Synthesis and Properties of Tris(octaethylporphyrin)s Connected with Vinylene Groups

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Tris(octaethylporphyrin)s, in which two octaethylporphyrin (OEP) rings are connected with vinylene groups at α,γ- and α,β-*meso* positions of the central OEP ring, were synthesized. The tris(OEP)s have similar conformational and configurational structures to the corresponding vinylene group-connected bis(OEP). Examination of both ^{1}H NMR and electronic absorption spectra of the tris(OEP)s showed the behavior reflecting the highly symmetrical structure and the mutual interaction between the three OEP rings through the vinylene linkages.

In recent years, porphyrin-based oligomers have received much attention in the studies on the optical, electronical, photophysical, and biological properties of various functionalizing organic assemblies.[1] The vinylene group-connected bis(octaethylporphyrin) [bis(OEP)] **1-H$_2$**, which was first synthesized by Ponomarev and Shul'ga,[2] proved to be a useful model compound for the study on the primary charge separation process in photosynthesis.[3] We previously reported the features of the bis(OEP) **1-M** and showed that the electron-releasing ability of **1-M** increases by the electronic interaction between the two OEP rings through the vinylene-linkage, as compared with that of **OEP-M**.[4] To continue our investigations on the properties of OEP oligomers, we synthesized the tris(OEP)s **2**[5a] and **3**, in which two outer OEP rings are connected with the vinylene-linkage at α,γ- and α,β-*meso* positions of the central OEP ring, respectively. Here we describe the synthesis, spectral, and electrochemical properties of these isomeric tris(OEP)s **2** and **3** (Chart 1).

Results and Discussion

Synthesis. In 1977, Arnold et al. reported that the reaction of the **OEP-Ni** methanol **6** with concd H_2SO_4 gave the ethylene group-connected bis(OEP) **7-Ni**.[6] In 1986, Ponomarev and Shul'ga prepared **1-H$_2$** by dehydrogenation of **7-H$_2$** with refluxing AcOH.[2] According to their procedures, we synthesized **2** and **3**, employing the cross coupling of methanol **6** with bis(hydroxymethyl)porphyrin **10** or **11**, followed by dehydrogenation of the coupling product, as illustrated in Scheme 1.

The OEP nickel(II) complex **4**[7] reacted with 100 molar amounts of the Vilsmeier reagent ($POCl_3$/DMF) to **4**, affording the carbaldehyde **5** in ca. 90% yield.[6] Similarly, the formylation of **4** with 550 molar amounts of the Vilsmeier reagent gave a mixture of **8** and **9** in almost 1 : 1 ratio in ca. 70% yield, which can be separated by column chromatography on SiO_2. Reduction of **5**, **8**, and **9** with $NaBH_4$ gave the corresponding methanols, **6**, **10**, and **11**, respectively, in good yields.

According to the Arnold procedure,[6] a mixture of the methanols **6** and **10** in DMF containing concd H_2SO_4 was refluxed (Method A, see Experimental) to afford the crude **12-Ni** which contains partially dehydrogenated products along with the ethylene group-connected bis(OEP) **7-Ni**. The yield of the tris(OEP) products **12-Ni** was ca. 5%. Another synthesis of **12-Ni** was attempted by adding a solution of concd H_2SO_4 in DMF to the refluxing solution of **6** and **10** (Method B,[5a] see Experimental). Similar products to those obtained by Method A formed in ca. 15% yield. The coupling of **6** with the α,β-bis(methanol) **11** was also carried out by Method B to give the crude **13-Ni** in ca. 10% yield. However, neither **12-Ni** nor **13-Ni** could be separated to each product by means of either column chromatography or fractional recrystallization or both. Removal of the Ni(II) ion from **12-Ni** or **13-Ni** was performed by stirring the tris(OEP)s mixture in concd H_2SO_4 at room temperature to afford **12-H$_2$** or **13-H$_2$**, respectively, in quantitative yields. However, these products could not be separated by column chromatography either. Without further purification, the crude **12-H$_2$** or **13-H$_2$** was subjected to the following reaction employing Ponomarev procedure. Conversions from the ethylene group-connected tris(OEP)s **12-H$_2$** and **13-H$_2$** to the vinylene group tris(OEP)s **2-H$_2$** and **3-H$_2$**, respectively, smoothly proceeded in AcOH at 65 °C.[2,3] The products could be purified by column chromatography on SiO_2 to give pure **2-H$_2$** and **3-H$_2$**.

