Synthesis and Properties of Conjugated Porphyrins with a Diacetylene Spacer

Hiroshi IMAHORI, Hiroyuki HIGUCHI,† Yoshihiko MATSUDA,† Ayano ITAGAKI,† Yoshie SAKAI,† Jûro OJIMA,*,† and Yoshiteru SAKATA*

The Institute of Scientific and Industrial Research, Osaka University, Mihoga-oka, Ibaraki, Osaka 567

† Department of Chemistry, Faculty of Science, Toyama University, Gofuku, Toyama 930

(Received March 15, 1994)

A series of (porphyrin)–$(C\equiv C)_2$–C_6H_4–R^1 (R^1=NO_2, H, Me, and OMe) were synthesized by the oxidative coupling of ethynyl porphyrins and phenylacetylenes in the presence of copper(II) acetate in pyridine. Electronic and electrochemical spectra of the compounds with R^1=H, Me, and OMe are quite similar, while pronounced change was observed for the compound with R^1=NO_2, especially for the *meso*-substituted one, indicating that intramolecular charge transfer is responsible for the difference.

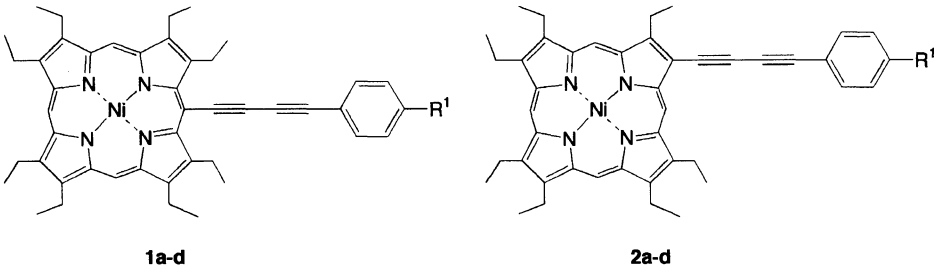
Porphyrin chromophores are widely found in animal and/or plant organisms and are responsible for the peculiar functions of photosynthesis, hemoglobin, P450, and so on.[1] To understand such biological functions, various modified porphyrins have so far been synthesized. On the other hand, the derivatization of porphyrins has also been carried out toward the development of new molecular devices[2] such as "molecular wire", photovoltaic devices, and nonlinear optics, since porphyrins have large π-systems with high HOMO and low LUMO levels. For the further improvement of the unique electronic levels, conjugated porphyrins are required. When a π system such as phenyl and ethylenic chromophores is introduced into the *meso* position of a porphyrin ring for this purpose, no conjugation takes place between the two chromophores due to the large steric hindrance for the planar conformation. Therefore, no substituent effect for absorption spectra of tetraarylporphyrin, where four aryl groups are introduced into the *meso* (5,10,15,20-tetraarylporphyrin)[3] or β position (2,7,12,17-tetraarylporphyrin)[4] of a porphyrin ring, is observed in changing the substituents at aryl ring. An acetylene group with small steric demand is an excellent building block for preparing conjugated arrays containing porphyrins with conformationally rigid structure. Several works along with this line have already appeared.[5—7] However, systematic studies are still lacking especially on push-pull conjugated systems.[8] Here we report the preparation and properties of compounds **1** and **2**, where one end of a diacetylene unit is directly connected to the *meso* or β position of a porphyrin ring and the other end is linked to a substituted phenyl ring. By changing the substituent of **1** and **2** from electron accepting to electron donating group, useful information on porphyrin conjugation is expected to be given (Chart 1).

Results and Discussion

Synthesis of 1 and 2. The synthesis of **1** and the corresponding reference **3** was carried out by using *meso*-ethynylporphyrinatonickel **4**,[9] which was prepared from octaethylporphyrin (OEP) according to Arnold's method,[5] as a key intermediate. Thus, **1a** was prepared by the coupling reaction of **4** with a large excess of 4-nitrophenylacetylene (**5a**)[10] in the presence of copper(II) acetate in pyridine. Purification of the crude products with column chromatography afforded **1a**, in addition to a trace amount of 1,4-bis[2,3,7,8,12,13,17,18-octaethylporphyrinatonickel(II)-5-yl]-1,3-butadiyne[5] and a large amount of 1,4-bis(4-nitrophenyl)-1,3-butadiyne (**6a**) (Chart 2). Similarly, compounds **1b—d** were obtained by the coupling reactions of **4** with the corresponding phenylacetylenes **5b—d**.[11] The reference compound **3** was also prepared by the coupling reaction of **4** with 3,3-dimethyl-1-butyne. Attempts of demetallation of **1** under various conditions were unsuccessful and only decomposed product was obtained.

