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Cooperative C3- and C13-Substituent Effects on Synthetic Chlorophyll Derivatives

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C3-vinyl and C13-keto-carbonyl groups of methyl pyropheophorbide-*a*, a chlorophyll-*a* derivative, were systematically modified to investigate the substituent effects along the y-axis of chlorin macrocycles. $C13^1$ deoxygenation resulted in blueshifts of the Q_y absorption maxima and a large reduction of their redox potentials, whereas introduction of the dicyanomethylene group at the 13^1-position caused the opposite effect on both optical and electrochemical properties. Among the nine chlorins examined, the Q_y peak positions could be varied from 647 to 736 nm by the cooperative effects of the diagonal substituents' combinations.

Introduction

Chlorophyll(Chl)-*a* (Figure 1, a) possessing the C3-vinyl group is a representative dye molecule in natural photosynthesis, and its C3-formyl analogue, Chl-*d*, is observed in some cyanobacteria.[1] This difference between the C3-vinyl and formyl groups causes a shift of the Q_y peak positions: 661 (Chl-*a*) and 686 nm (Chl-*d*) in ethyl ether.[2] On the other hand, bacteriochlorophyll-*d* has the C3-(1-hydroxyethyl) group on its chlorin macrocycle to give a blueshifted Q_y maximum at 650 nm as its monomeric form in ethyl ether.[3] To clarify such C3-substituent effects on optical properties, we reported a series of Chl derivatives possessing different C3-substituents.[4,5]

Since alteration of the C3-functional group brings visual color changes in solution and drastic Q_y peak shifts, introduction of a molecular recognition site at the 3-position successfully led to the development of chlorophyll-based chemosensors (Figure 1, b).[6] One of the advantages in using the chlorin unit for the design of chromo/fluororeceptors is its intense Q_y band, which is located at the longer-wavelength region. Because this characteristic band is dependent on the transition moment along the *y*-axis, transformation of the C13-functional group would also be useful for tuning the optical properties of the red-most bands. Thus spectral characteristics of C3-functionalized chlorins are expected to be effectively controlled by the simultaneous substituent effects at the diagonal 13-position.

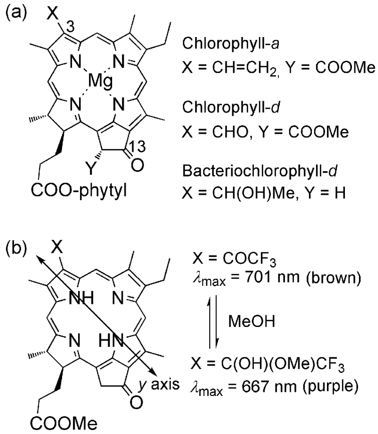

Figure 1. Chemical structures of (a) some natural (bacterio)chlorophylls and (b) an example of a chlorophyll-based chemosensor.

In this study we synthesized C3-substituted chlorins possessing a dicyanomethylene group at the 13^1-position or lacking any C13-functional group and compared their physical properties with those of the corresponding $C13^1$-oxochlorins. The cooperative effects of C3/C13-functional groups were elucidated based on absorption and emission spectroscopy together with cyclic voltammetry.

Results and Discussion

Synthesis of Chlorophyll Derivatives 1–9

Chl-*a* was extracted from *Spirulina geitleri* and converted to methyl pyropheophorbide-*a* (**1**)[7] and its $C13^1$-deoxo analogue **4**[8] according to the literature procedure. Oxidative cleavage of the C3-vinyl to formyl group (**1** → **2**,[7] **4** → **5**[9]; Scheme 1) and the successive Knoevenagel reaction of the 3-formylchlorins with malononitrile (**2** → **3**, **5** → **6**) were

