon$ ) of the solvents increased, the distinct decreases in the  $\Phi_{em}$ -values of **1d/e/f**, **2e/f**, and **3f** were observed:  $\Phi_{em}(\text{C}_6\text{H}_5\text{CH}_3) = 14/14/13\%$ ,  $23/25\%$ , and  $5\% \rightarrow \Phi_{em}(\text{CH}_3\text{CN}) = 10/3/1\%$ ,  $12/1\%$ , and  $2\%$ , respectively (Table 4). These observations are consistent with the reported data that the  $\Phi_{em}$ -value of **4f** bearing a nitro group was dependent on the solvent polarity (16). Consequently, the decrease in the  $\Phi_{em}$ -values of **1/2/3a** by the *p*-substitution with CF<sub>3</sub>, CN, and/or NO<sub>2</sub> groups on the C3<sup>3</sup>-phenyl ring would be caused by intramolecular photoinduced electron transfer quenching.

**Table 4.** Fluorescence emission quantum yields  $\Phi_{em}$  (%) of **1/2/3a-f** in various solvents (excitation at the intense Soret maxima).

Compound [R]	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	THF	CH <sub>2</sub> Cl <sub>2</sub>	DMF	CH <sub>3</sub> CN
<b>1a</b> [H]	16	14	14	13	17
<b>1d</b> [CF <sub>3</sub> ]	14	14	11	10	10
<b>1e</b> [CN]	14	13	4	5	3
<b>1f</b> [NO <sub>2</sub> ]	13	1	0	1	1
<b>2a</b> [H]	27	21	22	20	23
<b>2d</b> [CF <sub>3</sub> ]	24	22	19	21	20
<b>2e</b> [CN]	23	22	18	16	12
<b>2f</b> [NO <sub>2</sub> ]	25	8	1	1	1
<b>3a</b> [H]	5	4	3	2	4
<b>3d</b> [CF <sub>3</sub> ]	4	4	3	3	4
<b>3e</b> [CN]	4	4	3	2	3
<b>3f</b> [NO <sub>2</sub> ]	5	4	2	1	2

## CONCLUSIONS

Chalcone-(B)Chls **1a–f**, **2a–f**, and **3a–f** possessing bacteriochlorin, chlorin, and porphyrin  $\pi$ -systems, respectively, were successfully synthesized through a similar manner for the synthesis of isomeric reverse chalcone-chlorins **4a–f**. The redmost Qy absorption and main fluorescence emission maxima of all of the synthetic chalcone analogs **1/2/3/4a–f** were dependent on the *p*-substituents of the C3<sup>3</sup>-phenyl ring. The sensitivities to their Hammett  $\sigma$ -values decreased in the following order: **1** > **4** > **2** > **3**. Furthermore, the substitution effects on the quantum yields by the *p*-substituents are dependent on the  $\pi$ -conjugation degree of cyclic tetrapyrroles and the solvent polarities. These results indicate that the use of different fundamental  $\pi$ -systems and chemical modification of peripheral substituents of (B)Chls are techniques to regulate their singlet excited energy levels.

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## SUPPORTING INFORMATION

Additional Supporting Information may be found in the online version of this article:

**Figure S1.** Energy-minimized molecular models of **2a/2g/4a** estimated by MM+/PM3 calculations.

**Figure S2.** Normalized fluorescence emission spectra (excitation at the intense Soret maxima) of **1/2/3a** in CH<sub>2</sub>Cl<sub>2</sub>.

**Figures S3, S4, S5.** Correlation of main emission maxima  $\lambda_{em}$  of **1/2/3a-f** in CH<sub>2</sub>Cl<sub>2</sub> with Hammett substituent constants  $\sigma$ .

**Table S1.** Qy(0,0) absorption maxima  $\lambda_{abs}[Qy(0,0)]$  (nm) of **1/2/3a-f** in CH<sub>2</sub>Cl<sub>2</sub>.

**Table S2.** Stokes shifts  $\Delta$  (cm<sup>-1</sup>) of **1/2/3a-f** in CH<sub>2</sub>Cl<sub>2</sub>.

Spectral data of chalcone-bacteriochlorins/chlorins/porphyrins **1/2/3a-f**

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## FIGURE CAPTIONS

**Figure 1.** Chemical structures of naturally occurring (B)Chl pigments.

**Figure 2.** Chemical structure of reverse chalcone-type Chl derivatives **4a–f** as the isomers of **2a–f**.

**Figure 3.** UV-Vis absorption spectra of **2a** (green line), **2g** (black line), and **4a** (pink line) in CH<sub>2</sub>Cl<sub>2</sub>. All the spectra were normalized at the intense Soret maxima.

