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Synthesis and optical properties of C3-ethynylated chlorin and π-extended chlorophyll dyads

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ABSTRACT

A C3-ethynylated chlorophyll derivative was prepared from methyl pyropheophorbide-*d* possessing a 3-formyl group by treatment of Bestmann–Ohira reagent. The mono-substituted acetylene was subjected to coupling reactions at the terminal acetylenic carbon atom to form a series of π-extended chlorophyll derivatives. Replacement of the terminal hydrogen to phenyl, phenylethynyl and C3-chlorin-ethynyl caused red-shifts of their Q_y (0,0) maxima from 675 to 679, 686, and 696 nm, respectively. Optical properties of C3^2-substituted 3-ethynyl-chlorophyll derivatives including chlorophyll dyads were investigated in comparison with those of their related compounds. Partial quenching of the fluorescence emission (Φ_{flu}=0.14) was observed for *ortho*-substituted dyad, compared to *meta*- (Φ=0.27) and *para*-dyads (Φ=0.29), suggesting a through-space interaction between the two chlorin macrocycles in a molecule.

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1. Introduction

(Bacterio)chlorophylls [=(B)Chls] play the leading role in light absorption and energy/electron-transfer in natural photosynthesis. They have several kinds of C3-substituents on their cyclic tetrapyrrole macrocycles consisting of porphyrin, chlorin and bacteriochlorin π-systems (see Fig. 1). All Chls-*c* possess a C3-vinyl group on the porphyrin unit. Chls-*a*/*b* have the same C3-vinyl group on the chlorin π-system, while Chl-*d* has a formyl group at the 3-position, which causes a red-shift of the longest absorbing (Q_y) maxima from 662 (Chl-*a*) to 688 nm (Chl-*d*) in diethylether.[1] BChl-g also has a C3-vinyl group on the bacteriochlorin skeleton, and electron-withdrawing ability of the C3-acetyl group in BChls-*a*/*b* contributes to bathochromic shifts of the electronic absorption bands. Combination of the C3-functional group with the π-conjugated skeleton of (B)Chl pigments makes different ranges of light absorption possible as their monomeric states. On the contrary, BChls-*c*/*d*/*e* have a C3-1-hydroxyethyl group on the chlorin unit to form self-aggregates and absorb a wide range of light in a chlorosome.[2] Thus, naturally occurring (B)Chls realize light absorption at various wavelengths by tuning C3-substituents on their tetrapyrrole units. Synthetic modification of the C3-substituents has led to the development of new dye components with various functionalities, of which absorption bands at the long-wavelength region of (bacterio)chlorin skeleton are important for practical uses. For example, 3-trifluoroacetyl-(bacterio)chlorins were applied to an analytical ethanol sensor[3] as well as visual sensing reagents for alcohol/amine detection[4] and 3-(2-carboxyvinyl)-derivatives have successfully been applied to dye-sensitized solar cells.[5]

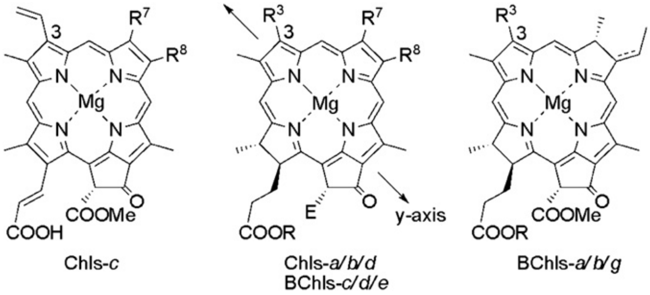

Fig. 1. Structures of naturally occurring (B)Chls possessing different π-skeletons: porphyrin, chlorin, and bacteriochlorin (left to right).

In view of the construction of artificial models of natural photosynthetic antennae, many porphyrin derivatives have been synthesized to form large oligomers covalently linked by π-conjugation units.[6] Since acetylene coupling is one of the most widely used techniques to form such porphyrin assembly, a chlorophyll-derived ethynyl-chlorin appears to be a more direct and suitable component for developing model compounds related to natural photosynthesis.[7] Although several covalently-linked chlorin dimers have been reported,[8] there are only limited

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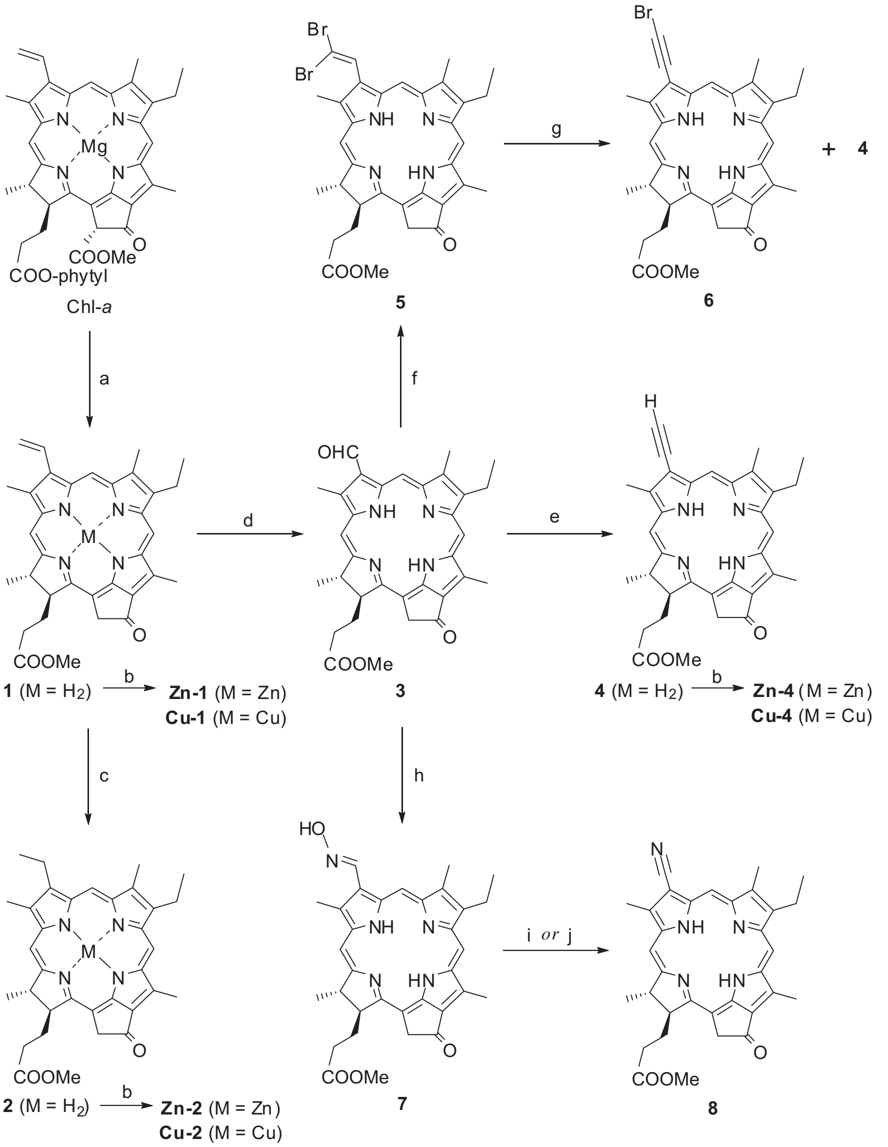
examples of chlorophyll dyads fixed with rigid spacers.[7,9] Moreover, alteration of the acetylene unit at the 3-position would lead to development of new types of chlorophyll derivatives, since transformation of the *C*3-substituent along the *y*-axis causes drastic spectral changes, especially at the Q_y peak position (vide supra).[1b,10]

We have preliminarily reported a synthetic route of *C*3-ethynylated chlorin and some of its derivatives.[11] Here we synthesized a series of rigid chlorin dimers using acetylene coupling, and optical properties of *C*3-ethynyl and its related chlorins as well as chlorin-dyads were elucidated by UV–vis, circular dichroism, and fluorescence emission spectroscopies.