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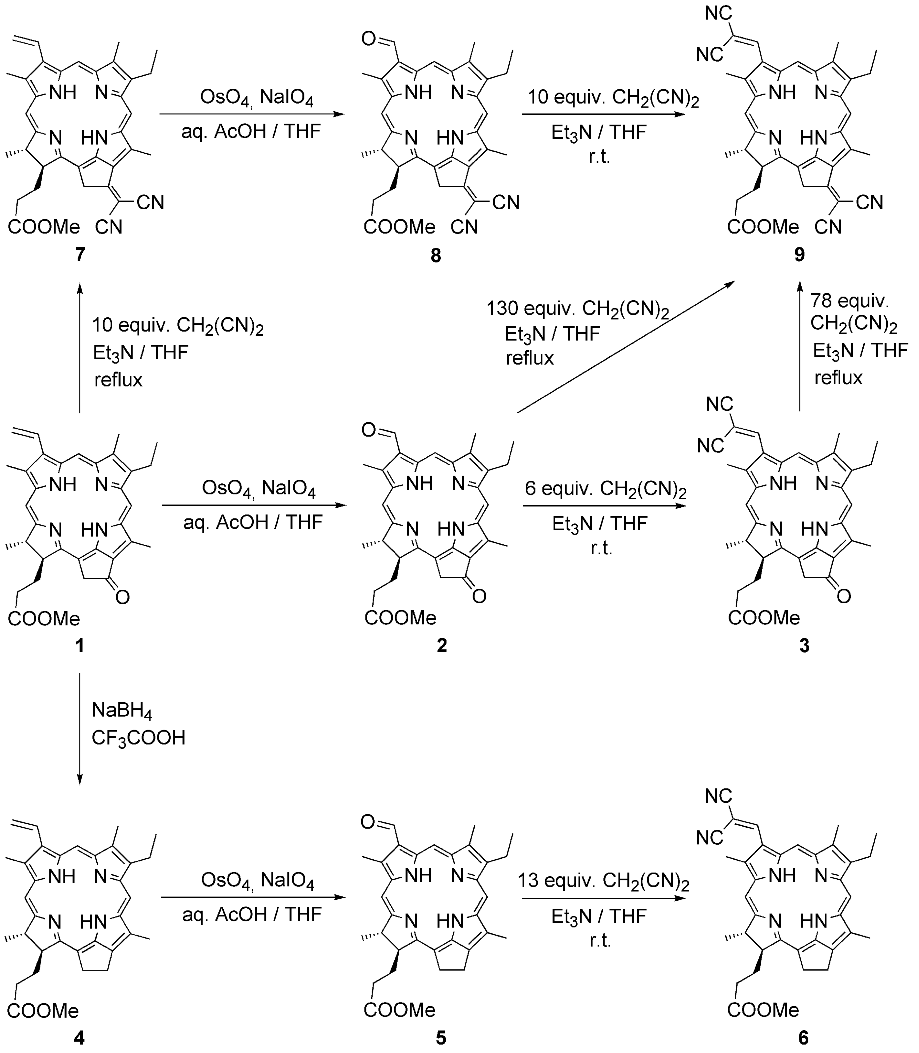


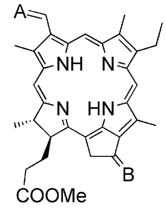
Scheme 1. Synthesis of chlorophyll derivatives **1**–**9**.

carried out by using previously reported procedures.[4] On the other hand, the Knoevenagel reaction was found to be applicable for the introduction of a dicyanomethylene group at the 13^1-position. When the C13-keto-carbonyl group on **1** was treated with excess malononitrile in the presence of triethylamine in refluxing THF, the corresponding C13^1-dicyanomethylene-chlorin **7** was obtained in 67% yield. The following oxidative cleavage of the C3-vinyl group of **7** and subsequent Knoevenagel reaction proceeded smoothly to afford **8** (70%) and **9** (41%) with less interference of the C13^1-dicyanomethylene group. Alternatively, one-pot reaction of the 3- and 13-positions of **2** with malononitrile afforded **9** via **3**, as its counterpart **8** was not isolated even under mild conditions: its stepwise synthesis from **2** slightly improved the yield of **9** (**2** → **9**: 7%, **2** → **3** → **9**: 88 × 12% = 11%).