The key intermediate for the synthesis of **2a—d** is β-ethynylporphyrinatonickel **7** (Chart 3). For the preparation of **7**, we tried at first dehydrobromination of 3-[(*E*)-2-bromovinyl]porphyrin **8**[12] using bases such as K_2CO_3, BuLi, and KOH. However, these attempts were unsuccessful, resulting in the almost recovery or the decomposition of **8**. This may be rationalized that the bulky porphyrin ring hinders the correct approach of the reagents. Therefore, we chose 3-(1-chlorovinyl)-porphyrin **9** instead of **8** with a hope that base is much easily accessible in **9** compared with **8**. Treatment of 3-acetylporphyrin **11**, which was obtained from OEP via 3 steps according to Chang's method,[13] with $POCl_3$ in DMF did not give 3-(1-chlorovinyl)porphyrin **9**,[14] but afforded 3-(1-chloro-2-formylvinyl)porphyrin **12** as a mixture of *Z*,*E*-isomers with 1 : 1 ratio. Dechloroformylation of **12** was successfully carried out by treatment of the isomeric mixture in DMF with an aqueous solution of potassium hydroxide at 0 °C for 30 min to give 3-ethynylporphyrin **13**. The oxidative coupling of **7**, which was derived from **13** with $Ni(OAc)_2$, with a large excess of **5a** gave diacetylene-linked compound **2a**, in addition to a large amount of **6a**. Similarly, compounds **2b—d** were obtained by the coupling reactions of **7** with the corresponding phenylacetylenes **5b—d**.

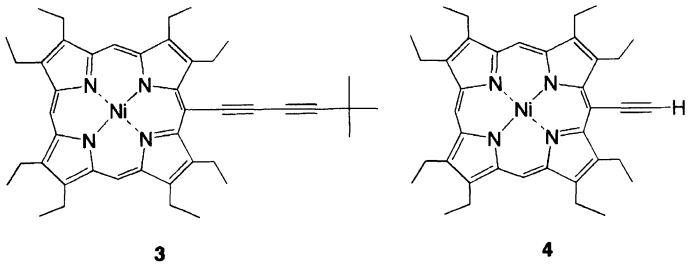
Redox Potentials of 1 and 2. Redox potentials of **1—3**, and **6** were measured with differential pulse voltammetry at a Pt electrode in dichloromethane. The results are summarized in Table 1. From the table,



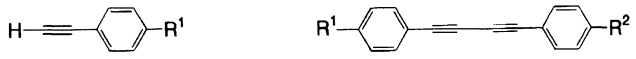
1a-d **2a-d**

a: R^1=NO_2
b: R^1=H
c: R^1=Me
d: R^1=OMe

Chart 1.



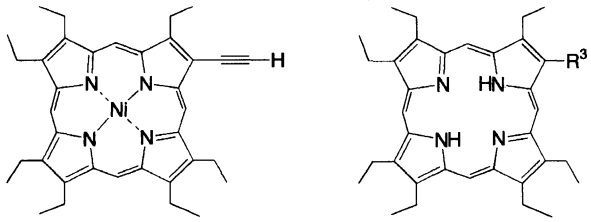
3 **4**



5a-d **6a-f**

a: R^1=R^2=NO_2
b: R^1=R^2=H
c: R^1=R^2=Me
d: R^1=R^2=OMe
e: R^1=H, R^2=NO_2
f: R^1=H, R^2=OMe

Chart 2.



7

8: R^3=-CH=CH-Br
9: R^3=-CCl=CH_2
10: R^3=-CHOH-CH_3
11: R^3=-$COCH_3$
12: R^3=-CCl=CH-CHO
13: R^3=-C≡C-H

Chart 3.

oxidation potentials of both **1** and **2** are higher than that of octaethylporphyrinatonickel(II) (OEP(Ni)) and oxidation potentials of **1** are lower than those of compounds **2**. This means that HOMO level of **1** is higher than that of **2**. Since electron density at the *meso* position of OEP in HOMO level is higher compared with the β position, direct introduction of 4-phenyl-1,3-butadiynyl group into the *meso* position may change the oxidation potential more dramatically than into the β position. Reduction potentials of **1** appears at around -1100 mV. On the other hand, **2b—d** have no signal in this area down to -1400 mV. Therefore, compounds **2** seem to have lower reduction potentials compared with those of **1**. This means that LUMO level of **1** is lower than that of **2**. These results together with the UV-vis spectral data described later indicate that there is more widespread π-conjugation in **1** compared with that in **2**. In contrast to one reduction potential in **1b—d**, **1a** has two peaks. We assigned the peak at -1070 mV of **1a** to be the one-electron reduction of the porphyrin

Table 1. Redox Potentials of **1**—**3**, and **6**[a)]

Compounds	Reduction potentials/mV		Oxidation potentials/mV	
OEP(Ni)			800	1200
1a	−1070	−860	880	1220
1b	−1150		850	1220
1c	−1180		860	1220
1d	−1160		850	1200
2a		−840	1020	1330
2b			990	1320
2c			1000	1320
2d			980	1330
3	−1200		850	1220
6a		−980		
6b	—[b)]			

a) Redox potentials (mV vs. Ag/Ag^+) were measured by differential pulse voltammetry at a Pt electrode, in CH_2Cl_2 containing 0.1 M tetrabutylammonium perchlorate at 20 °C. Experimental errors are within ±10 mV, M=mol dm^{-3}. b) No peak was observed within a sweep range of ±1400 mV.

moiety and the other peak at −860 mV to be that of the nitrophenyldiacetylene moiety, since **1b**—**d** have peaks at around −1100 mV and **2a** and **6a** showed peak at around −900 mV. Compared with **1b**—**d**, **1a** has higher reduction potential due to the porphyrin ring by 80—110 mV, indicating that the electronic state of **1a** is much perturbed by the introduction of nitro group.