2. Results and discussion

Synthetic routes of 3-ethynyl-chlorophyll derivative and its related compounds are shown in Scheme 1. The starting material is methyl pyropheophorbide-*a* (**1**) prepared by modifying Chl-*a* according to reported procedures.[12] Although the reduction (hydrogenation) of *C*3-vinyl to ethyl group (**1**→**2**)[13] and the oxidation to formyl group (**1**→**3**)[12] were reported, the oxidized (3^1,3^2-dehydrogenated) state of **1**, as in **4**, had not been prepared before our preliminary report.[11] Treatment of **3** with commercially available Bestmann–Ohira reagent [$(MeO)_2P(O)C(COMe)N_2$][14] in the presence of Cs_2CO_3 in THF and MeOH afforded a 3-ethynyl-chlorin **4** in 37% yield. To prepare other types of chlorins possessing a *C*3-triple bond substituent, the 3-formyl group of **3** was changed to a dibromoethylene unit[15] and the following dehydrobromination by tetrabutylammonium fluoride (TBAF) in DMF[16] gave 3-bromoethynyl-chlorin **6** (14% for the two-steps isolated yield) together with **4** (7%) as a side product. On the other hand, condensation of **3** with hydroxylamine gave oxime **7**,[17] which was dehydrated to give 3-cyano-chlorin **8**. Two different reaction conditions for the dehydration of **7** were examined, and treatment with $EtOPOCl_2$/DBU in CH_2Cl_2[18] (67%) was found to give a better yield than that with trichlorotriazine in DMF[19] (44%). Zinc- and copper-metallations of **4** at the central position were done as previously reported.[20]

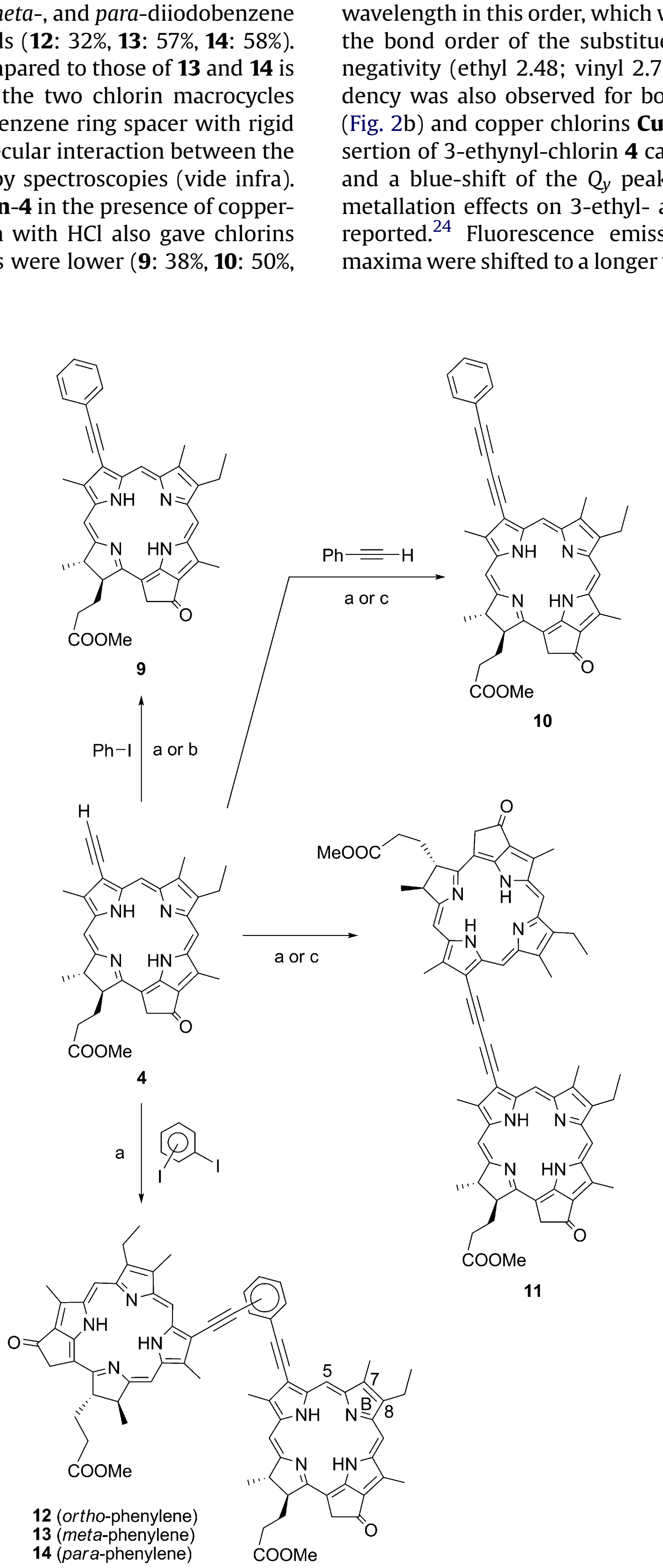
The reactivity of the terminal acetylene of **4** is expected to allow versatile reactions, such as Sonogashira-coupling with aromatic halides and Glaser-coupling with other ethynylated compounds.



Scheme 1. Reagents and conditions: (a) concd H_2SO_4, MeOH; collidine, reflux; (b) $M(OAc)_2\cdot xH_2O$, $MeOH/CH_2Cl_2$; (c) 10% Pd/C, H_2, acetone; (d) $NaIO_4$, OsO_4, THF-aq AcOH; (e) $(MeO)_2P(O)C(COMe)N_2$, Cs_2CO_3, THF/MeOH; (f) CBr_4, PPh_3, CH_2Cl_2; (g) TBAF, DMF; (h) $HONH_2\cdot HCl$, K_2CO_3, $MeOH/CH_2Cl_2$; (i) 2,4,6-trichloro-1,3,5-triazine, DMF; (j) $EtOPOCl_2$, DBU, MS 4 Å, CH_2Cl_2.

Scheme 2 overviews synthetic routes of π-extended chlorins derived from *C*3-ethynylated (**Zn**-)**4**. Copper-free Sonogashira-coupling[21] of free-base **4** using Pd-catalyst with excess iodobenzene or phenylacetylene gave the expected products in moderate yields (**9**: 70%, **10**: 67%). Without additional reactants, homocoupling of the terminal acetylene of **4** occurred under the same conditions to form chlorin dyad **11** in 88% yield. On the other hand, coupling reactions of **4** with 0.52 molar ratio of *ortho*-, *meta*-, and *para*-diiodobenzene gave the corresponding chlorin-dyads (**12**: 32%, **13**: 57%, **14**: 58%). The lower yield of *ortho*-dyad **12** compared to those of **13** and **14** is ascribed to the steric hindrance of the two chlorin macrocycles fixed on the *ortho*-positions of the benzene ring spacer with rigid acetylene unit. Actually, an intramolecular interaction between the chromophores of **12** was observed by spectroscopies (vide infra). Coupling reactions of zinc complex **Zn-4** in the presence of copper-catalyst[22] followed by demetallation with HCl also gave chlorins **9**–**11**, but their isolated overall yields were lower (**9**: 38%, **10**: 50%, **11**: 58%) than those of the above direct coupling of **4**. When free-base **4** was treated with $Cu(OAc)_2$ in pyridine, a doubly copper-metallated complex of **11** was obtained in 63% yield.