Optical Properties of Synthetic Chlorins 1–9

The electronic absorption and emission spectra of 3-vinyl-, 3-formyl-, and 3-(dicyanoethenyl)chlorins are shown in Figure 2, and their absorption maxima and fluorescence data are summarized in Table 1. When the C13-carbonyl group of chlorin derivatives is reduced to the C13-deoxo moiety, the Q_y peak maxima were shifted to a lower wavelength with a decrease of the relative peak absorbances (A_{rel}). On the contrary, replacement of the C13-carbonyl with the dicyanoethenyl group caused redshifts of the Q_y peak. The observed Q_y peak positions are apparently related to the electron-withdrawing ability of the C13-functional group [B = H$_2$ → O → C(CN)$_2$ in Table 1], which is similar to the C3-substituent effects previously reported.[5] In view of the C13-substituent effect, the Q_y peak shift (940 cm^{-1}) accompanied by the conversion of the C3-vinyl to dicyanoethenyl through the formyl group of C13^1-deoxochlorins **4** → **6** (B=H$_2$, λ_{abs} = 647 → 689 nm) is larger than that of C13^1-oxo-chlorins **1** → **3** (B = O, λ_{abs} = 667 → 706 nm, 830 cm^{-1}), whereas 13^1-(dicyanomethylene)chlorins **7** → **9** showed the least effect [B = C(CN)$_2$, λ_{abs} = 704 → 736 nm, 620 cm^{-1}]. An electron-withdrawing group seems to decrease the substituent effects at the diagonal position. Similar cooperative effects were also observed from changes

Table 1. Visible absorption (λ_{abs}), fluorescence emission maxima (λ_{em}), and fluorescence quantum yields (Φ) of chlorophyll derivatives **1**–**9** in CH_2Cl_2.



Compound	A	B	Absorption, λ_{abs} (A_{rel}[a]) [nm] [fwhm[b] [cm^{-1}]		Fluorescence emission[c]		
			Q_x	Q_y	λ_{em} [nm]	Δ [cm^{-1}][d]	Φ [%]
1	CH_2	O	509, 539	609, 667 (0.44) [473]	672	110	22
2	O	O	521, 554	632, 694 (0.81) [435]	699	100	18
3	$C(CN)_2$	O	522, 568	643, 706 (0.55) [803]	725	370	17
4	CH_2	H_2	501	592, 647 (0.24) [407]	650	70	17
5	O	H_2	514, 551	610, 665 (0.34) [452]	667	50	14
6	$C(CN)_2$	H_2	580	636, 689 (0.34) [928]	715	530	10
7	CH_2	$C(CN)_2$	534, 574	643, 704 (1.10) [505]	712	160	25
8	O	$C(CN)_2$	543, 584	663, 727 (1.30) [492]	733	110	21
9	$C(CN)_2$	$C(CN)_2$	545, 590	669, 736 (0.97) [802]	749	250	20

[a] Relative peak absorbance (A_{rel}) was based on the most intense Soret peak. [b] Full width at half maximum. [c] Excited at Soret band. [d] Stokes shift (Δ/cm^{-1}) = [$1/\lambda_{abs}(Q_y(0,0)) - 1/\lambda_{em}$] × 10^7.

of the C3-position; the Q_y peak shifts of **4** to **7** (A = CH_2, λ_{abs} = 647 → 704 nm, 1250 cm^{-1}) and **5** to **8** (A = O, λ_{abs} = 665 → 727 nm, 1280 cm^{-1}) are larger than that of 3-(dicyanoethenyl)chlorins **6** to **9** [A = $C(CN)_2$, λ_{abs} = 689 → 736 nm, 930 cm^{-1}].