UV-visible Spectra of 1 and 2. Electronic spectra of **1**—**3** and octaethylporphyrinatonickel(II) (OEP(Ni)) were measured in dichloromethane. The results are shown in Figs. 1 and 2. Soret and Q bands of **1** and **2** shifted to longer wavelength compared with those of OEP(Ni).[15)] Degree of the red shift for **1** is much larger than that for **2**. Considering the similar tendency observed in redox potentials of **1** and **2**, this may also be due to higher electron density at the *meso* position in HOMO level compared with the β position. Thus, direct introduction of 4-phenyl-1,3-butadiynyl group into the *meso* position changes the electronic state more extensively than into the β position. Compared with the spectrum of the reference compound **3**, both Soret and Q bands of **1b**—**d** are shifted to longer wavelength by about 5—10 nm, due to conjugation between the phenyl group and the porphyrin ring through a diacetylene spacer. The spectra of **1b**—**d** are quite similar in shape as well as in peak position, while pronounced change was observed for **1a**. In the spectrum of **1a** Soret band is splitted into three and Q band becomes quite broad. In a series of **2a**—**d** similar tendency was observed. Thus, only the spectrum of **2a** was different from those of **2b**—**d** as shown in Fig. 2. Characteristics in **2a** are broad Soret band and red-shifted Q band by about 5 nm compared with **2b**—**d**.

To clarify the unusual behavior of **1a** and **2a**, solvent effect was examined for **1a** and **1b** in various solvents with different polarity.[16)] As seen in Figs. 3 and 4, no solvent effect was observed for **1b**, while appreciable change of the spectra was observed for **1a** changing the solvents, from nonpolar hexane to polar acetonitrile. Absorption band at the longest wavelength among the three splitted Soret bands showed blue shift with an increase of the polarity of the solvents, while no solvent effect was observed for the middle band.[17)] The Q band also showed similar blue shift, but the degree of the shift is smaller than that of the Soret bands. The solvent effect described above clearly shows that the ground state of **1a** has polar structure probably due to intramolecular charge transfer (CT).[18)] This situation is quite different in small π-system like benzene. Thus, no CT band is observed for the corresponding phenyl analog **6e**. In conjugated porphyrins intramolecular CT interaction may become more significant due to high HOMO and low LUMO levels.

It is interesting to compare the role of porphyrin ring in π-conjugation with that of phenyl ring. Yen reported[19)] the electronic spectra of **6b**, **6e**, and **6f**, where the porphyrin rings of **1** and **2** are replaced by phenyl rings. The data are summarized in Table 2. The absorption band at the longest wavelength of the parent compound **6b** shifted to longer wavelength by 30 and 9 nm with an introduction of nitro and methoxyl groups, respectively. On the other hand, the absorption band at the longest wavelength of the parent compound **1b** and **2b** showed no shift with an introduction of methoxyl group and shifted to shorter and longer wavelength by 6 nm with an introduction of nitro group, respectively. This may be explained by the large π-electron "pool" of porphyrin ring. Thus, only small perturbation will be given by an introduction of an electron donating or accepting group into conjugated porphyrin system. It should be pointed out that the perturbation is effective only when the electron accepting π-system is linked, especially at the meso position, as shown in Figs. 1 and 2.

In summary, conjugation of porphyrin chromophore with phenyl ring has been achieved in **1** and **2** by using a diacetylene spacer and the conjugation is larger at *meso* position than at β position. Furthermore, appreciable

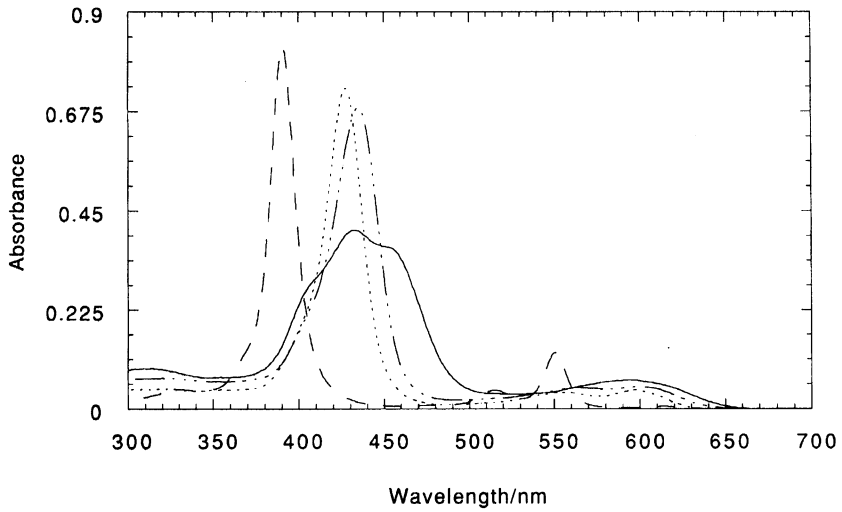


Fig. 1. UV-vis spectra of **1a** (—), **1b** (–···–), **3** (····), and OEP(Ni) (- - -) in CH_2Cl_2 (4.0×10^{-6} mol dm^{-3}).