Fig. 2a shows the absorption spectra of three kinds of chlorins, **2**, **1**, and **4**, possessing ethyl, vinyl, and ethynyl groups, respectively, at the 3-position in CH_2Cl_2. The Soret (300–450 nm), Q_x (450–600 nm) and Q_y bands (550–700 nm) were shifted to a longer wavelength in this order, which were consistent with an increase in the bond order of the substituents reflecting the group electronegativity (ethyl 2.48; vinyl 2.79; ethynyl 3.07).[23] The same tendency was also observed for both zinc chlorins **Zn-2**, **Zn-1**, **Zn-4** (Fig. 2b) and copper chlorins **Cu-2**, **Cu-1**, **Cu-4** (Table 1). Metal insertion of 3-ethynyl-chlorin **4** caused a red-shift of the Soret band and a blue-shift of the Q_y peak (Fig. 2), which is similar to the metallation effects on 3-ethyl- and 3-vinyl-chlorins as previously reported.[24] Fluorescence emission peaks excited at the Soret maxima were shifted to a longer wavelength in the same order of 3-



Scheme 2. Reagents and conditions: (a) $Pd_2(dba)_3$, P(*o*-tolyl)$_3$, Et_3N, toluene; (b) $Zn(OAc)_2\cdot 2H_2O$, $MeOH/CH_2Cl_2$; $Pd(PPh_3)_2Cl_2$, $Cu(OAc)_2\cdot H_2O$, Et_3N; aq HCl; (c) $Zn(OAc)_2\cdot 2H_2O$, $MeOH/CH_2Cl_2$; $Cu(OAc)_2\cdot H_2O$, pyridine; aq HCl.

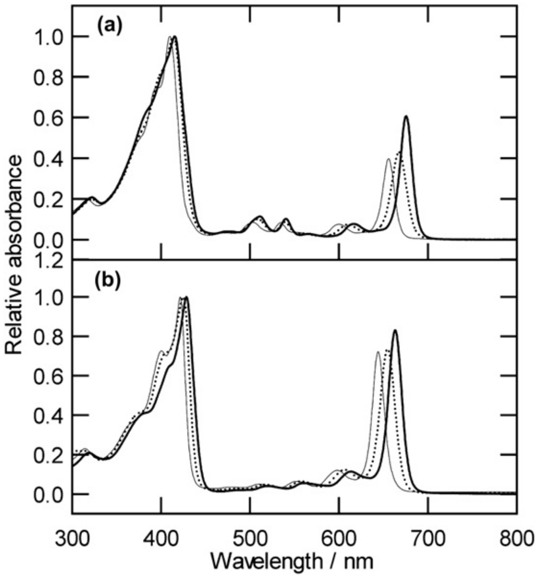
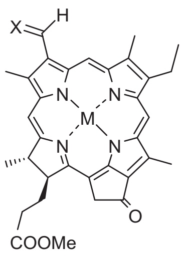


Fig. 2. Electronic absorption spectra of (a) 3-ethyl-chlorin **2** (solid thin line), 3-vinyl-chlorin **1** (dotted line), and 3-ethynyl-chlorin **4** (solid thick line) and (b) zinc 3-ethyl-chlorin **Zn-2** (solid thin line), zinc 3-vinyl-chlorin **Zn-1** (dotted line), and zinc 3-ethynyl-chlorin **Zn-4** (solid thick line) in CH$_2$Cl$_2$. All spectra were normalized at their Soret peaks.

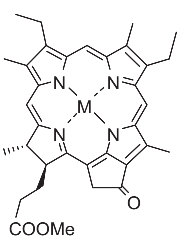
ethyl, 3-vinyl and 3-ethynyl group as those of absorption bands. The Stokes shifts of 3-ethynyl-chlorins (**4**, **Zn-4**) were comparable to those of 3-ethyl-chlorins (**2**, **Zn-2**), and were smaller than those of 3-vinyl-chlorins (**1**, **Zn-1**). Zinc insertion caused decrease of the fluorescence quantum yield, and copper-metallation completely quenched the emission.

Optical properties of the selected chlorophyll derivatives are summarized in Table 1 to compare the substituent effects at the 3-position, CH=X and C≡Y. Replacement of the C3^2-carbon atom with oxygen or nitrogen atom (**1**→**3** or **7**) caused a red-shift of the peak of both absorption and fluorescence emission spectra, apparently due to the nature of their electronegativities. On the other hand, substitution of the two hydrogen atoms on the C3^2-carbon of **1** with bromine atoms (**1**→**5**) had little effect on the peak positions of the spectra, while decreasing the fluorescence emission quantum yield (21→8%) mainly due to a heavy atom effect. Similar effects of heteroatom or halogen were also observed for three kinds of chlorins possessing a triple bond at the *C*3-position. Change of the CH to nitrogen atom in the 3^2-position of the *C*3-triple bond (**4**→**8**) caused red-shifts of the peak maxima of the spectra, because a cyano moiety strongly withdraws conjugated π-electron. Although the spectra of **4** and **6** appear to be almost the same, replacement of the hydrogen with bromine atom on the C3^2-carbon slightly decreased the fluorescence quantum yield (26→17%) as expected (vide supra). Full widths at half maxima (FWHM) of the Q_y (0,0) absorption and the main fluorescence emission bands appear to reflect the nature of the bond character: chlorins **4**, **6** and **8**

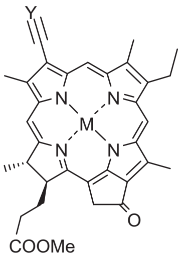
Table 1
Optical properties of chlorophyll derivatives in CH$_2$Cl$_2$