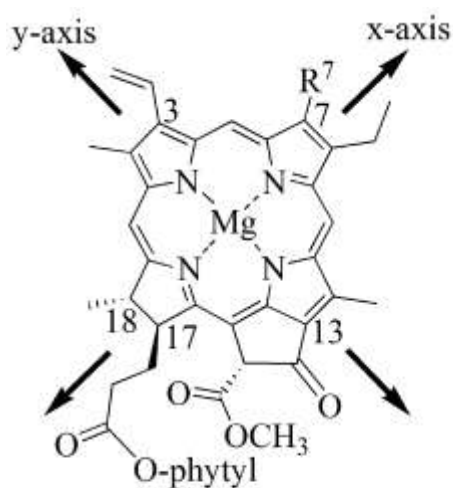
**Figure 4.** Correlation of Qy(0,0) absorption maxima  $\lambda_{\text{abs}}[\text{Qy}(0,0)]$  of **2a–f** in CH<sub>2</sub>Cl<sub>2</sub> with Hammett substituent constants  $\sigma$ .

**Figure 5.** Electronic absorption spectra of **1a** (red line), **2a** (green line), and **3a** (blue line) in CH<sub>2</sub>Cl<sub>2</sub>. All the spectra were normalized at the intense Soret maxima.

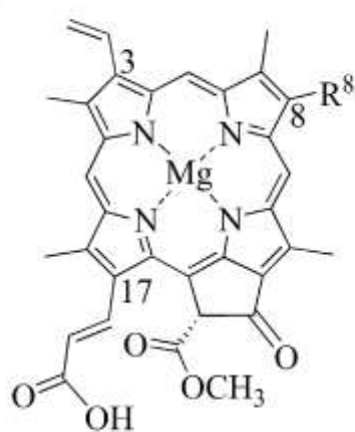
**Figure 6.** Correlation of Qy(0,0) absorption maxima  $\lambda_{\text{abs}}[\text{Qy}(0,0)]$  of **1a–f** in CH<sub>2</sub>Cl<sub>2</sub> with Hammett substituent constants  $\sigma$ .

**Figure 7.** Correlation of Qy(0,0) absorption maxima  $\lambda_{\text{abs}}[\text{Qy}(0,0)]$  of **3a–f** in CH<sub>2</sub>Cl<sub>2</sub> with Hammett substituent constants  $\sigma$ .

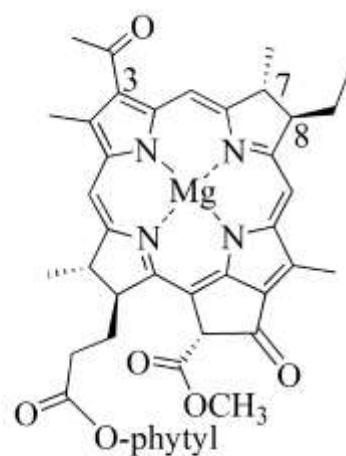
**Scheme 1.** Synthesis of chalcone-type (B)Chl derivatives bearing a bacteriochlorin **1a–f**, chlorin **2a–f**, or porphyrin skeleton **3a–f** through Claisen-Schmidt condensation of **1/2g** with *p*-(un)substituted benzaldehyde: (i) CH<sub>3</sub>OH, acetone; (ii) (a) aq. 2% HCl/CH<sub>2</sub>Cl<sub>2</sub>, (b) collidine, reflux, (c) H<sub>2</sub>SO<sub>4</sub>/CH<sub>3</sub>OH; (iii) *p*-RC<sub>6</sub>H<sub>4</sub>CHO, NaOCH<sub>3</sub>/CHCl<sub>3</sub>–CH<sub>3</sub>OH [R = H (**a**), OCH<sub>3</sub> (**b**), CH<sub>3</sub> (**c**), CF<sub>3</sub> (**d**), CN (**e**), and NO<sub>2</sub> (**f**)]; (iv) CH<sub>3</sub>OH; (v) (a) H<sub>2</sub>SO<sub>4</sub>/CH<sub>3</sub>OH, (b) collidine, reflux; (vi) (a) HBr/AcOH, (b) H<sub>2</sub>O, (c) CH<sub>2</sub>N<sub>2</sub>/Et<sub>2</sub>O, (d) CH<sub>3</sub>N(O)(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>O, Pr<sub>4</sub>NRuO<sub>4</sub>/CH<sub>2</sub>Cl<sub>2</sub>; (vii) (a) Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O/CH<sub>2</sub>Cl<sub>2</sub>–CH<sub>3</sub>OH; (b) DDQ/dry acetone, (c) H<sub>2</sub>SO<sub>4</sub>/CH<sub>3</sub>OH.



Chl-*a*: R<sup>7</sup> = CH<sub>3</sub>  
 Chl-*b*: R<sup>7</sup> = CHO



Chl-*c*<sub>1</sub>: R<sup>8</sup> = CH<sub>2</sub>CH<sub>3</sub>  
 Chl-*c*<sub>2</sub>: R<sup>8</sup> = CH=CH<sub>2</sub>



BChl-*a*