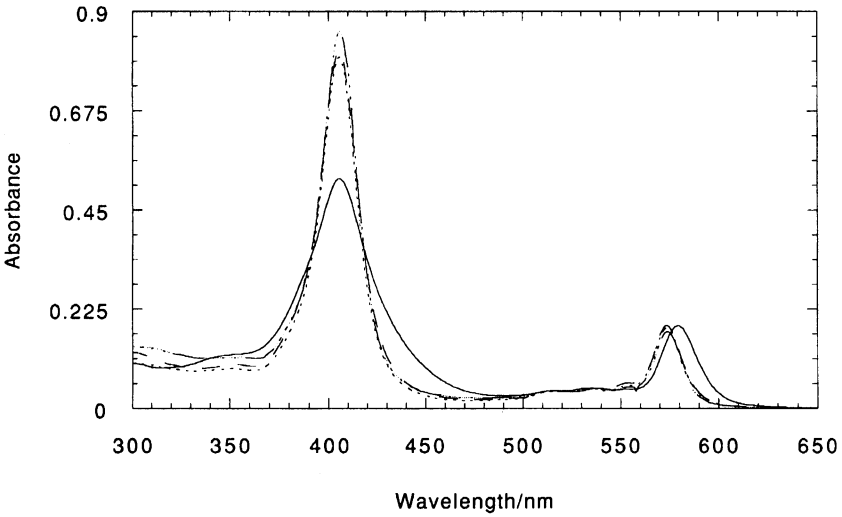


Fig. 2. UV-vis spectra of **2a** (—), **2b** (–···–), **2c** (····), and **2d** (- - -) in CH_2Cl_2 (4.0×10^{-6} mol dm^{-3}).

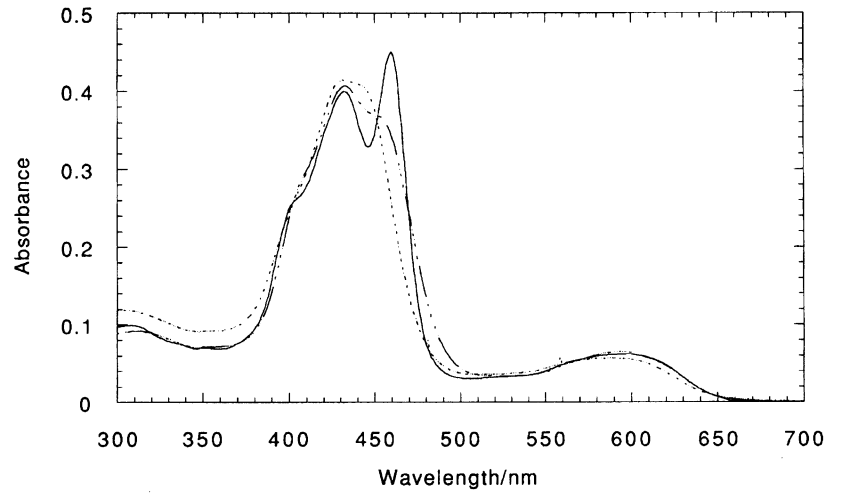


Fig. 3. UV-vis spectra of **1a** (4.0×10^{-6} mol dm^{-3}) in hexane (—), dichloromethane (–···–), and acetonitrile (····).

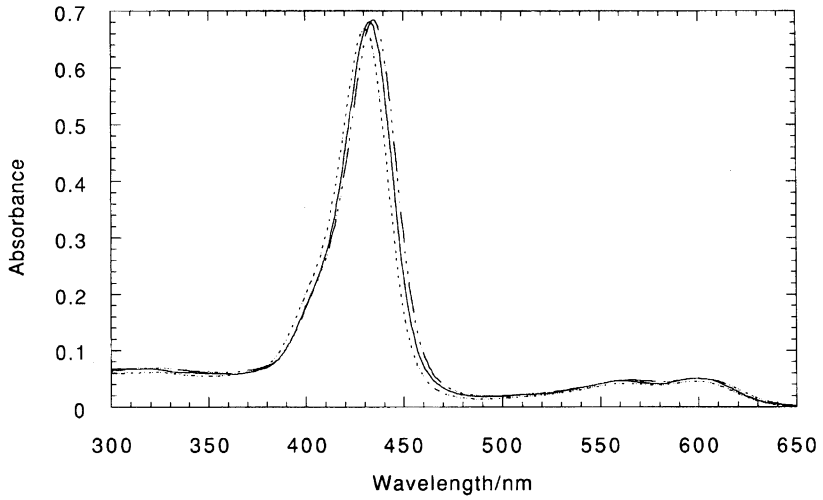


Fig. 4. UV-vis spectra of **1b** (4.0×10^{-6} mol dm^{-3}) in hexane (—), dichloromethane (–···–), and acetonitrile (····).