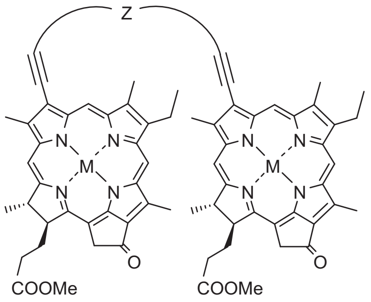
M-1, 3, 5, 7



M-2



M-4, 6, 8~10



11~14

Compound	λ_{abs}/nm					Int (Q_y (0,0)/Int (Soret)	λ_{em}/nm (FWHM^a/cm^{-1})	Φ_{flu}	Stokes shift/cm^{-1}
	Soret	Q_x		Q_y (FWHM^a/cm^{-1})					
		(0,1)	(0,0)	(0,1)	(0,0)				
1 (X=CH$_2$, M=H$_2$)	414	508	539	610	667 (450)	0.43	672 (470)	0.21	110
Zn-1 (X=CH$_2$, M=Zn)	425	518	557	606	655 (460)	0.74	660 (480)	0.16	120
Cu-1 (X=CH$_2$, M=Cu)	425	507	552	605	653 (600)	0.72	[b]	[b]	[b]
2 (M=H$_2$)	410	504	534	600	656 (390)	0.40	658 (390)	0.20	50
Zn-2 (M=Zn)	422	510	554	598	644 (390)	0.72	647 (430)	0.12	70
Cu-2 (M=Cu)	422	503	547	597	642 (520)	0.66	[b]	[b]	[b]
3 (X=O, M=H$_2$)	428	522	554	633	694 (430)	0.81	698 (470)	0.21	80
4 (Y=CH, M=H$_2$)	415	511	540	616	675 (360)	0.61	677 (380)	0.22	40
Zn-4 (Y=CH, M=Zn)	427	519	560	613	662 (410)	0.75	665 (430)	0.15	70
Cu-4 (Y=CH, M=Cu)	428	510	555	611	660 (530)	0.74	[b]	[b]	[b]
5 (X=CBr$_2$, M=H$_2$)	413	507	537	611	668 (410)	0.48	671 (460)	0.08	70
6 (Y=CBr, M=H$_2$)	415	511	541	618	677 (370)	0.58	678 (360)	0.17	20
7 (X=NOH, M=H$_2$)	420	514	543	619	679 (410)	0.59	682 (420)	0.22	70
8 (Y=N, M=H$_2$)	415	514	544	626/647	685 (320)	0.84	686 (320)	0.23	20
9 (Y=CC$_6$H$_5$, M=H$_2$)	419	513	542	620	679 (380)	0.56	681 (400)	0.26	40
10 (Y=CC≡CC$_6$H$_5$, M=H$_2$)	423	517	546	626	686 (380)	0.64	688 (400)	0.27	40
11 (Z=none)	419	519	552	628	696 (440)	0.95	700 (410)	0.34	80
12 (Z=*o*-C$_6$H$_4$)	411	514	545	628	683 (690)	0.54	687 (570)	0.14	90
13 (Z=*m*-C$_6$H$_4$)	420	515	545	621	681 (420)	0.59	686 (420)	0.27	110
14 (Z=*p*-C$_6$H$_4$)	419	516	545	624	685 (450)	0.68	689 (430)	0.29	80

[a] Full width at half maximum.

[b] Non-fluorescence.

possessing a linear triple bond substituent (3-C≡Y) showed a sharper peak compared to the corresponding chlorins **1**, **5**, and **7** (3-CH=X), respectively. More conformationally flexible *C*3-substituents with a double bond can take various rotamers including two energetically stable conformers coplanar with a chlorin π-system, and their rotational deviations from the chlorin π-plane enhance the energy levels of their Q_y bands, while there is no possible conformational pattern of the linear triple bond substituents.[25]

Fig. 3a gives absorption spectra of three types of chlorins **9**–**11** derived from 3-ethynyl-chlorin **4**. Replacement of the terminal hydrogen to phenyl group (**4**→**9**) and further π-extension by the phenylethynyl to phenylbutadiynyl unit (**4**→**10**) caused slight red-shifts of their absorption maxima (Table 1). The Q_y peak maximum of chlorin dimer **11** appeared at a longer-wavelength region (696 nm) with a high intensity [Int(Q_y)/Int(Soret)=0.95] than those of **10** possessing a phenylacetylene unit (686 nm and 0.64), suggesting that the two chlorin macrocycles interacted in a molecule through the linear butadiyne spacer along the *y*-axis. As can be seen in Figs. 3b and 3c, chlorin-dyads **13** and **14** showed similar absorption and CD spectra, which also resemble those of **10**. On the contrary, *ortho*-substituted **12** had a little broader spectrum than did **10**, **13**, and **14** (FWHM; **10**: 380, **12**: 690, **13**: 420, **14**: 450 cm^{-1}). Because the fluorescence quantum yield of **12** (14%) is lower than those of the other chlorins (**10**: 27%, **13**: 27%, **14**: 29%), it is reasonable to assume that the two chlorin macrocycles fixed at the *ortho*-position interacted with each other in the ground state to cause partial fluorescence quenching and also gave the lower synthetic yield due to the steric hindrance. Although the ^{1}H NMR spectrum of **12** indicated the free-rotation of the two chlorin macrocycles along the 3-ethynyl bridge at room temperature, apparent up-field shifts of several proton signals were observed. As summarized in Table 2, chemical shifts of the *C*7/*C*8-substituents of **12** appeared more than 1 ppm upper-field compared to those of the other chlorin-dyads. A molecular modelling study[26] suggests that chlorin **12** tends to form an intramolecular partially stacked conformation, in which the B-ring is located in the shielding region of the neighbouring chlorin π-system in a molecule (Fig. S1).

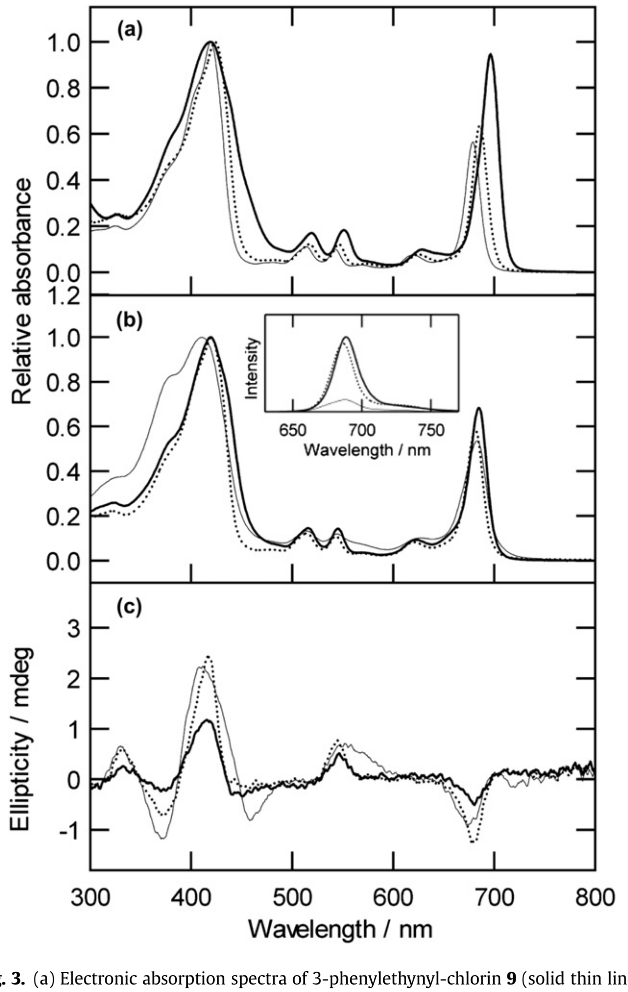


Fig. 3. (a) Electronic absorption spectra of 3-phenylethynyl-chlorin **9** (solid thin line), 3-phenylbutadiynyl-chlorin **10** (dotted line), and chlorin dimer **11** (solid thick line) in CH_2Cl_2 and (b) electronic absorption and (c) circular dichroism of *ortho*-dyad **12** (solid thin line), *meta*-dyad **13** (dotted line), and *para*-dyad **14** (solid thick line) in CH_2Cl_2. Inset of (b) indicates fluorescence emission spectra (excited at their Soret bands) of **12**–**14** in CH_2Cl_2. Absorption spectra were normalized at their Soret peaks.