An attempt of metallation for **2-H$_2$** was first carried out with nickel(II) acetate tetrahydrate [$Ni(OAc)_2 \cdot 4H_2O$] in refluxing $CHCl_3$–MeOH[7] to give a mixture of the partially

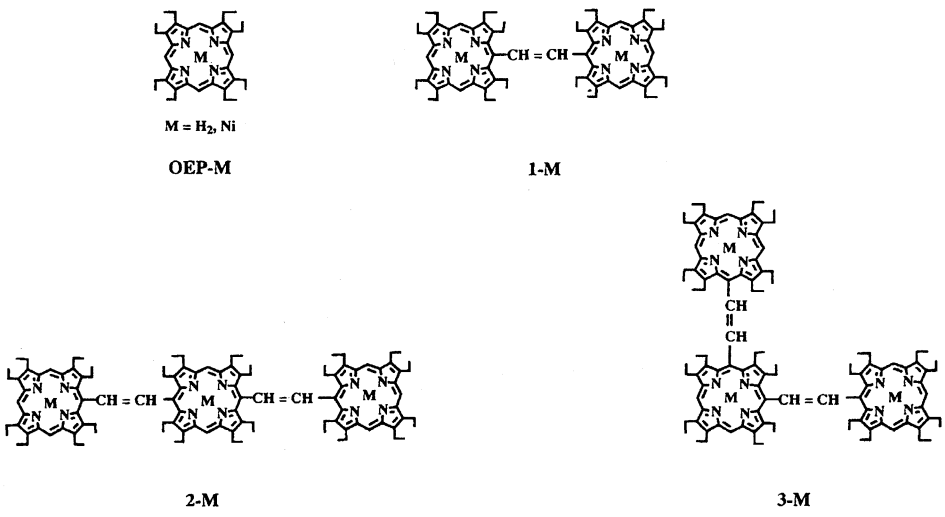
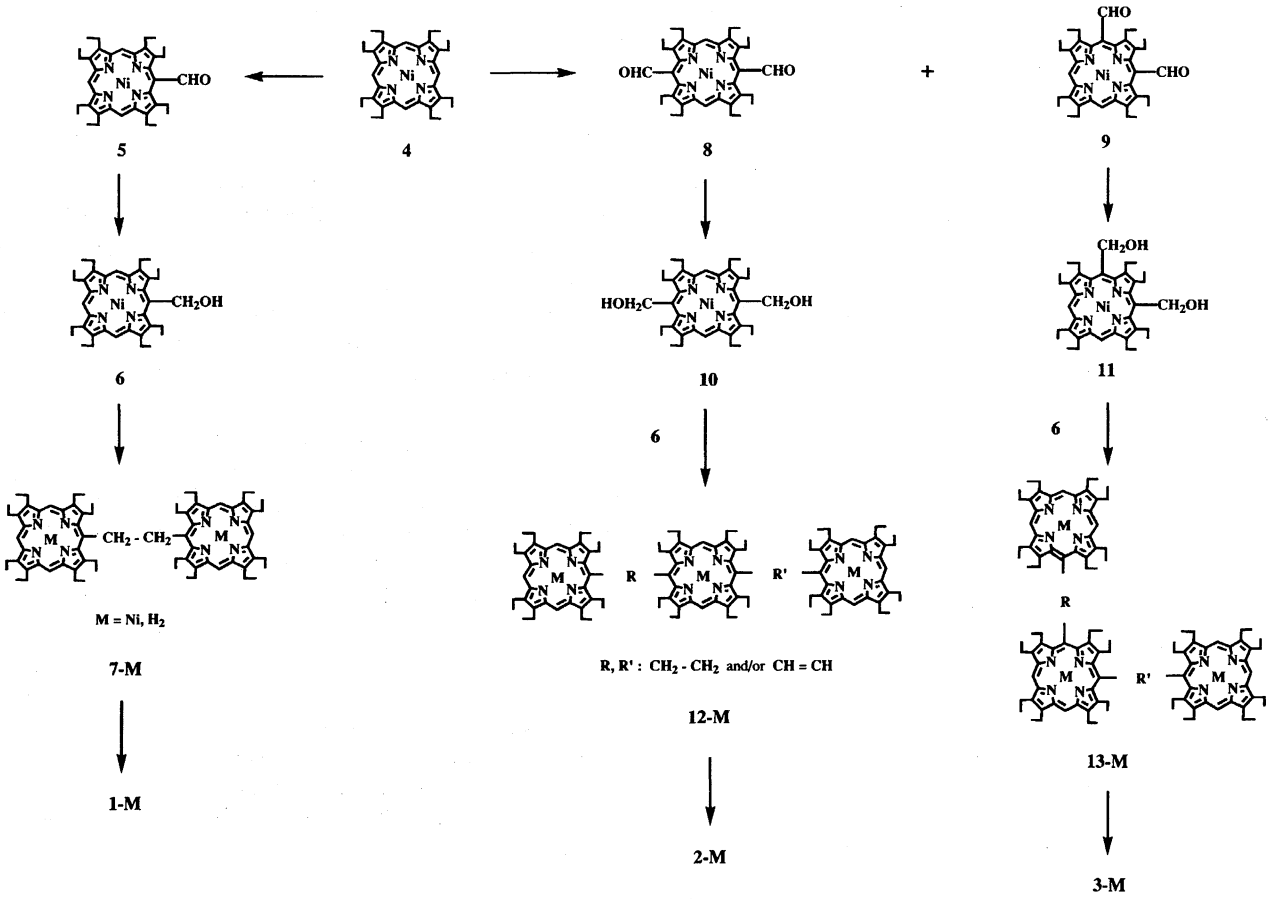