Table 2. UV-vis Spectra of **6** in EtOH

Compounds	λ_{max}/nm (log ε)
6e	264 (4.12), 279 (4.12), 298 (4.12), 333 (4.36), 356 (4.25)
6b	247 (4.45), 259 (4.42), 287 (4.31), 305 (4.49), 326 (4.46)
6f	259 (4.30), 265 (4.28), 296 (4.33), 315 (4.44), 335 (4.30)

CT interaction is seen only in **1a**, where conjugation of porphyrin takes place at the *meso* position.

Experimental

General. Melting points were recorded on a Yanagimoto apparatus and are not corrected. ^{1}H NMR spectra were measured on a JEOL FX-90Q or a JEOL EX-270. Mass spectra were obtained on a JEOL JMS-DX300. IR and UV-visible spectra were measured on a Hitachi 260-50 spectrophotometer as KBr disks and on a Hitachi 330, respectively. Redox potentials were recorded on Bioanalytical Systems, Inc. CV-50W. Elemental analyses were performed on a Perkin–Elmer Model 240C elemental analyzer.

Starting Material. OEP was prepared by the method given in the literature.[4] Substituted phenylacetylenes were synthesized according to the reported method.[10]

Preparation of 1 and 2. Typical procedure is as follows. To a suspension of copper(II) acetate monohydrate (44 mg, 0.22 mmol) in pyridine (15 ml) was added a solution of ethynylporphyrin **4** or **7** (0.038 mmol) and substituted phenylacetylene **5** (0.14 mmol) in pyridine (15 ml) at 45 °C in a period of 2 h. After additional stirring for 1 h, the reaction mixture was poured onto water and extracted with dichloromethane (150 ml). The combined extract was dried (Na_2SO_4) and the solvent was evaporated. Purification of the crude products was accomplished by column chromatography on silica gel with hexane–benzene (3 : 2) or hexane–chloroform (3 : 1).

1-(4-Nitrophenyl)-4-(2,3,7,8,12,13,17,18-octaethylporphyrinatonickel(II)-5-yl)-1,3-butadiyne (1a): Black-purple crystals from chloroform–methanol; 12% yield; mp 290—292 °C; MS (FAB) *m/z* 762 (MH^+); IR (KBr) 2960, 2925, 2850, 2360, 2340, 2195, 1635, 1460, 1380, 1335, 1060, 1020, 850, 800, 675 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ=1.6—1.9 (24H, m), 3.7—3.9 (12H, m), 4.13 (4H, q, J=7.6 Hz), 7.75 (2H, d, J=9.1 Hz), 8.26 (2H, d, J=9.1 Hz), 9.41 (1H, s), 9.43 (2H, s); UV-vis (CH_2Cl_2) 406 (log ε 4.83), 433 (5.00), 455 (4.97), 594 nm (4.27).

4-(2,3,7,8,12,13,17,18-Octaethylporphyrinatonickel-(II)-5-yl)-1-phenyl-1,3-butadiyne (1b): Black-purple crystals from chloroform–methanol; 12% yield; mp 219—221 °C; MS (FAB) *m/z* 717 (MH^+); IR (KBr) 2960, 2925, 2870, 2350, 2335, 2200, 2135, 1630, 1465, 1450, 1370, 1055, 1020, 960, 840, 665 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ=1.6—1.9 (24H, m), 3.7—3.9 (12H, m), 4.14 (4H, q, J=8.0 Hz), 7.37 (3H, m), 7.62 (2H, m), 9.40 (1H, s), 9.42 (2H, s); UV-vis (CH_2Cl_2) 435 (log ε 5.23), 565 (4.10), 600 nm (3.14).

1-(4-Methylphenyl)-4-(2,3,7,8,12,13,17,18-octaethylporphyrinatonickel(II)-5-yl)-1,3-butadiyne (1c): Black-purple crystals from chloroform–methanol; 16% yield; mp 252—254 °C; MS (FAB) *m/z* 731 (MH^+). IR (KBr) 2965, 2940, 2875, 2360, 2295, 2195, 1560, 1435, 1375, 1060, 1055, 1020, 960, 845, 810, 690 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ=1.6—1.9 (24H, m), 2.37 (3H, s), 3.7—3.9 (12H, m), 4.15 (4H, q, J=7.3 Hz), 7.17 (2H, d, J=7.9 Hz), 7.51 (2H, d, J=7.9 Hz), 9.38 (1H, s), 9.41 (2H, s); UV-vis (CH_2Cl_2) 436 (log ε 5.23), 564 (4.10), 600 nm (3.14).

1-(4-Methoxyphenyl)-4-(2,3,7,8,12,13,17,18-octaethylporphyrinatonickel(II)-5-yl)-1,3-butadiyne (1d): Black-purple crystals from chloroform–methanol; 15% yield; mp 241—243 °C; MS (FAB) *m/z* 747 (MH^+). IR (KBr) 2950, 2905, 2850, 2355, 2325, 2135, 1605, 1510, 1250, 1175, 1060, 1015, 965, 845, 835, 675 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ=1.6—1.9 (24H, m), 3.7—3.9 (12H, m), 3.83 (3H, s), 4.15 (4H, q, J=7.3 Hz), 6.90 (2H, d, J=8.9 Hz), 7.56 (2H, d, J=8.9 Hz), 9.39 (1H, s), 9.41 (2H, s); UV-vis (CH_2Cl_2) 438 (log ε 5.23), 564 (4.10), 600 nm (3.14).