Table 2
Selected ^{1}H NMR chemical shifts (δ/ppm) of chlorin-dyads **11**–**14** in $CDCl_3$

Proton	*o*-Dyad **12**	*m*-Dyad **13**	*p*-Dyad **14**	Dimer **11**
5-H	9.25	9.70	9.65	9.50
7-CH_3	1.91	3.37	3.35	3.27
8-CH_2	1.80	3.73	3.73	3.58
8^1-CH_3	0.67	1.72	1.74	1.66

3. Conclusions

We have shown a facile synthetic route of transforming the *C*3-formyl to the ethynyl group on a chlorin macrocycle, and the strategy of π-extension directly connected to the 3-position of the chlorin ring is demonstrated. Coupling reactions were performed to synthesize a series of π-conjugated chlorin-dyads, among which dyad **11** connecting two chlorin rings via butadiyne spacer showed Q_y peak maximum at the longest wavelength region. On the other hand, relative broadening of visible bands and partial quenching of the fluorescence were observed for *ortho*-substituted dyad **12**, suggesting a through-space interaction between the two chlorin macrocycles in a molecule.

4. Experimental section

4.1. General

Electronic absorption and fluorescence emission spectra were measured on a Hitachi U-3500 and F-4500 spectrometer, respectively. Fluorescence quantum yields were measured at room temperature using a Hamamatsu Photonics absolute PL quantum yield measurement system C9920-02. All melting points were measured with a Yanagimoto micro melting apparatus and were uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-ECA-600HR spectrometer in $CDCl_3$. Chemical shifts are reported relative to the residual solvent peak: δ=7.26 ppm ($CHCl_3$) for ^{1}H NMR and δ=77.0 ppm ($^{13}CDCl_3$) for ^{13}C NMR. Proton peaks were assigned by ^{1}H–^{1}H COSY and NOESY or ROESY spectra, and carbon signals except for quaternary peaks were assigned by DEPT and ^{13}C–^{1}H COSY spectra. FTIR spectra in CH_2Cl_2 were measured with a Shimadzu IRAffinity-1 spectrophotometer. Atmospheric pressure chemical ionization (APCI) quadrupole mass spectra (MS) and laser desorption ionization time of flight (TOF) MS were measured by Shimadzu LCMS-2010 EV and AXIMA-CFR+ apparatus, respectively; methanol solutions were injected for APCI-MS and no matrix was used for TOF-MS. Fast atom bombardment-mass spectroscopy (FAB-MS) data were measured by a JEOL GCmate II spectrophotometer; FAB-MS samples were dissolved in CH_2Cl_2, *m*-nitrobenzyl alcohol and glycerol were used as the matrix, and PEG600 was added as an internal reference. Flash column chromatography (FCC) was performed with silica gel (Merck, Kieselgel

60). HPLC was done with a packed column (Nacalai, Cosmosil 5SL-II, 10$\phi\times$250 mm).

Methyl pyropheophorbide-*a* (**1**),[12] zinc methyl pyropheophorbide-*a* (**Zn-1**),[27] copper methyl pyropheophorbide-*a* (**Cu-1**),[28] methyl mesopyropheophorbide-*a* (**2**),[13] zinc methyl mesopyropheophorbide-*a* (**Zn-2**),[20b] copper methyl mesopyropheophorbide-*a* (**Cu-2**),[13a] methyl pyropheophorbide-*d* (**3**),[12] methyl 3-devinyl-3-ethynyl-pyropheophorbide-*a* (**4**)[11] and methyl pyropheophorbide-*d* oxime (**7**)[17] were prepared as previously reported. THF was distilled over CaH_2 before use. Other solvents and reagents were used as purchased without further purification. All synthetic procedures were done in the dark.

4.2. Metallation of 3-ethynyl-chlorin

Zinc- and copper-metallation of free-base **4** were done according to the reported procedure[20] to give **Zn-4** and **Cu-4** in quantitative yields.

*4.2.1. Zinc methyl 3-devinyl-3-ethynyl-pyropheophorbide-a (**Zn-4**).* Green solid; mp >300 °C; VIS (CH_2Cl_2) λ_{max} 663 (relative intensity, 0.83), 613 (0.11), 560 (0.06), 520 (0.04), 428 (1.00), 319 nm (0.21); ^{1}H NMR ($CDCl_3$) δ 9.18 (1H, s, 5-H), 9.15 (1H, s, 10-H), 8.42 (1H, s, 20-H), 4.91, 4.81 (each 1H, d, J=19 Hz, 13^1-CH_2), 4.44 (1H, dq, J=2, 7 Hz, 18-H), 4.22 (1H, dt, J=8, 2 Hz, 17-H), 4.10 (1H, s, 3^1-CH), 3.52 (2H, q, J=8 Hz, 8-CH_2), 3.47 (3H, s, 12-CH_3), 3.41 (3H, s, 17^2-CO_2CH_3), 3.38 (3H, s, 2-CH_3), 3.08 (3H, s, 7-CH_3), 2.59–2.54 (1H, m, 17-CH), 2.49–2.43 (1H, m, 17^1-CH), 2.31–2.26 (1H, m, 17-CH), 2.24–2.19 (1H, m, 17^1-CH), 1.86 (3H, d, J=7 Hz, 18-CH_3), 1.56 (3H, t, J=8 Hz, 8^1-CH_3); HRMS (FAB) found: m/z 608.1752, calcd for $C_{34}H_{32}N_4O_3Zn$: M^+, 608.1766.

*4.2.2. Copper methyl 3-devinyl-3-ethynyl-pyropheophorbide-a (**Cu-4**).* Black crystals; mp >300 °C; MS (TOF) found: m/z 607, calcd for $C_{34}H_{32}N_4O_3Cu$: M^+, 607.

4.3. Synthesis of 3-bromoethynyl-chlorin

*4.3.1. Methyl 3^2,3^2-dibromo-pyropheophorbide-a (**5**).* Triphenylphosphine (980 mg, 3.7 mmol) and CBr_4 (600 mg, 1.8 mmol) were dissolved in CH_2Cl_2 (4 ml) and the mixture was stirred for 5 min at 0 °C, then aldehyde **3** (300 mg, 0.54 mmol) was added. After stirring for additional 5 min under nitrogen, the mixture was diluted with CH_2Cl_2 and washed by aqueous saturated $NaHCO_3$. The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified by FCC (Et_2O/CH_2Cl_2=7:93) followed by recrystallization from CH_2Cl_2 and hexane to give **5** (192 mg, 50%) as a black solid: mp 212–214 °C (lit.[15] 205–208 °C); VIS (CH_2Cl_2) λ_{max} 668 (relative intensity, 0.48), 611 (0.09), 537 (0.10), 507 (0.12), 413 (1.00), 320 nm (0.23); ^{1}H NMR ($CDCl_3$) δ 9.48 (1H, s, 10-H), 9.01 (1H, s, 5-H), 8.58 (1H, s, 20-H), 8.45 (1H, s, 3^1-H), 5.27, 5.12 (each 1H, d, J=19 Hz, 13^1-CH_2), 4.50 (1H, dq, J=2, 7 Hz, 18-H), 4.31 (1H, dt, J=8, 2 Hz, 17-H), 3.67 (2H, q, J=8 Hz, 8-CH_2), 3.65 (3H, s, 12-CH_3), 3.62 (3H, s, 17^2-CO_2CH_3), 3.30 (3H, s, 2-CH_3), 3.22 (3H, s, 7-CH_3), 2.71–2.68 (1H, m, 17-CH), 2.59–2.55 (1H, m, 17^1-CH), 2.31–2.25 (2H, m, 17-CHCH), 1.83 (3H, d, J=7 Hz, 18-CH_3), 1.69 (3H, t, J=8 Hz, 8^1-CH_3), 0.26, −1.86 (each 1H, s, NH×2); MS (TOF) found: m/z 704, calcd for $C_{34}H_{34}Br_2N_4O_3$: M^+, 704.

