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Synthesis, Structure, and Optical and Redox Properties of Chlorophyll Derivatives Directly Coordinating Ruthenium Bisbipyridine at the Peripheral β-Diketonate Moiety

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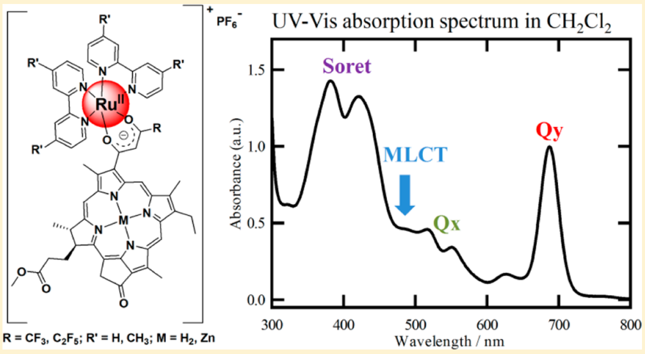
Supporting Information



R = CF_3, C_2F_5; R' = H, CH_3; M = H_2, Zn

ABSTRACT: The diketonate group of the peripheral position in chlorophyll derivatives **1** and **2** coordinated ruthenium bisbipyridine to give direct linkages **3**–**5** of the chlorin ring with the Ru(II) complex. Zinc metalation of the central position in the chlorin ring of free base **3** afforded the Ru–Zn binuclear complex **3-Zn**. Because the diketonate group at the C3 position of chlorophyll derivatives coordinated to bulky $Ru(bpy)_2^{2+}$, the plane of the diketonate group was twisted from the chlorin π ring in synthetic **3**–**5** and **3-Zn** to lead to a partial deconjugation and a slight blue shift of the longest wavelength electronic absorption band in dichloromethane. A broad metal-to-ligand charge-transfer absorption band derived from the Ru complex was observed around 500 nm, in addition to visible absorption bands from the chlorophyll moiety. Chlorophyll derivatives **3**–**5** and **3-Zn** directly coordinating the ruthenium complex were less fluorescent in dichloromethane than chlorophyll–diketonate ligands **1**, **2**, and **1-Zn** due to the heavy atom effect of the ruthenium in a molecule. The coordination to the ruthenium complex moiety at the peripheral position shifted the electrochemical reduction of the chlorin part in acetonitrile to a negative potential, and the coordination to zinc at the central position decreased the redox potentials. Chemical modification of the bipyridine and diketonate ligands of the ruthenium complexes greatly affected the redox potentials of Ru(II)/(III) and/or Ru(II)/(I) but minimally the redox properties of the chlorin moiety. Substitution with electron-donating groups shifted the former to a negative potential but only barely shifted the latter. The zinc metalation caused no apparent shifts for the redox potentials of the Ru center.

■ INTRODUCTION

β-Diketonates are such interesting functional groups that they have been investigated from various aspects.[1−3] In coordination chemistry, β-diketonates are effective for the ligand of metal complexes (Figure 1, left). Negatively charged oxygen atoms of the β-diketonates tightly coordinate a cationic metal through their strong σ-donation to stabilize the metal complex. The electron-donating ability of the oxygen sites is tunable by the three substituents R^1–R^3 in the diketonate group and produces the desired electron environment for any metal centers. The chelate effect of bidentate diketonate ligands further stabilizes the metal complexes.

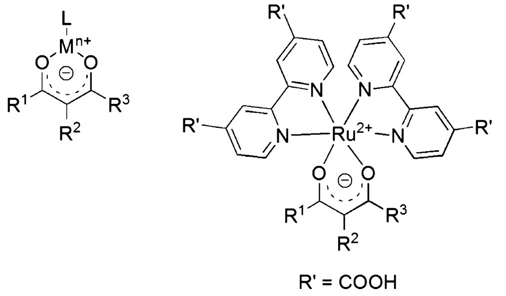


Figure 1. Chemical structures of metal complexes possessing a β-diketonate.

When a diketonate ligand coordinated to bis(4,4′-dicarboxy-2,2′-bipyridine)ruthenium (Figure 1, right), the resulting complex gave the metal-to-ligand charge-transfer (MLCT) absorption band in a wide visible region and acted as an efficient sensitizer of a solar cell.[4,5] The conversion efficiency reached 6% and was comparable to that of a Ru complex possessing two thiocyanate ligands. Moreover, in the case of R^1 = CF_3, the ruthenium complexes widely absorbed light from the visible to the near infrared (NIR) region and were effective dyes for solar cells, whose conversion efficiencies were enhanced by an increase of the alkyl chain length in the R^3 group.[6−9]

On the other hand, chlorophylls (Chls) play important roles in light-harvesting, energy-transferring, and charge-separating processes in photosynthesis.[10−12] Chls show characteristic absorption spectra in the ultraviolet (UV), visible, and NIR

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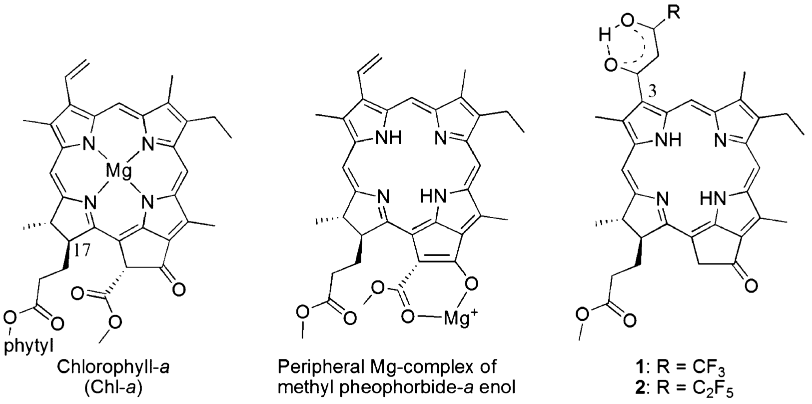


Figure 2. Chemical structures of Chl-*a*, peripheral Mg complex of methyl pheophorbide-*a* enol, and *β*-diketonated chlorophyll derivatives **1** and **2**.

regions, of which the two intense bands are called Qy and Soret bands in the longer and shorter wavelengths, respectively. Chls have several kinds of substituents at the peripheral positions of the chlorin ring. These substituents greatly affect the electronic absorption bands. Chls usually have a magnesium (Mg) dication at the central position of the chlorin ring (Chl-*a* in Figure 2). Additionally, a Chl possessing a zinc (Zn) dication was identified as a photosynthetically active pigment in specific purple bacteria.[13] Central metals are requisite for the construction of photosynthetic apparatuses, including light-harvesting antennas and reaction centers. In these apparatuses, the four-coordinated metals in naturally occurring Chls are bound with several functional groups at the axial position to form five-coordinated Chl−peptide[14,15] and Chl−Chl complexes.[16] Metalation of chlorin rings has been readily achieved, and various synthetic metallochlorophylls have proven to be useful as models of natural Chls.[17,18]

Coordination to the peripheral position of synthetic porphyrins has attracted some attention in the preparation of supramolecular assemblies.[19−21] Several porphyrins coordinating a bipyridineruthenium complex at the peripheral position are available for important complexes possessing photophysical, redox-active, electron-transferring, and light-harvesting properties.[22−25] The porphyrin−Ru conjugates were useful for dye sensitizers of solar cells,[26−29] molecular switches,[30,31] and molecular motors.[32,33] The peripheral coordination of a chlorin to a metal ion has been primarily studied in the field of photodynamic therapy (PDT).[34,35] Pyropheophorbide-*a*, one of the Chl-*a* derivatives, was connected with a potassium tetrachloroplatinate at the terminal position of the C17 substituent, and the resulting chlorin−Pt conjugate showed a greater cytotoxic effect than the original cisplatin.[36] A similar chlorin−Gd conjugate was prepared to use as an in vivo PDT and a fluorescent imaging agent based on the chlorophyll moiety, as well as a magnetic resonance imaging agent based on the gadolinium moiety.[37] All of the isolated chlorin−metal linkages investigated so far have been indirect conjugates of chlorin π ring systems with metal complexes. A Chl derivative directly conjugating Mg at the peripheral position of the chlorin π ring was prepared, as shown in the center drawing of Figure 2.[38] The chlorin−Mg conjugate was identified in a solution by both NMR and IR spectroscopy; the complex could not be obtained in the solid state due to its instability even in a solution.