4-(3,7,8,12,13,17,18-Heptaethylporphyrinatonickel-(II)-2-yl)-1-(4-nitrophenyl)-1,3-butadiyne (2a): Red-

purple crystals from hexane–benzene; 90% yield; mp 266 °C (decomp); MS (EI) m/z 731 (M^+); MS (High-resolution) Found: m/z 731.2740. Calcd for $C_{44}H_{43}N_5O_2Ni$: M, 731.2766. IR (KBr) 2965, 2930, 2870, 2200, 1590, 1520, 1340, 1055, 1020, 850, 745 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ=1.6—2.1 (21H, m), 3.7—4.3 (14H, m), 7.68 (2H, d, J=8.4 Hz), 8.23 (2H, d, J=8.4 Hz), 9.71 (2H, br.s), 9.81 (1H, s), 9.94 (1H, s); UV-vis (CH_2Cl_2) 405 ($\log\varepsilon$ 5.27), 514 (4.14), 538 (4.19), 579 nm (4.82).

4-(3,7,8,12,13,17,18-Heptaethylporphyrinatonickel-(II)-2-yl)-1-phenyl-1,3-butadiyne (2b): Red-purple crystals from chloroform–methanol; 98% yield; mp 270 °C (decomp); MS (EI) m/z 686 (M^+); MS (High-resolution) Found: m/z 686.3019. Calcd for $C_{44}H_{44}N_4Ni$: M, 686.2918. IR (KBr) 2965, 2930, 2870, 2205, 2140, 1630, 1550, 1225, 1020, 755, 690 cm^{-1}; ^1H NMR (90 Mz, $CDCl_3$) δ=1.7—2.0 (21H, m), 3.6—4.1 (14H, m), 7.2—7.5 (3H, m), 7.6—7.9 (2H, m), 9.64 (2H, br.s), 9.69 (1H, s), 9.91 (1H, s); UV (CH_2Cl_2) 406 ($\log\varepsilon$ 5.40), 534 (4.06), 573 nm (4.75).

4-(3,7,8,12,13,17,18-Heptaethylporphyrinatonickel-(II)-2-yl)-1-(4-methylphenyl)-1,3-butadiyne (2c): Red-purple crystals from hexane–benzene; 80% yield; mp 273 °C (decomp); MS (EI) m/z 700 (M^+); MS (High-resolution) Found: m/z 700.3075. Calcd for $C_{45}H_{46}N_4Ni$: M, 700.3075. IR (KBr) 2960, 2930, 2870, 2200, 2140, 1545, 1465, 1450, 1225, 1020, 815, 755, 700 cm^{-1}; ^1H NMR (90 Mz, $CDCl_3$) δ=1.7—2.0 (21H, m), 2.42 (3H, s), 3.7—4.3 (12H, m), 7.29 (2H, d, J=8.1 Hz), 7.63 (2H, d, J=8.1 Hz), 9.67 (2H, br.s), 9.73 (1H, s), 9.94 (1H, s); UV-vis (CH_2Cl_2) 405 ($\log\varepsilon$ 5.40), 536 (4.10), 551 (4.20), 573 nm (4.76).

4-(3,7,8,12,13,17,18-Heptaethylporphyrinatonickel-(II)-2-yl)-1-(4-methoxyphenyl)-1,3-butadiyne (2d): Red-purple crystals from hexane–benzene; 75% yield; mp 271 °C (decomp); MS (EI) m/z 716 (M^+); MS (High-resolution) Found: m/z 716.3057; Calcd for $C_{45}H_{46}N_4ONi$: M, 716.3022. IR (KBr) 2965, 2930, 2870, 2200, 2140, 1640, 1605, 1510, 1250, 1055, 1020, 830, 750 cm^{-1}; ^1H NMR (90 Mz, $CDCl_3$) δ=1.7—2.0 (21H, m), 3.7—4.3 (14H, m), 3.89 (3H, s), 6.98 (2H, d, J=9.4 Hz), 7.67 (2H, d, J=9.4 Hz), 9.71 (2H, br.s), 9.78 (1H, s), 9.97 (1H, s); UV-vis (CH_2Cl_2) 405 ($\log\varepsilon$ 5.41), 532 (4.06), 553 (4.25), 573 nm (4.77).

5,5-Dimethyl-1-(2,3,7,8,12,13,17,18-octaethylporphyrinatonickel(II)-5-yl)-1,3-hexadiyne (3):[15] Red-purple crystals from chloroform–methanol; 36% yield; mp 260—262 °C; MS (FAB) m/z 697 (MH^+); IR (KBr) 2985, 2880, 2825, 2355, 2340, 2220, 1645, 1450, 1235, 1145, 1055, 1020, 960, 840, 690 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ=1.48 (9H, s), 1.8—2.0 (24H, m), 4.0—4.2 (12H, m), 4.33 (4H, q, J=7.3 Hz), 9.97 (1H, s), 10.05 (2H, s); UV-vis (CH_2Cl_2) 428 ($\log\varepsilon$ 5.26), 556 (3.88), 598 nm (4.00).