*4.3.2. Methyl 3-bromoethynyl-3-devinyl-pyropheophorbide-a (**6**).* To a solution of **5** (20 mg, 0.028 mmol) in anhydrous DMF (8 ml) was added tetrabutylammonium fluoride trihydrate (16 mg, 0.05 mmol) and the mixture was stirred at room temperature under nitrogen. The reaction was monitored by visible spectrometry for 2 h until the Q_y peak (668 nm) of **5** completely disappeared. The reaction mixture was poured into aqueous saturated $NaHCO_3$, and extracted with CH_2Cl_2. The extract was washed with H_2O, dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified by FCC (Et_2O/CH_2Cl_2=7:93) followed by recrystallization from CH_2Cl_2 and hexane to give a 1:2 mixture of **4** and **6** (7.4 mg, 42%) The mixture was separated by HPLC (CH_2ClCH_2Cl/CH_3OH=99.5:0.5, 4 ml/min) at retention time (t_R)= 15 min for **6** and t_R=16 min for **4**. **6**: black solid; mp >300 °C; VIS (CH_2Cl_2) λ_{max} 677 (relative intensity, 0.58), 618 (0.08), 541 (0.10), 511 (0.12), 415 (1.00), 321 nm (0.22); IR (CH_2Cl_2) ν_{max} 3299 (alkyne-C–H), 2193 (C≡C), 1734 (ester-C=O), 1696 (keto-C=O), 1618, 1499 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 9.57 (1H, s, 10-H), 9.50 (1H, s, 5-H), 8.62 (1H, s, 20-H), 5.31, 5.15 (each 1H, d, J=19 Hz, 13^1-CH_2), 4.52 (1H, dq, J=2, 7 Hz, 18-H), 4.34 (1H, dt, J=8, 2 Hz, 17-H), 3.72 (2H, q, J=8 Hz, 8-CH_2), 3.70 (3H, s, 12-CH_3), 3.62 (3H, s, 17^2-CO_2CH_3), 3.48 (3H, s, 2-CH_3), 3.29 (3H, s, 7-CH_3), 2.75–2.69 (1H, m, 17-CH), 2.61–2.54 (1H, m, 17^1-CH), 2.35–2.28 (2H, m, 17-CHCH), 1.83 (3H, d, J=7 Hz, 18-CH_3), 1.70 (3H, t, J=8 Hz, 8^1-CH_3), 0.06, −1.98 (each 1H, s, NH×2); MS (TOF) found: m/z 624, calcd for $C_{34}H_{33}BrN_4O_3$: M^+, 624.

4.4. Synthesis of 3-cyano-chlorin

*4.4.1. Methyl 3-cyano-3-devinyl-pyropheophorbide-a (**8**).* To a solution of chlorin **7** (30 mg, 0.053 mmol) in CH_2Cl_2 (8 ml) was added $EtOPOCl_2$ (13 mg, 0.082 mmol), DBU (42 mg, 0.27 mmol), molecular sieve 4 Å, and the suspension was stirred for 6 h at room temperature under nitrogen. The reaction mixture was poured into aqueous 2% HCl and extracted with Et_2O. The extract was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified by FCC (Et_2O/CH_2Cl_2=7:93) followed by recrystallization from CH_2Cl_2 and hexane to give **8** as dark brown plates (20 mg, 67%): mp 218–219 °C; VIS (CH_2Cl_2) λ_{max} 685 (relative intensity, 0.81), 647 (0.08), 626 (0.08), 573 (0.02), 544 (0.13), 514 (0.12), 474 (0.04), 415 (1.00), 382 (0.74), 323 nm (0.22); IR (CH_2Cl_2) ν_{max} 2226 (C≡N), 1734 (ester-C=O), 1697 (keto-C=O), 1618, 1501, 1224, 1200, 1159, 977 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 9.50 (1H, s, 10-H), 9.42 (1H, s, 5-H), 8.76 (1H, s, 20-H), 5.35, 5.20 (each 1H, d, J=19 Hz, 13^1-CH_2), 4.58 (1H, dq, J=7, 2 Hz, 18-H), 4.37 (1H, dt, J=9, 2 Hz, 17-H), 3.63 (2H, q, J=8 Hz, 8-CH_2), 3.67 (3H, s, 17^2-CO_2CH_3), 3.64 (3H, s, 2-CH_3), 3.63 (3H, s, 12-CH_3), 3.19 (3H, s, 7-CH_3), 2.76–2.73 (1H, m, 17-CH), 2.64–2.58 (1H, m, 17^1-CH), 2.35–2.28 (2H, m, 17-CHCH), 1.86 (3H, d, J=7 Hz, 18-CH_3), 1.66 (3H, t, J=8 Hz, 8^1-CH_3), −0.49, −2.38 (each 1H, s, NH×2); MS (APCI) found: m/z 548, calcd for $C_{33}H_{34}N_5O_3$: MH^+, 548.

2,4,6-Trichloro-1,3,5-triazine (12 mg, 0.067 mmol) was dissolved in anhydrous DMF (1 ml) and the solution was stirred for 20 min at room temperature under nitrogen, then chlorin **7** (14 mg, 0.025 mmol) in anhydrous DMF (4 ml) was added and the mixture was stirred for 6 h. The reaction mixture was poured into H_2O and extracted with CH_2Cl_2. The extract was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified as mentioned above to afford **8** (6.0 mg, 44%).

4.5. Coupling reactions of (zinc) 3-ethynyl-chlorin (Zn)-4

*4.5.1. Methyl 3-devinyl-3-phenylethynyl-pyropheophorbide-a (**9**).* To a solution of **4** (20 mg, 0.037 mmol) in toluene (8 ml) and Et_3N (2 ml) was added iodobenzene (200 mg, 0.99 mmol), $Pd_2(dba)_3$ (8.9 mg, 0.010 mmol), P(o-tolyl)$_3$ (11 mg, 0.036 mmol) and the mixture was stirred for 12 h at 60 °C under nitrogen. The reaction mixture was poured into aqueous saturated $NaHCO_3$, and extracted with CH_2Cl_2. The extract was washed with H_2O, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by FCC (Et_2O/CH_2Cl_2=7:93) followed by recrystallization from CH_2Cl_2 and hexane to afford **9** (16 mg, 70%) as a black solid: mp 221–223 °C; VIS (CH_2Cl_2) λ_{max} 679 (ε, 6.3×10^4), 620 (8.6×10^3), 542 (1.1×10^4), 513 (1.2×10^4), 419 (1.11×10^5), 324 nm (2.3×10^4); IR (CH_2Cl_2) ν_{max} 2209 (C≡C), 1734 (ester-C=O), 1694 (keto-C=O), 1620, 1551, 1498 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.40 (1H, s, 5-H), 9.38 (1H, s, 10-H), 8.55 (1H, s, 20-H), 7.88 (2H, d, J=7 Hz, 2-H of 3^2-Ph), 7.56 (2H, t, J=7 Hz, 3-H of 3^2-Ph), 7.51 (1H, t, J=7 Hz, 4-H of 3^2-Ph), 5.26, 5.11 (each 1H, d, J=19 Hz, 13^1-CH_2), 4.48 (1H, br dq, 18-H), 4.30 (1H, br dt, 17-H), 3.63 (3H, s, 17^2-CO_2CH_3), 3.62 (3H, s, 12-CH_3), 3.59 (2H, q, J=8 Hz, 8-CH_2), 3.47 (3H, s, 2-CH_3), 3.16 (3H, s, 7-CH_3), 2.73–2.68 (1H, m, 17-CH), 2.60–2.55 (1H, m, 17^1-CH), 2.32–2.27 (2H, m, 17-CHCH), 1.83 (3H, d, J=7 Hz, 18-CH_3), 1.65 (3H, t, J=8 Hz, 8^1-CH_3), 0.17, −1.98 (each 1H, s, NH×2); ^{13}C NMR ($CDCl_3$) δ 196.8 ($C13^1$), 174.1 ($C17^3$), 171.5 (C19), 161.1 (C16), 155.4 (C6), 151.6 (C9), 149.4 (C14), 145.6 (C8), 141.4, 137.7 (C1, C2), 139.0, 129.4 (C11, C12), 137.4 (C4), 136.9 (C7), 132.5 ($C3^4$×2), 131.5 (C13), 129.6 ($C3^6$), 129.3 ($C3^5$×2), 124.0, 100.8 ($C3^2$, $C3^3$), 122.6 (C3), 106.9 (C15), 104.5 (C10), 98.4 (C5), 94.1 (C20), 83.7 ($C3^1$), 52.5 (C17), 52.4 ($C17^5$), 50.4 (C18), 48.8 ($C13^2$), 31.6 ($C17^2$), 30.5 ($C17^1$), 23.9 ($C18^1$), 20.0 ($C8^1$), 18.1 ($C8^2$), 13.2 ($C2^1$), 12.7 ($C12^1$), 11.7 ($C7^1$); HRMS (FAB) found: m/z 623.2999, calcd for $C_{40}H_{39}N_4O_3$: MH^+, 632.3022.