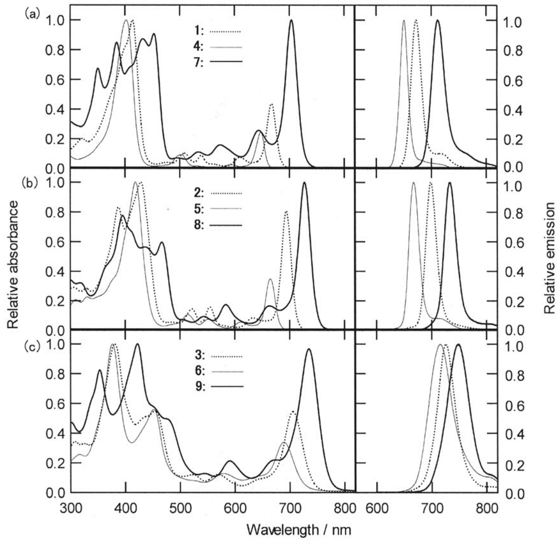


Figure 2. Electronic absorption (left) and fluorescence emission spectra (right) of (a) 3-vinylchlorins **1** (dotted line), **4** (solid thin line), and **7** (solid thick line), (b) 3-formylchlorins **2** (dotted line), **5** (solid thin line), and **8** (solid thick line), and (c) 3-(dicyanoethenyl)-chlorins **3** (dotted line), **6** (solid thin line), and **9** (solid thick line) in CH_2Cl_2. All spectra were normalized at their most intense maxima.

It should be noted that the dicyanomethylene group causes not only the redshifts of the Q_x/Q_y maxima but also characteristic peak broadening of the Soret band, regardless of the 3/13-positions of the group. This functional group seems to bring a large Stokes shift relative to other types of combinations of the substituents (A = CH_2, O; B=H_2, O). The fluorescence quantum yields were varied between 10 and 25%, and specific increase or quenching was not observed. Although the differences are not very large, electron-withdrawing groups at the 3-position decrease the Φ values, whereas the C13-functional groups appear to have the opposite effect.

Electrochemical Properties of Synthetic Chlorins 1–9

Redox potentials of chlorins **1**–**9** are summarized in Table 2.[10] Oxidation potentials ($E^{ox}_{1/2}$) of three-type C3-substituted chlorins [A = CH_2, O, or $C(CN)_2$] increased in the

Table 2. Redox potentials of chlorophyll derivatives **1**–**9**.[a]

	A[b]	B[b]	$E^{ox}_{1/2}$ [mV]	$E^{red}_{1/2}$ [mV]	ΔE [mV][c]	$10^7/\lambda_{abs}$ [cm^{-1}][d]
1	CH_2	O	390	–1590	1980	15000
2	O	O	480	–1400	1880	14400
3	$C(CN)_2$	O	500	–[e]	–	14200
4	CH_2	H_2	110	–1930	2040	15500
5	O	H_2	240	–1720	1960	15000
6	$C(CN)_2$	H_2	280	–[e]	–	14500
7	CH_2	$C(CN)_2$	450	–1370	1820	14200
8	O	$C(CN)_2$	540	–1260	1800	13800
9	$C(CN)_2$	$C(CN)_2$	580	–[e]	–	13600

[a] Cyclic voltammograms were recorded in CH_2Cl_2/0.1 M Bu_4NClO_4 with a scan rate of 10 mV/s at ca. 1 mM sample solutions. The redox potential values are reported based on the oxidation potential of ferrocene as a standard. [b] Refer to the structure in Table 1. [c] The difference between oxidation and reduction potentials: ΔE = $E^{ox}_{1/2} - E^{red}_{1/2}$. [d] The wavenumber of the Q_y(0,0) peak maxima. [e] Peaks were not clearly observed.

order of B = $CH_2 \rightarrow O \rightarrow C(CN)_2$ and reduction potentials ($E_{1/2}^{red}$) showed more positive values in this sequence. A similar tendency was observed in changes of A = $CH_2 \rightarrow O \rightarrow C(CN)_2$ for C13^1-substituted chlorins [B = O, H_2, or $C(CN)_2$]. Electron-withdrawing substituents at the 3/13-positions decrease the electron density on the chlorin macrocycle and make the release of one electron more difficult. As expected, an almost linear relationship (correlation coefficient $r^2 = 0.966$) can be seen when the potential differences of ΔE (= $E_{1/2}^{ox} - E_{1/2}^{red}$) are plotted versus the energy level of Q_y maxima ($10^7/\lambda_{abs}$) in wavenumber units (see Figure S5 in the Supporting Information).