Recently, we synthesized Chl derivatives **1** and **2**, which have a trifluoro- or pentafluoro-*β*-diketonate group at the C3 position (Figure 2), and we reported their optical properties, as well as the crystal structure of **1**.[39] Here, we used synthetic molecules **1** and **2** as the *β*-diketonate ligand and prepared their Chl derivatives, which coordinated Ru complexes bearing two bipyridines. The synthetic Chl derivatives possessing Ru complexes at the peripheral position were isolated and fully identified, and one of them was further zinc-metalated at the central position to give the binuclear Chl complex. In addition, their optical properties and redox potentials in a solution were measured, and their substitution effect was investigated.

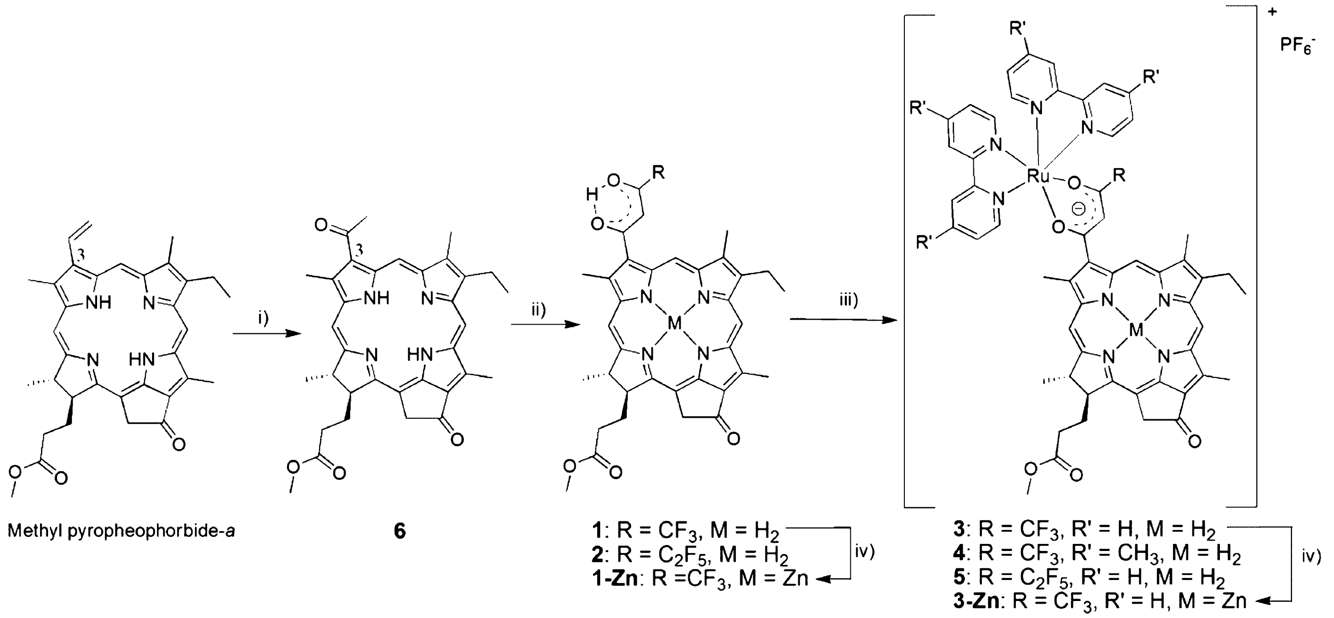
■ EXPERIMENTAL SECTION

General. Electronic absorption was measured in CH_2Cl_2 at room temperature on a Hitachi U-3500 spectrophotometer. Fluorescence quantum yields in air-saturated CH_2Cl_2 were determined using a Hamamatsu Photonics C9920-02 spectrometer. ^1H NMR and ^{19}F NMR spectra were recorded in $CDCl_3$ at room temperature on a JEOL ECA-600 (600 and 565 MHz) spectrometer; $CHCl_3$ ($\delta_H = 7.26$ ppm) was used as an internal reference and CF_3COOH ($\delta_F = -79.0$ ppm) as an external reference. Peaks were assigned by ^1H−^1H COSY and NOESY spectra. Electrospray ionization (ESI) high-resolution mass (HRMS) data were obtained with a Bruker micrOTOF-II. Flash column chromatography (FCC) was carried out on silica gel (Merck silica gel 60, 230−400 mesh). Electrochemical measurements were carried out by a BAS CV-50W voltammeric analyzer with a conventional three-electrode system.

Methyl 3-devinyl-3-(4,4,4-trifluoro-1,3-dioxo-butan-1-yl)-pyropheophorbide-*a* enol (**1**),[39] methyl 3-devinyl-3-(4,4,5,5,5-pentafluoro-1,3-dioxo-pentan-1-yl)-pyropheophorbide-*a* enol (**2**),[39] methyl 3-acetyl-3-devinyl-pyropheophorbide-*a* (**6**),[40] bis(2,2′-bipyridine)-dichlororuthenium(II) [$Ru(bpy)_2Cl_2$],[41] bis(4,4′-dimethyl-2,2′-bipyridine)dichlororuthenium(II) [$Ru(dmb)_2Cl_2$],[41,42] and [$Ru(bpy)_2(CF_3COCHCOC_6H_5)$]$PF_6$ (7)[43,44] were prepared according to reported procedures. Commercially available CH_2Cl_2, MeOH, and EtOH (Nacalai Tesque, extra pure reagents) were used as reaction solvents. For measurements of electronic absorption spectra, CH_2Cl_2 was purchased from Nacalai Tesque as a grade of reagent prepared specially for spectroscopy and used without further purification.