1,4-Bis(4-nitrophenyl)-1,3-butadiyne (6a): Pale yellow needles from dichloromethane; mp 272—273 °C; MS (EI) m/z 292 (M^+); Found: C, 65.90; H, 2.90; N, 9.59%. Calcd for $C_{16}H_8N_2O_4$: C, 65.75; H, 2.76; N, 9.40%. IR (KBr) 3050, 2840, 2155, 1590, 1510, 1340, 1320, 1105, 860, 850, 745 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ=7.62 (4H, d, J=8.9 Hz), 8.18 (4H, d, J=8.9 Hz).

2-Acetyl-3,7,8,12,13,17,18-heptaethylporphyrin (11): To a solution of (1-hydroxyethyl)porphyrin **10**[13] (50 mg, 0.091 mmol) in dichloromethane (10 ml) and acetone (5 ml) was added Jone's reagent (50 µl, prepared from CrO_3 (5.3 g), concd H_2SO_4 (4.6 ml), and H_2O (20 ml)). The mixture was stirred at 0 °C for 2.5 h, diluted with dichloromethane (100 ml), washed with water, and then dried. After removal of the solvent the residue was chromatographed on silica gel with benzene. Crude product (32 mg, 64% yield) was recrystallized from dichloromethane–hexane to form **11** as purple crystals **11**: Mp >300°C; MS (EI) m/z, 548 (M^+); Found: C, 78.65; H, 8.12; N, 10.26%. Calcd for $C_{36}H_{44}N_4O$: C, 78.79; H, 8.08; N, 10.21%. IR (KBr) 3300, 2850, 2730, 1660 cm^{-1}; ^1H NMR (90 Mz, $CDCl_3$) δ=−3.63 (2H, br.s), 1.7—2.1 (21H, m), 3.34 (3H, s), 3.8—4.5 (14H, m), 9.99 (2H, br.s), 10.13 (1H, s), 10.73 (1H, s).

2-(1-Chloro-2-formylvinyl)-3,7,8,12,13,17,18-heptaethylporphyrin (12): To a stirred solution of acetylporphyrin **11** (630 mg, 1.15 mmol) in dry DMF (250 ml) and dry benzene (210 ml) was added phosphoryl chloride (3.4 ml). Stirring was continued at room temperature overnight. The mixture was diluted with benzene, poured onto water, extracted with benzene, washed with water successively, and then dried. After removal of the solvent the residue was chromatographed on silica gel with benzene to give a 1:1 isomeric mixture (400 mg, 59%) of **12a** and **12b**. Preparative separation of the mixture with benzene afforded **12a** in the upper band and **12b** in the lower one.

12a: Bluish purple plates; mp 229—230 °C; MS (EI) m/z, 594 (M^+); Found: C, 74.36; H, 7.37; N, 9.17%. Calcd for $C_{37}H_{43}N_4ClO$: C, 74.66; H, 7.28; N, 9.41%. IR (KBr) 3300, 2870, 1680, 1615 cm^{-1}; ^1H NMR (90 MMz, $CDCl_3$) δ=−3.70 (2H, br.s), 1.8—2.1 (21H, m), 3.9—4.3 (14H, m), 7.36 (1H, d, J=7.7 Hz), 9.48 (1H, d, J=7.7 Hz), 10.02 (1H, s), 10.09 (1H, s), 10.11 (1H, s), 10.22 (1H, s); UV-vis (THF) 406 ($\log\varepsilon$ 5.09), 505 (3.94), 542 (4.10), 568 (3.86), 576 (3.83).

12b: Black purple micro crystals; mp 257—259 °C; MS (EI) m/z, 594 (M^+); Found: C, 74.42; H, 7.36; N, 9.38%. Calcd for $C_{37}H_{43}N_4ClO$: C, 74.66; H, 7.28; N, 9.41%. IR (KBr) 3300, 2870, 1675, 1605 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ=−3.69 (2H, br.s), 1.8—2.1 (21H, m), 3.9—4.4 (14H, m), 7.04 (1H, d, J=7.1 Hz), 10.09 (2H, br.s), 10.19 (2H, br.s), 10.73 (1H, d, J=7.1 Hz); UV-vis (THF) 408 ($\log\varepsilon$ 5.01), 504 (3.84), 542 (4.03), 568 (3.80), 576 nm (3.74).