Conclusions

We have demonstrated the transformation of methyl pyropheophorbide-*a* to 13^1-(dicyanomethylene)chlorin derivatives, which caused drastic spectral changes, especially in their Q_y bands. The modified dye molecules should be useful for the development of new chromo/fluororeceptors[6] and for application to dye-sensitized solar cells,[11] as the C3-formyl groups of **2**, **5**, and **8** could be further altered.[4–6,12]

Experimental Section

General Methods: Electronic absorption and fluorescence emission spectra were measured on Hitachi U-3500 and F-4500 spectrometers, respectively. Fluorescence quantum yields in CH_2Cl_2 were determined by using a Hamamatsu Photonics C9920-02 spectrometer. All melting points were measured with a Yanagimoto micro melting apparatus and were uncorrected. ^1H NMR spectra were measured with a JEOL-JNM-600HR spectrometer; chemical shifts (δ) in $CDCl_3$ are expressed in parts ppm relative to TMS (δ = 0.00 ppm) as an internal reference and peaks were assigned by ^1H-^1H COSY and NOESY spectra. FTIR spectra were measured with a Shimadzu IRAffinity-1 spectrophotometer. Electrochemical measurements were carried out by a BAS CV-50W voltammetric analyzer with a conventional three-electrode system. FAB-MS were measured with a JEOL GCmate II spectrometer. FAB-MS samples were dissolved in CH_2Cl_2 and *m*-nitrobenzyl alcohol and glycerol were used as the matrixes and PEG600 was added as an internal reference.

Methyl pyropheophorbide-*a* (**1**),[7] methyl pyropheophorbide-*d* (**2**),[7] methyl 3^2,3^2-dicyano-pyropheophorbide-*a* (**3**),[4] methyl 13^1-deoxo-pyropheophorbide-*a* (**4**),[8] and methyl 13^1-deoxo-pyropheophorbide-*d* (**5**)[9] were prepared as previously reported. THF was distilled from CaH_2 before use. Other solvents and reagents were employed as purchased without further purification. All synthetic procedures were carried out in the dark.

Methyl 3^2,3^2-Dicyano-13^1-deoxo-pyropheophorbide-*a* (6): According to the reported procedure,[4] Knoevenagel reaction of 3-formylchlorin **5** (30 mg, 0.056 mmol) was performed by malononitrile (50 mg, 0.76 mmol) and Et_3N (24 mg, 0.24 mmol) in refluxing THF (20 mL) for 6 h. The crude product was purified by chromatography on silica gel (Et_2O/CH_2Cl_2, 1:99) followed by recrystallization from CH_2Cl_2/MeOH to give **6** (16 mg, 48%) as brown crystals; m.p. 208–209 °C. UV/Vis (CH_2Cl_2): λ_{max} (A_{rel}) = 689 (0.34), 636 (0.10), 580 (0.13), 451 (0.56), 376 (1) nm; Flu (CH_2Cl_2: λ_{ex} = 450 nm): λ_{em} = 715 nm; Φ_{Flu} (CH_2Cl_2: λ_{ex} = 450 nm) = 10%. IR (film): $\tilde{\nu}$ = 2228 (C≡N), 1744 (17^2-C=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 9.54 (s, 1 H, 5-H), 9.52 (s, 1 H, 3-CH), 9.40 (s, 1 H, 10-H), 8.94 (s, 1 H, 20-H), 4.93–4.88, 4.81–4.76 (m, each 1 H, 13^1-CH_2), 4.60 (dq, *J* = 2, 7 Hz, 1 H, 18-H), 4.46–4.43 (br-d, 1 H, 17-H), 4.09–3.99 (m, 2 H, 13-CH_2), 3.80 (q, *J* = 8 Hz, 2 H, 8-CH_2), 3.64, 3.60 (s, each 3 H, 2-CH_3, 17^2-CO_2CH_3), 3.45 (s, 3 H, 12-CH_3), 3.41 (s, 3 H, 7-CH_3), 2.82–2.76, 2.66–2.60, 2.32–2.23 (m, 1 H, 1 H, 2 H, 17-CH_2CH_2), 1.83 (d, *J* = 7 Hz, 3 H, 18-CH_3), 1.75 (t, *J* = 8 Hz, 3 H, 8^1-CH_3), –1.08, –2.46 (s, each 1 H, NH×2) ppm. MS (FAB): calcd. for $C_{36}H_{36}N_6O_2$ 584.2900; found 584.2946 $[M]^+$.