Synthesis of [$Ru(bpy)_2$(1−H)]PF_6 (3). $Ru(bpy)_2Cl_2$ (96.5 mg, 0.20 mmol) was dissolved in EtOH (10 mL) and CH_2Cl_2 (90 mL) with stirring. Compound **1** (100 mg, 0.15 mmol) was added to the solution, and the mixture was refluxed overnight under nitrogen in the dark. The reaction mixture was cooled to room temperature and added to MeOH saturated with NH_4PF_6 (100 mL) with stirring. The solvents were evaporated in vacuo, and the resulting residue was dissolved in CH_2Cl_2. The solution was washed with water twice, dried over Na_2SO_4, and filtered. After evaporation of the solution in vacuo, the residue was purified by FCC using 1.5% MeOH−CH_2Cl_2 as eluents, and recrystallization from CH_2Cl_2 and hexane gave a pure sample of **3** (67 mg, 0.055 mmol, 36%): VIS (CH_2Cl_2) λ_{max} 687 (relative intensity, 71%), 627 (11), 550 (23), 516 (31), 420 (92), 382

Scheme 1. Synthetic Scheme of Chlorophyll Derivatives 1 and 2, Their Ruthenium Complexes 3−5, and 1/3-Zn[a]



[a]Conditions: (i) HBr/AcOH, H_2O, CH_2N_2/Et_2O, Pr_4NRuO_4−Me(O)N$(CH_2CH_2)_2O/CH_2Cl_2$; (ii) $RCOOC_2H_5$−$NaOCH_3/CH_3OH$−$CHCl_3$; (iii) $Ru(bpy)_2Cl_2$ or $Ru(dmb)_2Cl_2/C_2H_5OH$−$CHCl_3$, NH_4PF_6/CH_3OH; (iv) $Zn(OAc)_2\cdot 2H_2O/CH_3OH$−$CH_2Cl_2$.

nm (100). ^{1}H NMR ($CDCl_3$) δ (1/1): 9.51/9.50 (1H, s, 10-H), 9.46 (1H, s, 5-H), 9.18/9.15 (1H, d, J = 5 Hz, 6-H of bpy-I), 9.01 (1H, d, J = 5 Hz, 6-H of bpy-II), 8.66/8.63 (1H, d, J = 8 Hz, 3-H of bpy-II), 8.63/8.62 (1H, s, 20-H), 8.54 (1H, d, J = 8 Hz, 3-H of bpy-I), 8.44/8.42 (1H, d, J = 8 Hz, 3′-H of bpy-I), 8.33 (1H, d, J = 8 Hz, 3′-H of bpy-II), 8.27/8.26 (1H, t, J = 8 Hz, 4-H of bpy-II), 8.22, (1H, t, J = 8 Hz, 4-H of bpy-I), 7.92/7.89 (1H, d, J = 5 Hz, 6′-H of bpy-I), 7.89/7.88 (1H, d, J = 5 Hz, 6′-H of bpy-II), 7.83/7.82 (1H, dd, J = 5, 8 Hz, 5-H of bpy-II), 7.758/7.752 (2H, t, J = 8 Hz, 4′-H of bpy-I and II), 7.69/7.68 (1H, dd, J = 5, 8 Hz, 5-H of bpy-I), $7.21_5/7.21_1$ (1H, dd, J = 5, 8 Hz, 5′-H of bpy-II), 7.15/7.14 (1H, dd, J = 5, 8 Hz, 5′-H of bpy-I), 6.962/6.958 (1H, s, 3^1-CH), 5.271/5.269, 5.124/5.121 (each 1H, J = 19 Hz, 13^1-CH_2), 4.49/4.48 (1H, dq, J = 1, 7 Hz, 18-H), 4.30 (1H, m, 17-H), 3.70−3.65 (2H, m, 8-CH_2), 3.63/3.62 (3H, s, 12-CH_3), 3.58/3.57 (3H, s, 17^2-$COOCH_3$), 3.05 (3H, s, 7-CH_3), 3.02/2.99 (3H, s, 2-CH_3), 2.70−2.64, 2.58−2.50, 2.29−2.20 (1H+1H+2H, m, 17-CH_2CH_2), 1.77/1.73 (3H, d, J = 7 Hz, 18-CH_3), 1.682/1.676 (3H, t, J = 8 Hz, 8^1-CH_3) −0.13, −2.18 (each 1H, s, NH × 2). ^{19}F NMR ($CDCl_3$) δ: −74.4 (6F, d, J = 713 Hz, PF_6), −75.3 (3F, s, 3^3-CF_3). HRMS (ESI) m/z : $[M - PF_6]^+$ calcd for $C_{56}H_{50}F_3N_8O_5Ru$, 1073.2894; found, 1073.2848 .

Synthesis of $[Ru(dmb)_2(1-H)]PF_6$ (4). Similar to the synthesis of **3**, peripheral metalation of **1** (23.3 mg, 0.035 mmol) with $Ru(dmb)_2Cl_2$ (21.9 mg, 0.041 mmol) gave ruthenium complex **4** (18.9 mg, 0.015 mmol, 42%) after FCC (CH_2Cl_2/MeOH = 99:1): VIS (CH_2Cl_2) λ_{max} 686 (relative intensity, 70%), 625 (12), 548 (24), 515 (34), 417 (98), 384 nm (100). ^{1}H NMR ($CDCl_3$) δ (1/1): 9.57/9.56 (1H, s, 10-H), 9.46/9.45 (1H, s, 5-H), 9.00/8.97 (1H, d, J = 6 Hz, 6-H of dmb-I), 8.81 (1H, d, J = 6 Hz, 6-H of dmb-II), 8.63/8.62 (1H, s, 20-H), 8.47/8.45 (1H, s, 3-H of dmb-II), 8.34 (1H, s, 3-H of dmb-I), 8.25/8.24 (1H, s, 3′-H of dmb-I), 8.16 (1H, s, 3′-H of dmb-II), 7.72/7.69 (1H, d, J = 6 Hz, 6′-H of dmb-I), 7.69 (1H, d, J = 6 Hz, 6′-H of dmb-II), 7.59/7.58 (1H, d, J = 6 Hz, 5-H of dmb-II), 7.46/7.45 (1H, d, J = 6 Hz, 5-H of dmb-I), 7.04 (1H, d, J = 6 Hz, 5′-H of dmb-II), 6.96/6.94 (1H, d, J = 6 Hz, 5′-H of dmb-I), 6.90/6.89 (1H, s, 3^1-CH), 5.30/5.29, 5.144/5.142 (each 1H, J = 19 Hz, 13^1-CH_2), 4.50 (1H, dq, J = 3, 7 Hz, 18-H), 4.32 (1H, m, 17-H), 3.71 (2H, q, J = 7 Hz, 8-CH_2), 3.699/3.697 (3H, s, 12-CH_3), 3.59/3.58 (3H, s, 17^2-$COOCH_3$), 3.038 (3H, s, 7-CH_3), 3.035/3.011 (3H, s, 2-CH_3), 2.80/2.78, 2.77, 2.53, 2.45 (each 3H, 4,4′-CH_3 of dmb-I and II), 2.73−2.63, 2.60−2.53, 2.33−2.21 (1H+1H+2H, m, 17-CH_2CH_2), 1.78/1.75 (3H, d, J = 7 Hz, 18-CH_3), 1.71 (3H, t, J = 7 Hz, 8^1-CH_3), −0.05, −2.14 (each 1H, s, NH × 2). ^{19}F NMR ($CDCl_3$) δ: −74.4 (6F, d, J = 713 Hz, PF_6), −75.3 (s, 3^3-CF_3). HRMS (ESI) m/z: $[M - PF_6]^+$ calcd for $C_{60}H_{58}F_3N_8O_5Ru$, 1129.3521; found, 1129.3520.