Chart 1.



Scheme 1.

metallated products. However, according to the successful procedure for metallation of the bis(OEP) **1-H_2** with $Ni(OAc)_2 \cdot 4H_2O$ in DMF at 105—110 °C,[4a] the α,γ-tris(OEP) nickel(II) complex **2-Ni** was obtained quantitatively. Employing the same procedure, the α,β-isomer **3-Ni** was obtained in ca. 90%.

It is noteworthy that the cross coupling reaction for the preparation of tris(OEP)s **12-Ni** and **13-Ni** gave a mixture of the ethylene and vinylene groups-connected tris(OEP)s. On the other hand, the homo coupling reaction of the methanol **6** for preparation of the bis(OEP) **7-Ni** gives only the ethylene connected bis(OEP), with no formation of the vinylene connected bis(OEP).[6] In the case of preparation of tris(OEP)s, the vinylene group-connected bis(OEP) **1-Ni** was not obtained either. These results indicate that the ethylene-linkage in the tris(OEP)s shows higher reactivity for dehydrogenation than that in the bis(OEP). The vinylene-linkage of the bis(OEP) **1-H_2** is reported to isomerize in refluxing

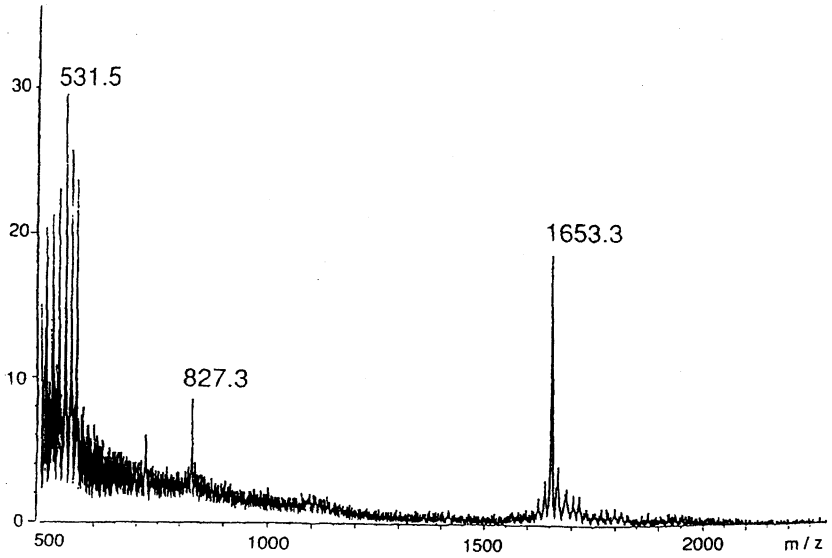


Fig. 1. FAB mass spectrum of **2-H_2**.

AcOH (115 °C) to give an equilibrium mixture of the trans and cis isomers.[4a] However, the geometry of the vinylene-linkages in the tris(OEP) **2-H_2** remained unchanged after refluxing in AcOH.