Methyl 13^1-Deoxo-13^1-(dicyanomethylene)pyropheophorbide-*a* (7): A mixture of chlorin **1** (27 mg, 0.050 mmol), malononitrile (33 mg, 0.50 mmol), and Et_3N (35 mg, 0.35 mmol) in THF (20 mL) was refluxed for 1 h. The solution was cooled to room temperature, poured into 1% aqueous HCl, and extracted with CH_2Cl_2. The extract was washed with water, dried with anhydrous Na_2SO_4, filtered, and concentrated. The crude product was purified by silica-gel chromatography (Et_2O/CH_2Cl_2, 1:99) followed by recrystallization from CH_2Cl_2/MeOH to give **7** (20 mg, 67%) as brown crystals; m.p. 232–236 °C. UV/Vis (CH_2Cl_2): λ_{max} (A_{rel}) = 704 (1.1), 643 (0.29), 574 (0.18), 534 (0.12), 453 (1), 433 (0.96), 385 (0.93), 351 (0.75) nm; Flu (CH_2Cl_2: λ_{ex} = 450 nm): λ_{em} = 712 nm; Φ_{Flu} (CH_2Cl_2: λ_{ex} = 450 nm) = 25%. IR (CH_2Cl_2): $\tilde{\nu}$ = 2220 (C≡N), 1733 (17^2-C=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 9.15 (s, 1 H, 5-H), 9.00 (s, 1 H, 10-H), 8.37 (s, 1 H, 20-H), 7.89 (dd, *J* = 18, 12 Hz, 1 H, 3-CH), 6.26 (dd, *J* = 18, 1 Hz, 1 H, 3^1-CH *trans* to 3-C-H), 6.16 (dd, *J* = 12, 1 Hz, 1 H, 3^1-CH *cis* to 3-C-H), 5.37, 5.26 (d, *J* = 20 Hz, each 1 H, 13^1-CH_2), 4.33 (dq, *J* = 2, 7 Hz, 1 H, 18-H), 4.10–4.07 (br-d, 1 H, 17-H), 3.65 (s, 3 H, 17^2-CO_2CH_3), 3.53 (q, *J* = 8 Hz, 2 H, 8-CH_2), 3.38 (s, 3 H, 12-CH_3), 3.33 (s, 3 H, 2-CH_3), 3.12 (s, 3 H, 7-CH_3), 2.58–2.52, 2.51–2.46, 2.29–2.24, 2.12–2.05 (m, each 1 H, 17-CH_2CH_2), 1.75 (d, *J* = 7 Hz, 3 H, 18-CH_3), 1.59 (t, *J* = 8 Hz, 3 H, 8^1-CH_3), 1.03, –1.03 (s, each 1 H, NH×2) ppm. MS (FAB): calcd. for $C_{37}H_{36}N_6O_2$ 596.2900; found 596.2898 $[M]^+$.