Synthesis of $[Ru(bpy)_2(2-H)]PF_6$ (5). Similar to the synthesis of **3**, metalation of **2** (22.5 mg, 0.034 mmol) with $Ru(bpy)_2Cl_2$ (29.9 mg, 0.062 mmol) gave ruthenium complex **5** (34.2 mg, 0.027 mmol, 79%) after FCC (CH_2Cl_2/CH_3OH = 98.5:1.5): VIS (CH_2Cl_2) λ_{max} 687 (relative intensity, 68%), 626 (11), 549 (23), 516 (32), 422 (89), 382 nm (100). ^{1}H NMR ($CDCl_3$) δ (1/1): 9.598/9.596 (1H, s, 10-H), 9.49/9.48 (1H, s, 5-H), 9.23/9.21 (1H, d, J = 5 Hz, 6-H of bpy-I), 9.00 (1H, d, J = 5 Hz, 6-H of bpy-II), 8.66/8.63 (1H, d, J = 8 Hz, 3-H of bpy-II), 8.63/8.62 (1H, s, 20-H), 8.51 (1H, d, J = 8 Hz, 3-H of bpy-I), 8.45/8.43 (1H, d, J = 8 Hz, 3′-H of bpy-I), 8.33 (1H, d, J = 8 Hz, 3′-H of bpy-II), 8.28/8.25 (1H, t, J = 8 Hz, 4-H of bpy-II), 8.21, (1H, t, J = 8 Hz, 4-H of bpy-I), 8.03/8.01 (1H, d, J = 6 Hz, 6′-H of bpy-I), 7.95/7.94 (1H, d, J = 5 Hz, 6′-H of bpy-II), 7.83−7.81 (2H, m, 4′-H of bpy-I and II), 7.79 (1H, dd, J = 5, 8 Hz, 5-H of bpy-II), 7.69/7.68 (1H, dd, J = 5, 8 Hz, 5-H of bpy-I), 7.27 (1H, m, 5′-H of bpy-II), 7.19 (1H, m, 5′-H of bpy-I), 7.02/7.01 (1H, s, 3^1-CH), 5.28, 5.13 (each 1H, J = 19 Hz, 13^1-CH_2), 4.50 (1H, dq, J = 1, 7 Hz, 18-H), 4.33 (1H, br, 17-H), 3.72 (2H, t, J = 8 Hz, 8-CH_2), 3.70 (3H, s, 12-CH_3), 3.59/3.58 (3H, s, 17^2-$COOCH_3$), 3.06 (3H, s, 7-CH_3), 3.00/2.97 (3H, s, 2-CH_3), 2.73−2.68, 2.58−2.51, 2.32−2.24 (1H+1H+2H, m, 17-CH_2CH_2), 1.78/1.76 (3H, d, J = 7 Hz, 18-CH_3), 1.72 (3H, t, J = 8 Hz, 8^1-CH_3), −0.09, −2.13 (each 1H, s, NH × 2). ^{19}F NMR ($CDCl_3$) δ (1/1): −74.4 (6F, d, J = 715 Hz, PF_6), −83.7/−84.1 (3F, br, 3^4-CF_3), −125.4 (2F, br, 3^3-CF_2). HRMS (ESI) m/z: $[M - PF_6]^+$ calcd for $C_{57}H_{50}F_5N_8O_5Ru$, 1123.2862; found, 1123.2800.

Synthesis of Zinc Methyl 3-devinyl-3-(4,4,4-trifluoro-1,3-dioxo-butan-1-yl)-pyropheophorbide-*a* enol (1-Zn). Enol compound **1** (6.0 mg, 0.0091 mmol) was dissolved in CH_2Cl_2 (50 mL), to which MeOH saturated with $Zn(OAc)_2\cdot 2H_2O$ was then added. The solution was stirred at room temperature for 2.5 h under nitrogen in the dark. The reaction mixture was washed with water, aq 4% $NaHCO_3$ and water, dried over Na_2SO_4, and filtered. The solvent was evaporated in vacuo, and the resulting residue was recrystallized from CH_2Cl_2 and hexane to give **1-Zn** (6.2 mg, 0.0085 mmol, 94%): VIS (THF) λ_{max} 685 (relative intensity, 80%), 433 (96), 388 (100), 319 nm (55). ^{1}H NMR ($CDCl_3$−1% pyridine-d_5) δ: 9.75 (1H, s, 5-H), 9.40 (1H, s, 10-H), 8.40 (1H, s, 20-H), 6.85 (1H, s, 3^1-CH), 5.20, 5.09

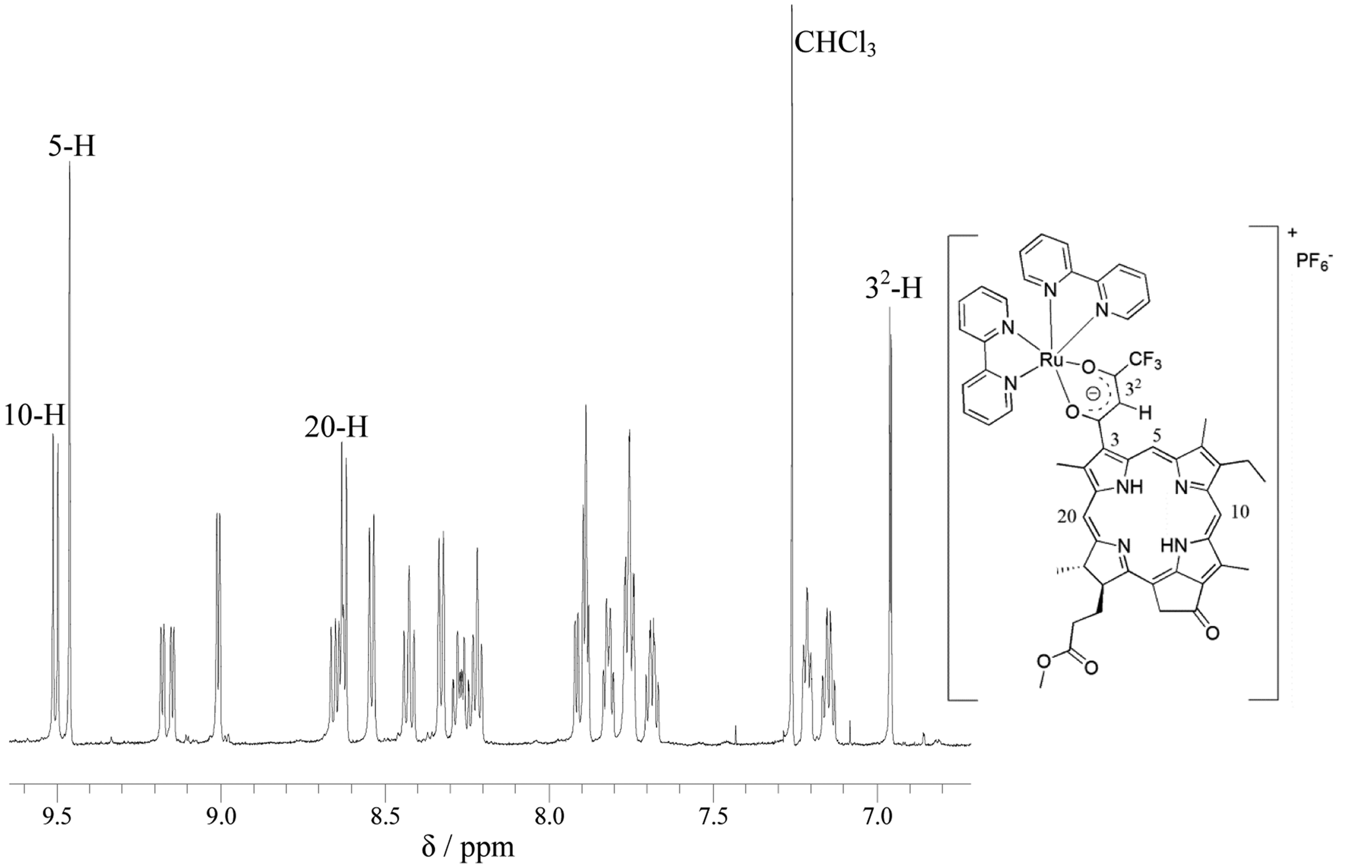


Figure 3. Partial ^{1}H NMR spectrum of **3** in $CDCl_3$ in >6.5 ppm.