Mass Spectra. It was useful to take the FAB mass spectra with a Profile program for the structural determination of the tris(OEP) products, because the molecular weights of the vinylene group-connected tris(OEP)s **2-H_2** and **3-H_2** and the ethylene group-connected tris(OEP)s **12-H_2** and **13-H_2** are very close to each other and differ in mass number only by four hydrogen atoms.

As shown in Fig. 1, the spectrum of **2-H_2** clearly exhibited the peak of *m/z* 1653.3 (M^++1) for the molecular weight (1652.3) of the tris(OEP) formula $C_{112}H_{138}N_{12}$ and of *m/z* 531.5 for the OEP formula $C_{36}H_{46}N_4$. No peak was observed between the *m/z* 1090 and 1120, corresponding to the mass numbers for the binucleic OEP spieces. A similar spectrum was obtained for **3-H_2**. It is known that the bis-

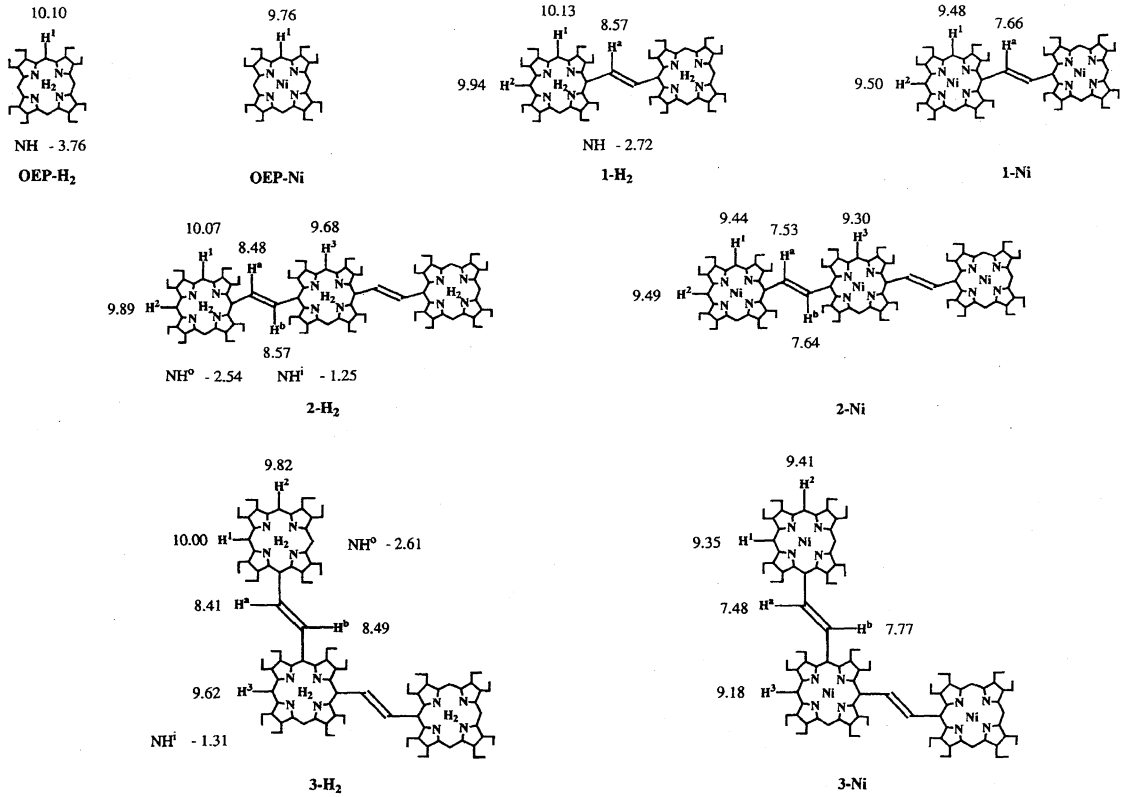
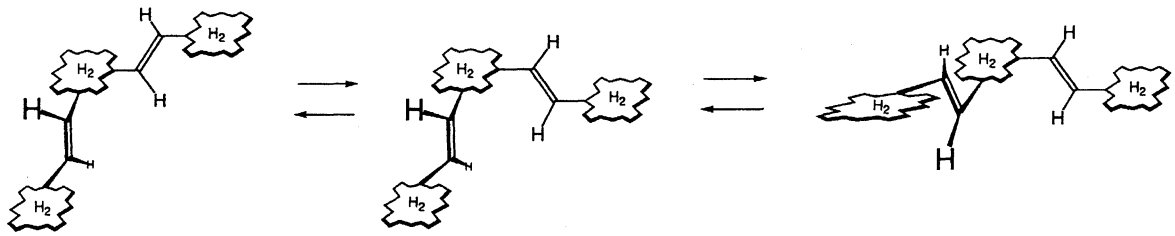


Chart 2.