Methyl 13^1-Deoxo-13^1-(dicyanomethylene)pyropheophorbide-*d* (8): According to the reported procedure,[7] 3-vinylchlorin **7** (50 mg, 0.084 mmol) was oxidized by OsO_4 (ca. 50 mg), $NaIO_4$ (300 mg, 1.4 mmol), and AcOH (1 mL) in water (2 mL) and THF (20 mL). The crude product was purified by silica-gel chromatography (Et_2O/CH_2Cl_2, 1:99) followed by recrystallization from CH_2Cl_2/MeOH to give **8** (35 mg, 70%) as green crystals; m.p. 239–242 °C. UV/Vis (CH_2Cl_2): λ_{max} (A_{rel}) = 727 (1.3), 663 (0.22), 584 (0.23), 543 (0.12), 467 (0.77), 437 (0.73), 395 (1) nm; Flu (CH_2Cl_2: λ_{ex} = 470 nm): λ_{em} = 733 nm; Φ_{Flu} (CH_2Cl_2: λ_{ex} = 470 nm) = 21%. IR (Film): $\tilde{\nu}$ = 2222 (C≡N), 1744 (17^2-C=O), 1668 (3-C=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 11.46 (s, 1 H, 3-CH), 10.17 (s, 1 H, 5-H), 9.46 (s, 1 H, 10-H), 8.69 (s, 1 H, 20-H), 5.78, 5.66 (d, *J* = 21 Hz, each 1 H, 13^1-CH_2), 4.49 (dq, *J* = 2, 8 Hz, 1 H, 18-H), 4.33–4.30 (br-d, 1 H, 17-H), 3.87 (s, 3 H, 12-CH_3), 3.71 (s, 3 H, 2-CH_3), 3.67 (q, *J* = 8 Hz, 2 H, 8-CH_2), 3.63 (s, 3 H, 17^2-CO_2CH_3), 3.26 (s, 3 H, 7-CH_3), 2.70–2.64, 2.63–2.59, 2.34–2.29, 2.27–2.23 (m, each 1 H, 17-CH_2CH_2), 1.81 (d, *J* = 8 Hz, 3 H, 18-CH_3), 1.69 (t, *J* = 8 Hz, 3 H, 8^1-CH_3), 0.75, –1.34 (s, each 1 H, NH×2) ppm. MS (FAB): calcd. for $C_{36}H_{34}N_6O_3$ 598.2692; found 598.2732 $[M]^+$.

Methyl 3^2,3^2-Dicyano-13^1-deoxo-13^1-(dicyanomethylene)pyropheophorbide-*a* (9): Reaction of **2** (35 mg, 0.06 mmol) with malononitrile (515 mg, 7.8 mmol) in refluxing THF in the presence of Et_3N for 3.5 h gave **9** in 7% yield, whereas a similar treatment of **3** (60 mg, 0.10 mmol) with malononitrile (515 mg, 7.8 mmol) gave **9** in 12% yield. Reaction of **8** (30 mg, 0.05 mmol) with malononitrile (33 mg, 0.50 mmol) in the presence of Et_3N (35 mg, 0.35 mmol) in

THF (20 mL) at room temperature for 2 h gave **9** as green crystals in 41% yield after purification by silica-gel chromatography (CH_2Cl_2) and recrystallization (CH_2Cl_2/MeOH); m.p. 138–143 °C. UV/Vis (CH_2Cl_2): λ_{max} (A_{rel}) = 736 (0.97), 669 (0.22), 590 (0.21), 545 (0.13), 422 (1), 353 (0.83) nm; Flu (CH_2Cl_2: λ_{ex} = 450 nm): λ_{em} = 749 nm; Φ_{Flu} (CH_2Cl_2: λ_{ex} = 450 nm) = 20%. IR (CH_2Cl_2): $\tilde{\nu}$ = 2228, 2216 (C≡N), 1743 (17^2-C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 9.29, 9.17, 9.05, 8.66 (s, each 1 H, 5-, 10-, 20-H, 3-CH), 5.56, 5.39 (d, J = 20 Hz, each 1 H, 13^1-CH_2), 4.48 (dq, J = 2, 8 Hz, 1 H, 18-H), 4.28–4.25 (br-d, 1 H, 17-H), 3.66 (q, J = 8 Hz, 2 H, 8-CH_2), 3.65, 3.51, 3.46, 3.25 (s, each 3 H, 2-, 7-, 12-CH_3, 17^2-CO_2CH_3), 2.65–2.59, 2.35–2.29, 2.22–2.17 (m, 2 H, 1 H, 1 H, 17-CH_2CH_2), 1.84 (d, J = 8 Hz, 3 H, 18-CH_3), 1.67 (t, J = 8 Hz, 3 H, 8^1-CH_3), 0.47, –1.36 (s, each 1 H, NH×2) ppm. MS (FAB): calcd. for $C_{39}H_{35}N_8O_2$ 647.2883; found 647.2918 $[M + H]^+$.

Supporting Information (see also the footnote on the first page of this article): ^{1}H NMR spectra of **6**–**9** in $CDCl_3$ (Figures S1–4) and relation of Q_y energy levels with redox potential differences (Figure S5).

Acknowledgments

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