(each 1H, d, J = 19 Hz, 13^1-CH_2), 4.38 (1H, dq, J = 2, 8 Hz, 18-H), 4.21 (1H, dt, J = 8, 2 Hz, 17-H), 3.68 (3H, s, 12-CH_3), 3.56 (3H, s, 17^2-$COOCH_3$), 3.43 (3H, s, 2-CH_3), 3.36 (2H, q, J = 8 Hz, 8-CH_2), 2.84 (3H, s, 7-CH_3), 2.60−2.52, 2.40−2.33, 2.28−2.20, 2.00−1.99 (each 1H, m, 17-CH_2CH_2), 1.68 (3H, d, J = 8 Hz, 18-CH_3), 1.49 (3H, t, J = 8 Hz, 8^1-CH_3) [the peak of OH could not be observed]. ^{19}F NMR ($CDCl_3$) δ: −78.3 (3F, s, 3^3-CF_3). HRMS (ESI) m/z: M$^+$ calcd for $C_{36}H_{33}F_3N_4O_5Zn$, 722.1695; found, 722.1694.

Synthesis of [Ru(bpy)$_2$(1-Zn−H)]PF$_6$ (3-Zn). Similar to the synthesis of **1-Zn**, zinc metalation of [Ru(bpy)$_2$(**1**−H)]PF$_6$ (**3**, 6.0 mg, 0.0049 mmol) gave the ruthenium−zinc binuclear complex **3-Zn** (6.2 mg, 0.0048 mmol, 99%): VIS (CH_2Cl_2) λ_{max} 678 (relative intensity, 89%), 627 (18), 567 (17), 428 (100), 386 nm (87). ^{1}H NMR ($CDCl_3$−1% pyridine-d_5) δ (1/1): 9.599/9.596 (1H, s, 10-H), 9.319/9.315 (1H, s, 5-H), 9.20/9.16 (1H, d, J = 5 Hz, 6-H of bpy-I), 8.98 (1H, d, J = 6 Hz, 6-H of bpy-II), 8.66/8.63 (1H, d, J = 8 Hz, 3-H of bpy-II), 8.48/8.47 (1H, d, J = 8 Hz, 3-H of bpy-I), 8.41/8.40 (1H, d, J = 8 Hz, 3′-H of bpy-I), 8.39/8.38 (1H, s, 20-H), 8.29 (1H, d, J = 8 Hz, 3′-H of bpy-II), 8.22/8.20 (1H, t, J = 8 Hz, 4-H of bpy-II), 8.16 (1H, t, J = 8 Hz, 4-H of bpy-I), 7.93/7.90 (1H, d, J = 6 Hz, 6′-H of bpy-I), 7.85/7.84 (1H, d, J = 6 Hz, 6′-H of bpy-II), 7.83−7.73 (3H, m, 5-H of bpy-II and 4′-H of bpy-I and II), 7.65−7.61 (1H, m, 5-H of bpy-I), 7.21 (1H, m, 5′-H of bpy-II), 7.18−7.13 (1H, m, 5′-H of bpy-I), 6.92/6.91 (1H, s, 3^1-CH), 5.16, 5.04, (each 1H, J = 19 Hz, 13^1-CH_2), 4.39/4.38 (1H, m, 18-H), 4.19/4.18 (1H, m, 17-H), 3.74 (2H, q, J = 7 Hz, 8-CH_2), 3.677/3.6675 (3H, s, 12-CH_3), 3.531/3.528 (3H, s, 17^2-$COOCH_3$), 3.016/3.014 (3H, s, 7-CH_3), 2.98/2.95 (3H, s, 2-CH_3), 2.55−2.49, 2.38−2.31, 2.24−2.17 (1H+1H+2H, m, 17-CH_2CH_2), 1.70/1.68 (3H, t, J = 7 Hz, 8^1-CH_3), 1.66/1.64 (3H, d, J = 7 Hz, 18-CH_3). ^{19}F NMR ($CDCl_3$) δ (1/1): −74.4 (6F, d, J = 711 Hz, PF_6), −75.14/−75.15 (3F, s, 3^3-CF_3). HRMS (ESI) m/z: [M − PF_6]$^+$ calcd for $C_{56}H_{48}F_3N_8O_5RuZn$, 1135.2029; found, 1135.2029.

Synthesis of [Ru(dmb)$_2$(CF$_3$COCHCOC$_6$H$_5$)]PF$_6$ (8). Similar to the synthesis of **3**, metalation of $CF_3COCH_2COC_6H_5$ (16.3 mg, 0.075 mmol) with Ru(dmb)$_2$Cl$_2$ (30.4 mg, 0.056 mmol) gave **8** (16.3 mg, 0.020 mmol, 35%): VIS (CH_2Cl_2) λ_{max} 491 (relative intensity, 100%), 425 (61), 365 nm (66). ^{1}H NMR ($CDCl_3$) δ: 8.49 (1H, d, J = 5 Hz, 6-H of dmb-I), 8.40 (1H, d, J = 5 Hz, 6-H of dmb-II), 8.25 (1H, s, 3-H of dmb-I), 8.20 (1H, s, 3-H of dmb-II), 8.13 (1H, s, 3′-H of dmb-I), 8.05 (1H, s, 3′-H of dmb-II), 7.58 (3H, m, 2-, 6-H of Ph, 6′-H of dmb-I), 7.51 (1H, d, J = 6 Hz, 6′-H of dmb-II), 7.46 (1H, t, J = 8 Hz, 4-H of Ph), 7.36 (1H, d, J = 5 Hz, 5-H of dmb-I), 7.31 (3H, m, 3-, 5-H of Ph, 5-H of dmb-II), 6.98 (1H, d, J = 6 Hz, 5′-H of dmb-I), 6.92 (1H, d, J = 6 Hz, 5′-H of dmb-II), 6.40 (1H, s, COCH), 2.68 (3H, s, 4-CH_3 of dmb-I), 2.66 (3H, s, 4-CH_3 of dmb-II), 2.49 (3H, s, 4′-CH_3 of dmb-I), 2.45 (3H, s, 4′-CH_3 of dmb-II). ^{19}F NMR ($CDCl_3$) δ: −74.1 (6F, d, J = 713 Hz, PF_6), −75.4 (3F, s, CF_3). HRMS (ESI) m/z: [M − PF_6]$^+$ calcd for $C_{34}H_{30}F_3N_4O_2Ru$, 685.1359; found, 685.1359.

■ RESULTS AND DISCUSSION

Synthesis of Chlorophyll Derivatives Coordinating Ruthenium Bisbipyridine Complex. Preparation of Chl derivatives **1** and **2** was preliminarily reported,[39] and their synthesis was described briefly. Methyl pyropheophorbide-*a* was prepared by modifying Chl-*a*,[40] and the 3-vinyl group was hydrated and oxidized to the 3-acetyl group in **6** (Scheme 1).[45] Claisen condensation of 3-acetyl-chlorin **6** with ethyl perfluorocarboxylates gave Chl derivatives **1** and **2** possessing a β-diketonate moiety at the C3 position.