U, U - Form U, D - Form D, D - Form

Fig. 2. Interconversion between the atropisomers, **U,U-**; **U,D-**; and **D,D-**Forms of **3-H$_2$**.

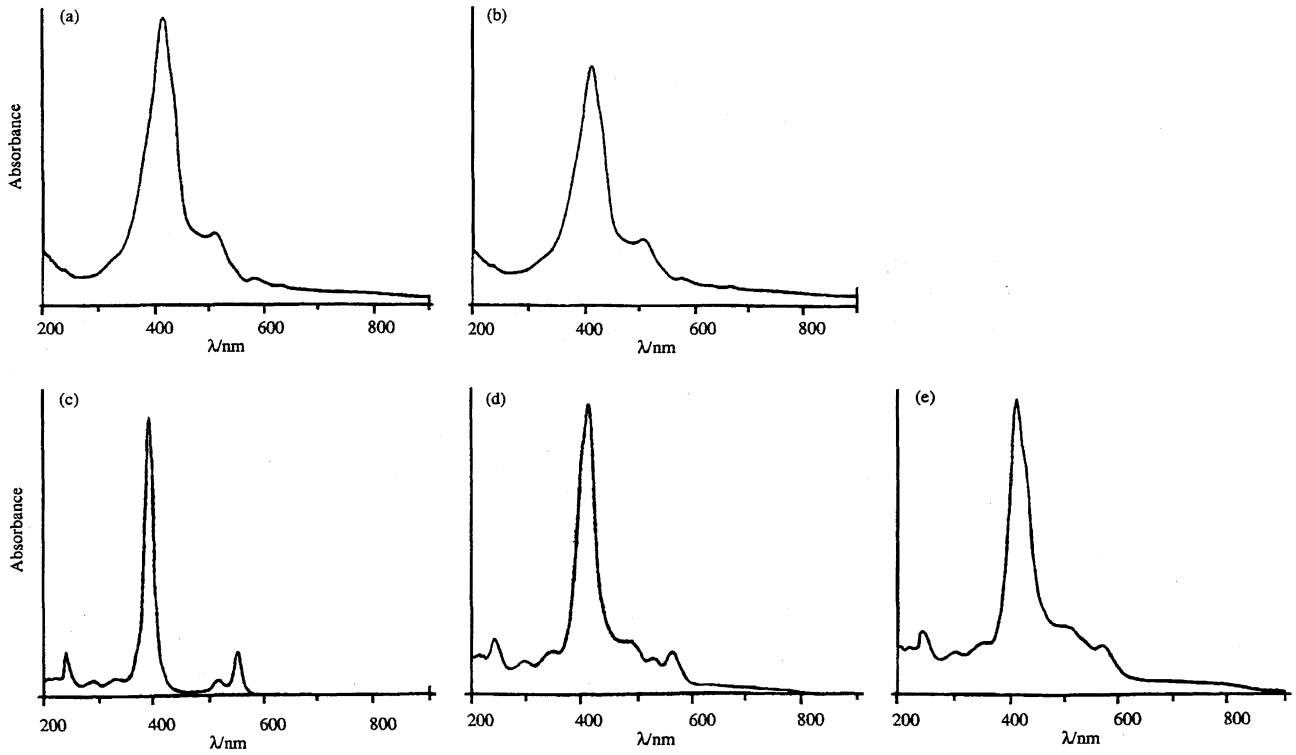


Fig. 3. Electronic absorption spectra of the OEP derivatives; (a) **2-H$_2$**, (b) **3-H$_2$**, (c) **OEP-Ni**, (d) **1-Ni**, and (e) **2-Ni**.