To a solution of **Zn-4** (11 mg, 0.017 mmol) in Et_3N (10 ml) was added iodobenzene (100 mg, 0.50 mmol), $Cu(OAc)_2\cdot H_2O$ (22 mg, 0.11 mmol), $Pd(PPh_3)_2Cl_2$ (60 mg, 0.086 mmol), and the mixture was stirred for 12 h at room temperature under nitrogen. The reaction mixture was poured into aqueous saturated $NaHCO_3$ solution and extracted with CH_2Cl_2. The extract was washed with H_2O and concentrated. The residue was dissolved in CH_2Cl_2, 18% aqueous HCl was added, and stirred for 1 h at room temperature. The mixture was then poured into H_2O, and the organic phase was washed successively with saturated aqueous $NaHCO_3$ and H_2O, dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified as mentioned above to give **9** (4.0 mg, 38%).

*4.5.2. Methyl 3-devinyl-3-phenylbutadiynyl-pyropheophorbide-a (**10**).* Similar to the synthesis of **9**, reaction of **4** with phenylacetylene instead of iodobenzene gave **10** in 67% yield as a black solid: mp 122–124 °C; VIS (CH_2Cl_2) λ_{max} 686 (ε, 6.3×10^4), 626 (7.8×10^3), 546 (1.1×10^4), 517 (1.1×10^4), 423 (9.4×10^4), 327 nm (2.2×10^4); IR (CH_2Cl_2) ν_{max} 2212 (C≡C), 1730 (ester-C=O), 1694 (keto-C=O), 1618, 1501 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.38 (1H, s, 10-H), 9.33 (1H, s, 5-H), 8.58 (1H, s, 20-H), 7.74 (2H, d, J=7 Hz, 2-H of 3^4-Ph), 7.47–7.37 (3H, m, 3-, 4-H of 3^4-Ph), 5.29, 5.14 (each 1H, d, J=19 Hz, 13^1-CH_2), 4.51 (1H, br dq, 18-H), 4.33 (1H, br dt, 17-H), 3.63 (3H, s, 17^2-CO_2CH_3), 3.62 (3H, s, 12-CH_3), 3.59 (2H, q, J=8 Hz, 8-CH_2), 3.49 (3H, s, 2-CH_3), 3.17 (3H, s, 7-CH_3), 2.72–2.68 (1H, m, 17-CH), 2.58–2.54 (1H, m, 17^1-CH), 2.30–2.26 (2H, m, 17-CHCH), 1.85 (3H, d, J=7 Hz, 18-CH_3), 1.64 (3H, t, J=8 Hz, 8^1-CH_3) 0.03, −2.18 (each 1H, s, NH×2); ^{13}C NMR ($CDCl_3$) δ 196.7 ($C13^1$), 174.0 ($C17^3$), 171.1 (C19), 161.3 (C16), 155.7 (C6), 151.6 (C9), 149.3 (C14), 145.5 (C8), 140.6, 140.3 (C1, C2), 139.3, 129.8 (C11, C12), 137.5 (C4), 137.2 (C7), 133.2 ($C3^6$×2), 131.7 (C13), 130.2 ($C3^8$), 129.2 ($C3^7$×2), 122.3 ($C3^5$), 120.8 (C3), 107.0 (C15), 104.4 (C10), 98.5 (C5), 94.4 (C20), 85.1, 74.5 ($C3^2$, $C3^3$), 84.6 ($C3^4$), 76.0 ($C3^1$), 52.5 (C17), 52.4 ($C17^5$), 50.2 (C18), 48.8 ($C13^2$), 31.5 ($C17^2$), 30.4 ($C17^1$), 23.9 ($C18^1$), 20.0 ($C8^1$), 18.0 ($C8^2$), 13.4 ($C2^1$), 12.7 ($C12^1$), 11.8 ($C7^1$); HRMS (FAB) found: m/z 647.3035, calcd for $C_{42}H_{39}N_4O_3$: MH^+, 647.3022.

Similar to the alternative synthesis of **9**, reaction of **Zn-4** with phenylacetylene in pyridine and successive demetallation gave **10** in 50% yield.

*4.5.3. Chlorin-dyad **11**.* Similar to the synthesis of **9**, homocoupling of **4** (20 mg, 0.037 mmol) in the presence of $Pd_2(dba)_3$ (8.4 mg, 0.009 mmol) and P(*o*-tolyl)$_3$ (11 mg, 0.036 mmol) in toluene (8 ml) and Et_3N (2 ml) gave **11** (18 mg, 88%) as a black solid after FCC (Et_2O/MeOH/CH_2Cl_2=10:1:89) followed by recrystallization from CH_2Cl_2-hexane: mp >300 °C; VIS (CH_2Cl_2) λ_{max} 696 (ε, 1.46×10^5), 628 (1.5×10^4), 552 (2.7×10^4), 519 (2.6×10^4), 419 (1.52×10^5), 326 nm (3.6×10^4); IR (CH_2Cl_2) ν_{max} 1734 (ester-C=O), 1693 (keto-C=O), 1618, 1551, 1498, 1222 cm^{-1} [ν(C≡C) was not observed]; ^1H NMR ($CDCl_3$) δ 9.50 (2H, s, 5-H×2), 9.29 (2H, s, 10-H×2), 8.65 (2H, s, 20-H×2), 5.28, 5.13 (each 2H, d, J=19 Hz, 13^1-CH_2×2), 4.53 (2H, br dq, 18-H×2), 4.35 (2H, br dt, 17-H×2), 3.65 (6H, s, 2-CH_3×2), 3.64 (6H, s, 17^2-CO_2CH_3×2), 3.58 (4H, br q, 8-CH_2×2), 3.55 (6H, s, 12-CH_3×2), 3.27 (6H, s, 7-CH_3×2), 2.75–2.71 (2H, m, 17-CH×2), 2.63–2.57 (2H, m, 17^1-CH×2), 2.34–2.28 (4H, m, 17-CHCH×2), 1.90 (6H, d, J=7 Hz, 18-CH_3×2), 1.66 (6H, t, J=8 Hz, 8^1-CH_3×2), −0.17, −2.17 (each 2H, s, NH×2×2); ^{13}C NMR ($CDCl_3$) δ 196.1 ($C13^1$×2), 173.5 ($C17^3$×2), 170.6 (C19×2), 161.0 (C16×2), 154.6 (C6×2), 151.3 (C9×2), 148.8 (C14×2), 145.0 (C8×2), 140.0, 139.7 (C1×2, C2×2), 138.9, 129.4 (C11×2, C12×2), 137.1 (C4×2), 136.7 (C7×2), 131.3 (C13×2), 120.1 (C3×2), 106.6 (C15×2), 103.7 (C10×2), 98.1 (C5×2), 94.0 (C20×2), 84.5 ($C3^2$×2), 78.6 ($C3^1$×2), 52.1 ($C17^5$×2), 51.9 (C17×2), 49.7 (C18×2), 48.2 ($C13^2$×2), 31.0 ($C17^2$×2), 29.9 ($C17^1$×2), 23.4 ($C8^2$×2), 19.5 ($C8^1$×2), 17.5 ($C18^1$×2), 13.1 ($C2^1$×2), 12.1 ($C12^1$×2), 11.3 ($C7^1$×2); MS (FAB) found: m/z 1091.4, calcd for $C_{68}H_{67}N_8O_6$: MH^+, 1091.5.