C3-trifluoroacetylacetonated chlorin **1** and Ru(bpy)$_2$Cl$_2$[41] were dissolved in ethanol and dichloromethane, and the solution was refluxed overnight under nitrogen in the dark. The reaction mixture was cooled to room temperature and added to methanol saturated with ammonium hexafluorophosphate (NH_4PF_6) to give ruthenium(II) complex **3**, containing the anionic species of **1**, two bpy molecules, and PF_6^- in 36% yield.

The resulting chlorin–Ru conjugate **3** was so stable that it could be purified by FCC on silica gel and characterized by its $^1H/^{19}F$ NMR and HRMS spectra.

The ^1H NMR spectra of **3** in $CDCl_3$ (1D, 2D $^1H-^1H$ COSY, and NOESY) showed 20 protons in a low magnetic field (> 6.5 ppm), which were assigned to three meso (5, 10, 20-H) and one diketonated proton (3^2-H) derived from the chlorin part and 16 aromatic protons of two bpy ligands (Figure 3). The detailed assignment of bis(2,2′-bipyridine) moiety was mentioned in the Experimental Section. ^1H NMR spectra of **3** in $CDCl_3$ at 20 °C showed that each proton signal at the C10 and C20 positions was split into two 1:1 signals (see Figure 3); the proton signal at C5 was not split by accidentally overlapping. When they were heated, their split signals coalesced to become relatively broad singlet signals in $CDCl_2CDCl_2$ at 120 °C (see Figure S1). The changes indicate that each split signal peaking at the C10 and C20 positions at room temperature should be ascribable to the two rotational isomers (about 1:1) around the C3–C3^1 bond; the more sterically crowded C3 substituent relative to the diketonate group is discussed later. A similar interconversion was reported in a Chl derivative possessing a bulky group at the C3 position.[46] On the other hand, the proton signal at the C3^2 position was split into two 1:1 singlet peaks even at 120 °C (Figure S1). This result shows that the split of the C3^2–H was due to the two 1:1 Δ/Λ-isomers of the ruthenium complex which were not isomerized thermally; the diastereomeric isomers could not be separated by conventional HPLC. Thus, **3** was a mixture of rotamers and stereoisomers, which could not be separated by FCC. ESI-HRMS of **3** was measured at a positive mode to show the parent peak as the cationic species of **3** lacking PF_6^- at m/z = 1073.284, and the observed isotopic pattern was in good agreement with the calculated distribution (Figure 4).

Instead of bpy, C4,4′-dimethylated bpy (dmb)[41,42] was used as the ligand of the Ru center. Similar to the preparation of **3**, the reaction of **1** with $Ru(dmb)_2Cl_2$ afforded **4** in 42% yield after purification by FCC. Its structure was confirmed by its $^1H/^{19}F$ NMR and MS spectra. In the ^1H NMR spectra of **4**, two sets of the proton signal of the dimethyl group at C4 and C4′ positions in bipyridine were observed around 3 ppm (Figure S2). Similar to the ESI-HRMS of **3**, that of **4** showed the parent peak as the cationic species of **4** lacking PF_6^- at m/z = 1129.3521. Moreover, complexation of chlorin **2** possessing a pentafluorinated β-diketonate group at the C3 position with $Ru(bpy)_2Cl_2$ gave **5** in 79% yield after FCC purification and characterized by ^1H NMR (Figure S3) and ESI-MS. The HRMS peak of **5** at m/z = 1123.2800 corresponded to the cationic species of **5** lacking PF_6^-.

Zinc metalation of **3** by a standard procedure[17,18] quantitatively afforded binuclear complex **3-Zn** after recrystallization. In the ^1H NMR spectrum of **3-Zn** in $CDCl_3$ and 1% pyridine, two NH signals disappeared in a high field region (<0 ppm, Figure S3), indicating that a zinc ion was introduced at the central position of the chlorin ring. The ESI-HRMS peak of **3-Zn** at m/z = 1135.2029 supports the cationic species of **3-Zn** lacking PF_6^-. As reference complexes of **3(-Zn)** and **4**, Ru complexes **7** and **8** possessing a phenyl group instead of a chlorin moiety were prepared by reaction of trifluoroacetylacetonated benzene with $Ru(bpy)Cl_2$ and $Ru(dmb)_2Cl_2$, respectively (Scheme 2).[43,44] Zinc complex **1-Zn** was synthesized as the additional reference of **3-Zn**.

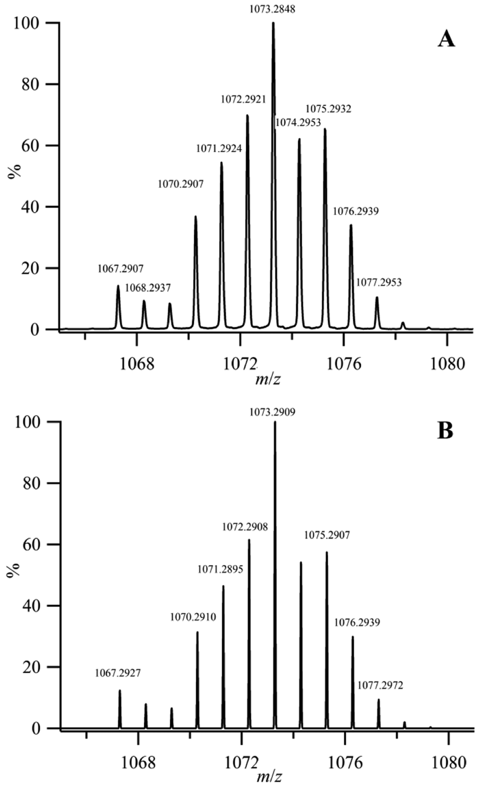
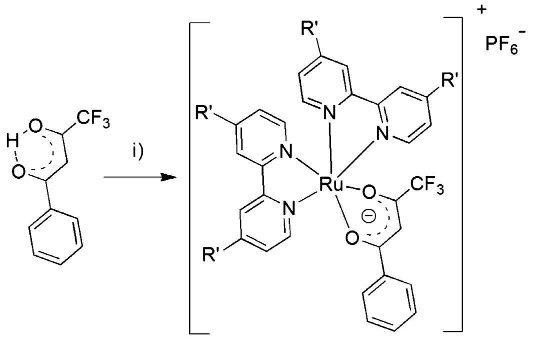


Figure 4. (A) Observed ESI-HRMS peaks of **3** and (B) calculated peaks of **3** lacking PF_6^- .

Scheme 2. Synthesis of Reference Ru(II) Complexes 7 and 8[a]



7: R′ = H, **8**: R′ = CH_3

[a]Conditions: (i) $Ru(bpy)Cl_2$ or $Ru(dmb)_2Cl_2/C_2H_5OH$, NH_4PF_6/CH_3OH.