(OEP) **1-H$_2$** exhibits the molecular ion peak *m/z* 1092 (M^+) clearly.[14] These results may suggest that the fragmentation by the fast atomic bombardment ionization begins with the simultaneous double fission of the C–C bond between the vinylene group carbon and the carbon at *meso* position of the central OEP ring in the trimers, producing three OEP rings, and/or that the bis(OEP) bearing the vinyl substituent at γ position to the vinylene-linkage is too labile to be observed within the time-scale of the spectrometer.

^{1}H NMR Spectra. The ^{1}H NMR spectra of all compounds described in this study were taken in $CDCl_3$ at 25 °C, unless otherwise stated. Chemical shifts of the selected protons are summarized in Chart 2.

The spectra of **2-H$_2$** and **3-H$_2$** exhibited two broad singlets of NH protons, multiplet of methylene protons at around 4 ppm, and a pair of doublets of the bridging CH=CH protons with a coupling constant of 15 Hz. If the tris(OEP) has one or two cis double bonds, in other words, partially or fully face-to-face structure, signals of methylene protons of ethyl groups adjacent to the vinylene-linkage should show a characteristic pattern with complex multiplet at higher field in the region of 2.5—4.0 ppm, as seen in the spectrum of the *cis* **1-H$_2$**.[4a] The *meso* protons appeared as three kinds of singlet signals in both cases of **2-H$_2$** and **3-H$_2$**. In a series of the free-bases, the *meso* H^1 proton signals of the **OEP-H$_2$**, the bis(OEP) **1-H$_2$**, and the tris(OEP)s **2-H$_2$** and **3-H$_2$** appeared at around 10 ppm. On the other hand, the signals of the H^2 protons attached at γ position to the vinylene group in both the bis- and tris(OEP)s shifted to higher field by 0.16—0.28 ppm from those of the *meso* proton of **OEP-H$_2$** and the *meso* H^3 proton signals of the central OEP rings in the tris(OEP)s shifted by more than 0.4 ppm. **2-Ni** and **3-Ni** showed spectra similar to those of **2-H$_2$** and **3-H$_2$**. These results suggest that the tris(OEP) **2-M** or **3-M** possesses the simply extended structure which retains the similar conformational and configurational properties to that of the bis(OEP) **1-M** (see below).[2,4a,8]

The NH proton signals shifted to the low field in the

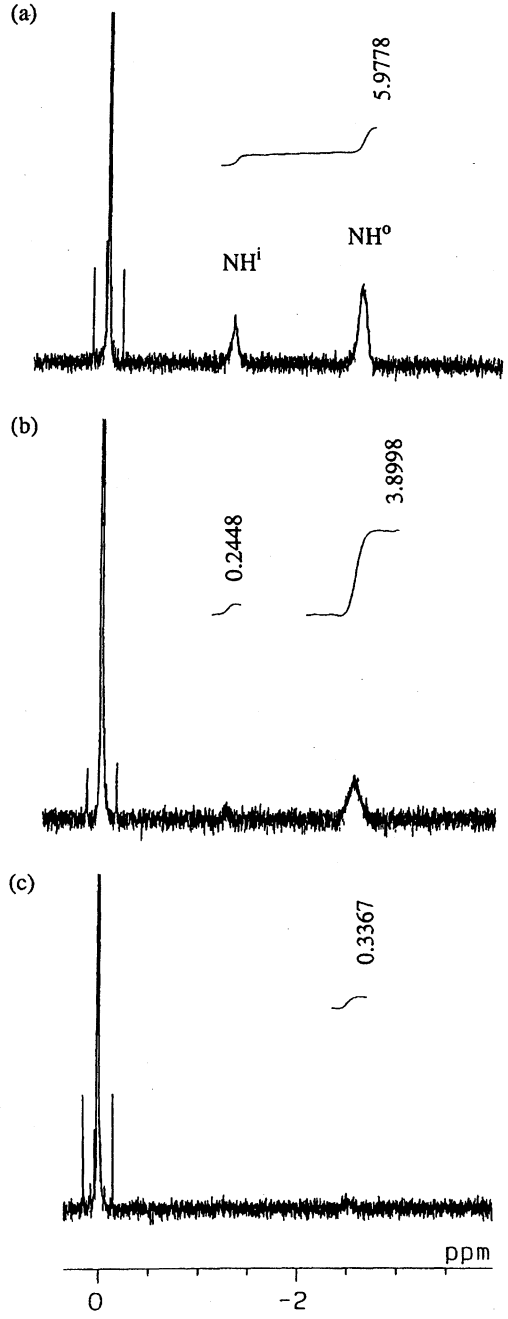


Fig. 4. ^{1}H NMR spectra for H–D exchange experiment of **2-H$_2$** in $CDCl_3$ solution (0.33 mg in 440×10^{-3} cm^3) after addition of D_2O (165×10^{-3} cm^3) at 30 °C; (a) without addition of D_2O (original), (b) after 1 min, and (c) after 42 min.