Similar to the synthesis of **9**, reaction of **Zn-4** (23 mg, 0.037 mmol) in the presence of $Cu(OAc)_2\cdot H_2O$ (22 mg, 0.11 mmol) in pyridine (12 ml) and successive demetallation gave **11** (13 mg, 58%).

*4.5.4. Chlorin-dyad **12**.* Similar to the synthesis of **11**, reaction of **4** (20 mg, 0.037 mmol) with 1,2-diiodobenzene (6.2 mg, 0.019 mmol) at 80 °C for 2 days gave **12** (6.7 mg, 32%) as a black solid: mp >300 °C; VIS (CH_2Cl_2) λ_{max} 683 (relative intensity, 0.53), 628 (0.10), 545 (0.12), 514 (0.13), 411 nm (1.00); IR (CH_2Cl_2) ν_{max} 2201 (C≡C), 1734 (ester-C=O), 1693 (keto-C=O), 1618, 1499 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.25 (2H, s, 5-H×2), 8.46 (2H, s, 20-H×2), 8.16, 7.69 (each 2H, m, 3^2-C_6H_4), 8.00 (2H, s, 10-H×2), 5.36, 5.19 (each 2H, d, J=19 Hz, 13^1-CH_2×2), 4.47 (2H, br q, 18-H×2), 4.32 (2H, br d, 17-H×2), 3.68 (6H, s, 17^2-CO_2CH_3×2), 3.47 (6H, s, 2-CH_3×2), 3.44 (6H, s, 12-CH_3×2), 2.78–2.74 (2H, m, 17-CH×2), 2.67–2.60 (2H, m, 17^1-CH×2), 2.44–2.30 (4H, m, 17-CHCH×2), 1.91 (6H, s, 7-CH_3×2), 1.80 (4H, q, J=8 Hz, 8-CH_2×2), 1.79 (6H, d, J=7 Hz, 18-CH_3×2), 0.67 (6H, t, J=8 Hz, 8^1-CH_3×2), −0.47, −2.25 (each 2H, s, NH×2×2); MS (TOF) found: m/z 1167, calcd for $C_{74}H_{70}N_8O_6$: M^+, 1167.

*4.5.5. Chlorin-dyad **13**.* Similar to the synthesis of **12**, reaction of **4** with 1,3-diiodobenzene gave **13** in 57% yield as a black solid after FCC (Et_2O/MeOH/CH_2Cl_2=10:1:89) followed by recrystallization from CH_2Cl_2–hexane: mp >300 °C; VIS (CH_2Cl_2) λ_{max} 681 (relative intensity, 0.59), 621 (0.08), 545 (0.12), 515 (0.12), 420 (1.00), 324 nm (0.22); IR (CH_2Cl_2) ν_{max} 2219 (C≡C), 1734 (ester-C=O), 1693 (keto-C=O), 1619, 1499 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.70 (2H, s, 5-H×2), 9.57 (2H, s, 10-H×2), 8.66 (2H, s, 20-H×2), 8.47 (1H, t, J=1 Hz, 2-H of Ph), 8.07 (2H, dd, J=8, 1 Hz, 4-, 6-H of Ph), 7.77 (1H, t, J=8 Hz, 5-H of Ph), 5.32, 5.16 (each 2H, d, J=19 Hz, 13^1-CH_2×2), 4.54 (2H, br q, 18-H×2), 4.36 (2H, br t, 17-H×2), 3.73 (4H, q, J=8 Hz, 8-CH_2×2), 3.70 (6H, s, 12-CH_3×2), 3.63 (6H, s, 17^2-CO_2CH_3×2), 3.62 (6H, s, 2-CH_3×2), 3.37 (6H, s, 7-CH_3×2), 2.76–2.71 (2H, m, 17-CH×2), 2.62–2.58 (2H, m, 17^1-CH×2), 2.34–2.27 (4H, m, 17-CHCH×2), 1.86 (6H, d, J=7 Hz, 18-CH_3×2), 1.72 (6H, t, J=8 Hz, 8^1-CH_3×2), 0.31, −1.81 (each 2H, s, NH×2×2); MS (TOF) found: m/z 1167, calcd for $C_{74}H_{70}N_8O_6$: M^+, 1167.

*4.5.6. Chlorin-dyad **14**.* Similar to the synthesis of **12**, reaction of **4** with 1,4-diiodobenzene gave **14** in 58% yield as a black solid: mp >300 °C; VIS (CH_2Cl_2) λ_{max} 685 (relative intensity, 0.68), 624 (0.09), 545 (0.14), 516 (0.14), 419 (1.00), 324 nm (0.26); IR (CH_2Cl_2) ν_{max} 2202 (C≡C), 1733 (ester-C=O), 1694 (keto-C=O), 1619, 1504 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.65 (2H, s, 5-H×2), 9.55 (2H, s, 10-H×2), 8.65 (2H, s, 20-H×2), 8.11 (4H s, 3^2-C_6H_4), 5.31, 5.16 (each 2H, d, J=19 Hz, 13^1-CH_2×2), 4.54 (2H, br q, 18-H×2), 4.35 (2H, br d, 17-H×2), 3.73 (4H, q, J=8 Hz, 8-CH_2×2), 3.69 (6H, s, 12-CH_3×2), 3.64 (6H, s,

17^2-CO_2CH_3×2), 3.60 (6H, s, 2-CH_3×2), 3.35 (6H, s, 7-CH_3×2), 2.76–2.70 (2H, m, 17-CH×2), 2.63–2.57 (2H, m, 17^1-CH×2), 2.34–2.28 (4H, m, 17-CHCH×2), 1.86 (6H, d, J=7 Hz, 18-CH_3×2), 1.74 (6H, t, J=8 Hz, 8^1-CH_3×2), 0.29, −1.83 (each 2H, s, NH×2×2); MS (TOF) found: m/z 1167, calcd for $C_{74}H_{70}N_8O_6$: M^+, 1167.

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Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.tet.2011.06.020.

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