Optical Properties of Chlorophyll Derivatives Coordinating Ruthenium Bisbipyridine Complex. Figure 5A shows UV–vis absorption spectra of **1**, **3**, **6**, and **7** in CH_2Cl_2. The Qx/Qy maxima of C3-trifluoroacetylacetonated chlorin **1** were located at 554/692 nm and were red-shifted compared with those of 3-acetyl-chlorin **6** due to the extension of π-conjugation at the C3-substitution (see also Table 1).[39] When the β-diketonate group of **1** coordinated to $Ru(bpy)_2^{2+}$, its Qx/Qy maxima were hypsochromically shifted to 551/687 nm in **3**. The blue shifts can be explained by the following steric effect. The crystal structure of **1** showed that the diketonate group at the C3 position was twisted at an angle of 25.8° from the plane of the chlorin π ring due to the steric repulsion from the two neighbors, the 2-methyl group and 5-hydrogen atom. Complex-

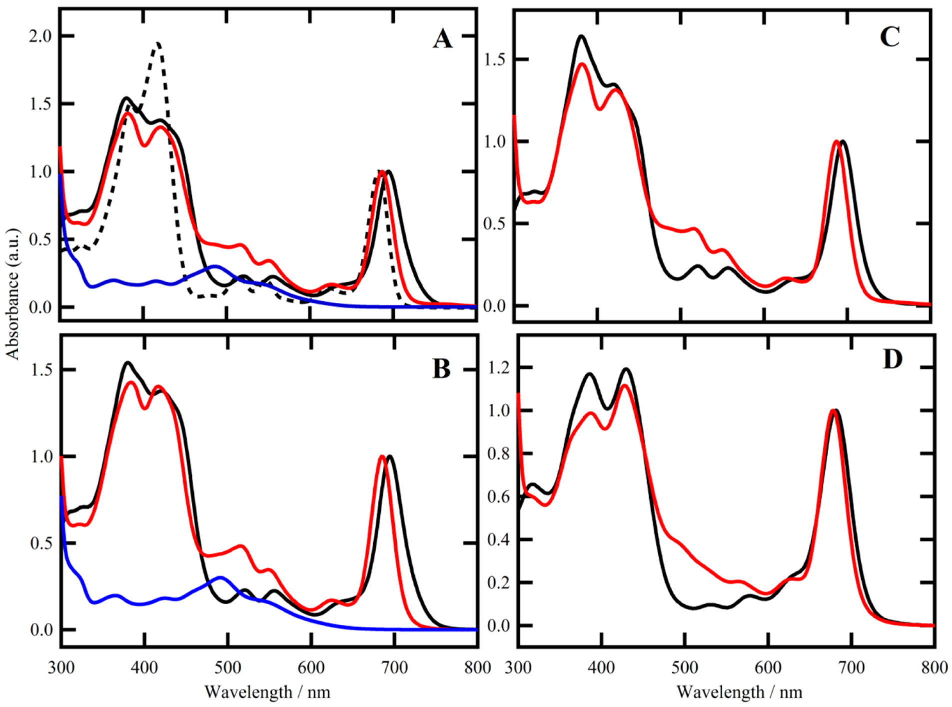


Figure 5. UV−vis absorption spectra of (A) **1** (black solid line), **3** (red), **6** (black broken), and **7** (blue); (B) **1** (black), **4** (red), and **8** (blue); (C) **2** (black) and **5** (red); and (D) **1-Zn** (black) and **3-Zn** (red). The spectra of chlorophyll derivatives were normalized at Qy maxima.

Table 1. Electronic Absorption Data of 1−6 and 1/3-Zn in CH_2Cl_2

	absorption maximum (nm)					
		Qx		Qy		
compound	Soret	(0,1)	(0,0)	(0,1)	(0,0)	dihedral angle[a]/°
1	382, 421	520	554	632	692	34
2	381, 418	520	557	633	695	34
3	382, 421	516	551	627	687	37
4	384, 416	516	548	624	685	39
5	382, 422	516	549	626	687	37
6	385, 417	514	547	622	683	
1-Zn	386, 430	532	579	–[b]	682	32
3-Zn	387, 428	–[b]	564	629	678	36

[a] The dihedral angles of C4−C3−C3^1−C3^2 were estimated by molecular models using MM+/PM3 calculations.[47] [b] Not apparently observed.

ation of a $Ru(bpy)_2^{2+}$ moiety with the diketonate group made the C3 substituent more bulky. The larger steric hindrance around the C3 position increased the dihedral angle of C4−C3−C3^1−C3^2 (27.2°, observed in crystallographic analysis) and 34° (estimated by molecular modeling)[47] in **1** to 37° (estimated) in **3**. The enhancement in the twist between the two moieties in **3** led to their lower conjugation to give blue shifts of Q absorption maxima.[†] Based on the UV−vis spectrum of reference compound **7** (blue line in Figure 5A), the absorbance at around 500 nm in **3** was primarily due to a MLCT absorption band. In a Soret region, **6** apparently gave two bands at 385 (minor) and 417 nm (major). More split and broadened Soret bands were visible in **1**. Ru-complexation of **1** to **3** afforded similar Soret maxima at 382 and 421 nm, which were comparably intense.

The Qx/Qy absorption maxima of compound **4** coordinating $Ru(dmb)_2^{2+}$ at the C3 diketonate moiety were shifted to longer wavelengths than those of ligand **1**. The blue shifts were ascribed to the twist of the diketonate group from the chlorin π-system by its coordination to the bulky ruthenium moiety; the estimated dihedral angle increased from 34 to 39°. In addition, the Qy maxima of **4** showed a slightly hypsochromical shift compared with those of compound **3** possessing a $Ru(bpy)_2^{2+}$ moiety (Figure 5B). The substitution of 4,4′-H in bpy with CH_3 in dmb would enhance the dihedral angle and slightly reduce the π-conjugation of the chlorin with the C3 substituent.[†] Considering that the methylation hardly increased the steric repulsion around the C3 position, the plane of the diketonate group would have been twisted from the chlorin ring by an electronic effect. This interpretation was supported by the molecular modeling which showed that the dihedral angle (39°) of C4−C3−C3^1−C3^2 in **4** was slightly larger than that in **3** (37°).

The Qx/Qy absorption bands of compound **5** coordinating the ruthenium complex at the diketonate group possessing a C_2F_5 group were hypsochromically shifted from those of ligand **2** (Figure 5C). The plane of the diketonate group in **5** was twisted from the chlorin ring slightly more than that in **2** (34° → 37°), similarly as in **1** → **3**. The absorption spectra of **3** and **5** were almost identical, and no remote substitution effect of CF_3 to C_2F_5 was observed in chlorin-specific absorption bands. This consistency was supported by the same estimated dihedral angles of **3** and **5** (37°). On the other hand, the terminal substitution of CF_3 with C_2F_3 at the diketonate group in chlorin ligand molecules moved the Qy band to a longer wavelength: 692 (**1**) → 695 nm (**2**). Because the estimated dihedral angles of **1** and **2** were the same (34°), a remote and electronic substitution effect on the Qy bands operated in ligands **1** and **2**.

Zinc metalation at the central position of **1** and **3** would shift the Qx/Qy maxima to a longer/shorter wavelength, respectively (Table 1), which was consistent with the observation reported previously.[17,18] The Qx/Qy bands of ruthenium−zinc

Table 2. Redox $E_{1/2}$ and Peak Potentials E_p (in mV) of **1**–**5**, **7**, **8**, and **3-Zn**[a]

	$E_{1/2}^{ox}$ (ΔE_p)			$E_{1/2}^{red}$ (ΔE_p)		
	Chl			Chl		
compound	first	second	Ru(II)/(III)	first	second	Ru(I)/(II)
1	533 (E_{pa})	870 (E_{pa})		−1516 (63)	−1780 (91)	
2	538 (E_{pa})	843 (E_{pa})		−[b]		
3	~500 (E_{pa})	842 (E_{pa})	533 (104)	−1320 (56)	−1457 (60)	−1988 (65)
4	577 (E_{pa})	835 (E_{pa})	419 (83)	−1332 (62)	−1477 (63)	−2079 (82)
5	−[c]	915 (E_{pa})	476 (91)	−[b]		
7			441 (70)	−[b]		
8			348 (66)			−1983 (82)
3-Zn	246 (70)	−[c]	544 (125)	−1511 (52)	−1677 (117)	−1988 (84)