2-Ethynyl-3,7,8,12,13,17,18-heptaethylporphyrin (13): To a stirred solution of an isomeric mixture of **12** in DMF (40 ml) was added aqueous potassium hydroxide (0.6 ml, prepared from KOH (90 mg) and H_2O (2.0 ml)). After additional stirring at 0 °C for 30 min, the mixture was diluted with benzene, poured onto water, extracted with benzene. The extracts were washed with water and dried. After removal of the solvent, the residue was chromatographed on silica gel with hexane and benzene (7:3) to give 20 mg (22%) of **13**. Recrystallization from hexane–dichloromethane gave pure **13** as black purple needles, mp >282°C (decomp); MS (EI) m/z, 530 (M^+); Found: C, 81.76; H, 8.04; N, 10.26%. Calcd for $C_{36}H_{42}N_4$: C, 81.47; H, 7.98; N, 10.56%. IR (KBr) 3375, 3280, 2090 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ=−3.70 (2H, br.s), 1.8—2.1 (21H, m), 3.9—4.3 (15H, m), 10.08 (1H, s), 10.10 (1H, s), 10.14 (1H, s), 10.37 (1H, s); UV-vis (THF) 391 ($\log\varepsilon$ 4.86), 402 (5.09), 503 (3.98), 507 (3.97), 542 (4.17), 570 (3.83), 578 (3.70), 625 (3.26), 633 nm (3.11).

2-Ethynyl-3,7,8,12,13,17,18-heptaethylporphyrinatonickel(II) (7): To a solution of ethynylporphyrin **13** (20 mg, 0.038 mmol) in chloroform (5 ml) was added a hot saturated methanol solution of nickel(II) acetate. The

mixture was refluxed under argon atmosphere for 30 h. After removal of the solvent, the residue was chromatographed on alumina with dichloromethane to give 18 mg (81%) of **7**. The spectra were in agreement with those in the literature.[5)]

We thank Material Analysis Center of ISIR for the measurement of mass spectra and elemental analyses. This work was supported by the Grant-in-Aids (No. 04403007 to Y. S., No. 05740393 to H. I., No. 05453029 to J. O., and No. 05640650 to H. H.) from the Ministry of Education, Science and Culture, a grant from The Tamura Foundation for the Promotion of Science and Technology, and a grant from The Japan Securities Scholarship Foundation.

References

1) "Porphyrins and Metalloporphyrins," ed by K. M. Smith, Elsevier, Amsterdam (1975); "The Porphyrins," ed by D. Dolphin, Academic Press, New York (1978).

2) J. M. Lehn, *Angew. Chem., Int. Ed. Engl.*, **27**, 89 (1988).

3) D. W. Thomas and A. E. Martell, *J. Am. Chem. Soc.*, **78**, 1338 (1956).

4) N. Ono, H. Kawamura, M. Bougauchi, and K. Maruyama, *Tetrahedron*, **46**, 7483 (1990).

5) D. P. Arnold, A. W. Johnson, and M. J. Mahendran, *J. Chem. Soc., Perkin Trans. 1*, **1978**, 366; D. P. Arnold and L. J. Nitschinsk, *Tetrahedron*, **48**, 8781 (1992).

6) K. Maruyama and S. Kawabata, *Bull. Chem. Soc. Jpn.*, **63**, 170 (1990).

7) H. L. Anderson and J. K. M. Sanders, *Angew. Chem., Int. Ed. Engl.*, **29**, 1400 (1990); H. L. Anderson and J. K. M. Sanders, *J. Chem. Soc., Chem. Commun.*, **1989**, 1714.

8) A. E. Stiegman, E. Graham, K. J. Perry, L. R. Khundkar, L. -T. Chang, and J. W. Perry, *J. Am. Chem. Soc.*, **113**, 7658 (1991); C. Dehu, F. Meyers, and J. L. Brédas, *J. Am. Chem. Soc.*, **115**, 6198 (1993); L. -T. Cheng, W. Tam, S. H. Stevenson, G. R. Meredith, G. Rikken, and S. R. Marder, *J. Phys. Chem.*, **95**, 10631 (1991).

9) *meso*-Ethynylporphyrinatonickel **4** was not stable so that **4** was used immediately after preparation from bromovinylporphyrin without purification.

10) T. Kurihara, E. Fumihira, and H. Tabei, *Chem. Abstr.*, **105**, 42449v (1986).

11) A. Uchida, T. Nakazawa, I. Kondo, N. Iwata, and H. Matsuda, *J. Org. Chem.*, **37**, 3749 (1972); M. Cariou, *Tetrahedron*, **47**, 799 (1991).

12) M. G. H. Vicente and K. M. Smith, *Synlett*, **1990**, 579.

13) C. K. Chang and C. Sotiriou, *J. Org. Chem.*, **52**, 926 (1987).

14) A. F. Mironov, D. T. Kozhich, V. I. Vasilevsky, and R. P. Evstigneenva, *Synthesis*, **1979**, 533.

15) H. Imahori, Y. Tanaka, T. Okada, and Y. Sakata, *Chem. Lett.*, **1993**, 1215.

16) Since **2a** was quite insoluble in hexane and acetonitrile, electronic spectra of **2a** could not be obtained.

17) Spectral fitting was carried out with gaussian function by using PeakFit v.3.0. We could not get reasonable result for fitting the absorption band at the shortest wavelength among the three splitted Soret bands.

18) F. Foster, "Organic Charge-Transfer Complexes," in "Organic Chemistry, A Series of Monographs," ed by A. T. Blomquist, Academic Press, New York (1969), Vol. 15, p. 33.

19) M. Vo-Quang Yen, *Ann. Chim.*, **7**, 785 (1962).