[a] Cyclic voltammograms were recorded in CH_3CN/0.1 M Bu_4NClO_4 with a scan rate of 10 mV/s at ≈1 mM sample solutions. The redox potential values are cited, based on the oxidation potential of ferrocene as a standard. E_{pa} and E_{pc} were the anodic and cathodic peak potentials, respectively. $\Delta E_{1/2} = (E_{pa} + E_{pc})/2$ and $\Delta E_p = E_{pa} - E_{pc}$. [b] Reversible peaks could not be apparently observed. [c] E_{pa} for a chlorin part could not be detected due to the overlap with the E_{pa} for Ru(II)/(III).

binuclear chlorin **3-Zn** were observed at a lower wavelength than those of **1-Zn**. The blue-shifted value of the Qy maxima (4 nm for **1-Zn** → **3-Zn**) was nearly identical to that by the coordination of **1** with $Ru(bpy)_2^{2+}$ to **3** (5 nm). This result was supported by the molecular modeling which showed that the dihedral angle in **3-Zn** (36°) increased from that of **1-Zn** (32°). Therefore, the diketonate group directly conjugated to the chlorin ring was twisted by the ruthenium complexation, and the Qy bands were hypsochromically shifted.

The fluorescence emission quantum yields of Chl derivatives **3**, **4**, **5**, and **3-Zn** coordinating the ruthenium complex at the diketonate group were less than 1% and much smaller than those of chlorin ligands; these values were ~20% for **1**, **2**, and **6** and ~10% for **1-Zn**. The quenching was ascribed to the heavy atom effect of the ruthenium center partially conjugated with the fluorescent chlorin π-system through the diketonate group.

Electrochemical Properties of Chlorophyll Derivatives Coordinating Ruthenium Bisbipyridine Complex. The cyclic voltammograms of **1**–**5**, **7**, **8**, and **3-Zn** were measured in acetonitrile containing 0.1 M tetrabutylammonim perchlorate (TBAP) as a supporting electrolyte[50] (see Figures S4–S10), and the data relative to ferrocene/ferrocenium are summarized in Table 2. During sweeping of the applied potential from 0 to 1.2 V, two oxidation (anodic) peaks of **1** were observed, but the reverse sweep resulted in no apparent reduction (cathodic) peaks (Figure S4A). The electrochemical oxidation of **1** was irreversible, which was consistent with previous reports for Chl derivatives.[51] When sweeping the potential from 0 to −2.4 V, two anodic peaks were observed, and the reverse sweep afforded two cathodic peaks. Thus, compound **1** gave two reversible and sequential one-electron reductions at $E_{1/2}^{red}$ = −1.52 (ΔE_p = 0.06 V) and = −1.78 V (0.09 V) (see Figure S4B).

In the positively applied-potential side of the cyclic voltammogram of chlorin–ruthenium conjugate **3**, two irreversible oxidations of chlorin and one reversible oxidation of Ru(II) to Ru(III) were observed (Figure S6A). The oxidation potential $E_{1/2}^{ox}$ of Ru(II)/(III) was 0.53 V, which was larger than the first anodic peak potential E_{pa} of the chlorin moiety and smaller than the second E_{pa}. In the negatively applied potential, three reversible reductions were observed, which included the two sequential one-electron reductions of chlorin in **3**, followed by Ru(II)/(I). The two $E_{1/2}^{red}$ of chlorin were positively shifted by about 0.2–0.3 V from the values in **1**. The coordination with $Ru(bpy)_2^{2+}$ at the peripheral position of chlorin **1** easily reduced the electrochemical chlorin part in **3**, mainly due to the presence of the cation (Ru^{2+}) near the chlorin π-system.

Comparing the voltammograms of **3** and **4**, no change was apparently observed in the redox properties of the chlorin moieties, but redox potentials of Ru(II)/(III) and Ru(II)/(I) were shifted to about 0.1 V on the negative side. Especially, reversible oxidation of Ru(II)/(III) first occurred in **4**, and then sequential oxidation of the chlorin moiety took place. The substitution of 4,4′-H with electron-donating CH_3 groups in bpy affected predominantly one-electron oxidation and reduction of the Ru center but minimally the redox in the chlorin part. This minimal electrochemical shift was consistent with the lack of change in electron absorption bands of chlorin chromophores in **3** and **4** (vide supra). The $E_{1/2}^{ox}$ for Ru(II)/(III) of **8** was shifted by 0.1 V to the negative side from that of **7**. This shift was almost the same as that from **3** to **4**. Moreover, the observed shift value (0.1 V) was consistent with that reported (~0.1 V) for the electrochemical oxidation of Ru(II) to Ru(III) in the complexes possessing $(bpy)_2$ or $(dmb)_2$.[52]

The oxidation potential of Ru(II)/(III) in **5** was negatively shifted by about 0.05 V from that in **2**. Substitution of CF_3 with a less-electron-withdrawing C_2F_5 group[53] on the diketonate ligand decreased $E_{1/2}^{ox}$ of Ru(II)/(III). The substitution effect is in good agreement with that in the aforementioned dimethylation. Introduction of electron-donating and electron-withdrawing groups to the ligands on Ru complexes decreased and increased, respectively, the redox potentials of the Ru center, Ru(II)/(III), and Ru(II)/(I).

After zinc metalation at the central position of a chlorin, the moiety is easily oxidized and difficult to reduce in comparison with the corresponding free base.[54] The cyclic voltammogram of ruthenium–zinc binuclear chlorin **3-Zn** showed several reversible redox potentials (Figure S9). The redox potentials of the chlorin moiety were shifted to negative sides (~0.2 V) by zinc metalation of the chlorin ring (**3** → **3-Zn**), but almost no shifts of the redox potentials of Ru(II)/(III) and (II)/(I) were observed. The above results indicate that the chlorin moiety did not electrochemically interact with the ruthenium center in a complex.

■ CONCLUSION

A ruthenium bisbipyridine complex was successfully coordinated with the diketonate group at the peripheral C3 position of Chl derivatives **1** and **2**, and the chlorin–ruthenium conjugates **3** and **5** were isolated after purification. The dimethyl substituent at the bpy of **3** as in **4** and the zinc complex of the central position of the chlorin ring of **3** as in **3-Zn** were obtained as chemically stable compounds. The synthetic chlorin−ruthenium conjugates had the electronic absorption bands characteristic of chlorin and ruthenium moieties. The apparent interaction between the two moieties in a complex was not observed in a solution. The fluorescence emission derived from the chlorin moiety was largely quenched by its coordination to the ruthenium moiety due to its internal heavy atom effect in the close situation. The redox properties of chlorin−ruthenium conjugates were affected largely by the substituents close to redox centers but minimally by those far from them. For example, the oxidation of Ru(II)/(III) in $Ru(bpy)_2^{2+}$ of **3** occurred at slightly more positive potential than that of the chlorin moiety, while that of Ru(II)/(III) in $Ru(dmb)_2^{2+}$ occurred before that of the chlorin moiety. In the zinc chlorin−ruthenium conjugate **3-Zn**, the chlorin moiety was obviously oxidized first, followed by the ruthenium center.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^1H NMR spectra and cyclic voltammograms have been provided. This material is available free of charge via the Internet at http://pubs.acs.org/.

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Notes

The authors declare no competing financial interest.

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■ ADDITIONAL NOTE

[†]Similar steric effects in the other C3-substituted Chl derivatives were available in previous reports.[48,49] Inductive effect of the C3 substituent could not be ruled out.

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