order of **OEP-H$_2$** > bis(OEP) > tris(OEP), suggesting that oligomerization causes a decrease in the diamagnetic ring current of **OEP-H$_2$**. The ring current of **OEP-H$_2$** also decreases by metallation with the Ni(II) ion,[7,9] resulting in the up-field shift of the *meso* proton signal of **OEP-Ni** by 0.34 ppm above that of **OEP-H$_2$**. The tendency of shifting to the up-field of the *meso* proton signals in the Ni(II) complexes is more pronounced in the bis- and tris(OEP)s. Furthermore, a large up-field shift of the signals of the vinylene-linkage protons of the Ni(II) complexes from those of the corresponding free-bases was observed, probably due to the conformational changes around the vinylene-linkage arising from metallation rather than from the ring current effect.[10] However, the extent of up-field shift for those protons was almost the same for the α,β- and the α,γ-tris(OEP)s, although these have different structures.

In contrast with the appearance of the sharp signals for all protons of **1-H$_2$**,[2–4] one of the three *meso* protons (H^3) and the olefinic proton at the low field (H^b) of **3-H$_2$** showed broader signals, as compared with the other *meso* and olefinic protons. Thus, the coupling constant of the olefinic H^b proton was ambiguous at room temperature, though it was confirmed by the C–H COSY measurement that H^b protons are correlated with H^a. The signals due to these H^3 and H^b protons in **3-H$_2$** became sharp and showed large intensities with the increasing temperature. Similar spectral behavior was also observed for **2-H$_2$**.[5a] It was reported that the *meso*-protons of α,γ-dialkylporphyrins show the same spectral changes with the increasing temperature,[11] as observed for these tris(OEP)s. The spectral properties for the *meso* protons of α,γ-dialkyl-OEP were ascribed to a dynamic interconversion between two conformers which have a 'roof-like' structure (*syn*-form) and 'twisted' structure (*anti*-form), arising from the steric hindrance between the *meso* alkyl substituents and the nearby ethyl groups.[11] In the case of the vinylene group-connected tris(OEP) **3-H$_2$**, it is suggested that an interconversion between the atropisomers such as **U,U**-form (or **D,D**-form) and **U,D**-form isomers becomes slow at room temperature, as shown in Fig. 2. The kinetic and dynamic studies of this possibility, however, were not successful because of low solubility of the tris(OEP)s in ordinary organic solvents.

Electronic Spectra. Electronic absorption spectra were measured in $CHCl_3$. As compared with the Soret band in the spectrum of **OEP-Ni** (Fig. 3c), the spectrum of the bis(OEP) **1-Ni** (Fig. 3d) shows the Soret band with a new band as a shoulder. This was suggested to result from the exciton coupling between the two transition dipoles of the OEP chromophores.[4a,8] As shown in Fig. 3e, **2-Ni** showed quite a similar spectrum, but with a larger intensity, to the spectrum of **1-Ni** (Fig. 3d), with Soret band at 405 and 421 nm (sh), Q band at 490, 520, and 565 nm, and the weak bands up to 1100 nm. There were, however, only little differences in both absorption maxima and molar extinction coefficients between the tris(OEP)s **2-Ni** and **3-Ni**. This spectral behavior was also observed between the free-bases **2-H$_2$** (Fig. 3a) and **3-H$_2$** (Fig. 3b), except for the fact that the Soret bands of the free-bases are slightly broadened as compared with those of the corresponding nickel(II) complexes. These results allow one to suggest that the difference in the connecting positions of the three OEP rings with the vinylene-linkages does not affect the electronic absorption spectra of the tris(OEP)s, and that the isomeric **2** and **3** have the similar conformational and configurational structures to the bis(OEP) **1**,[2,8] in contrast with their electrochemical properties (see below).

H–D Exchange Experiment. An experiment for H–D exchange of the NH protons in **2-H$_2$** using D_2O was at-

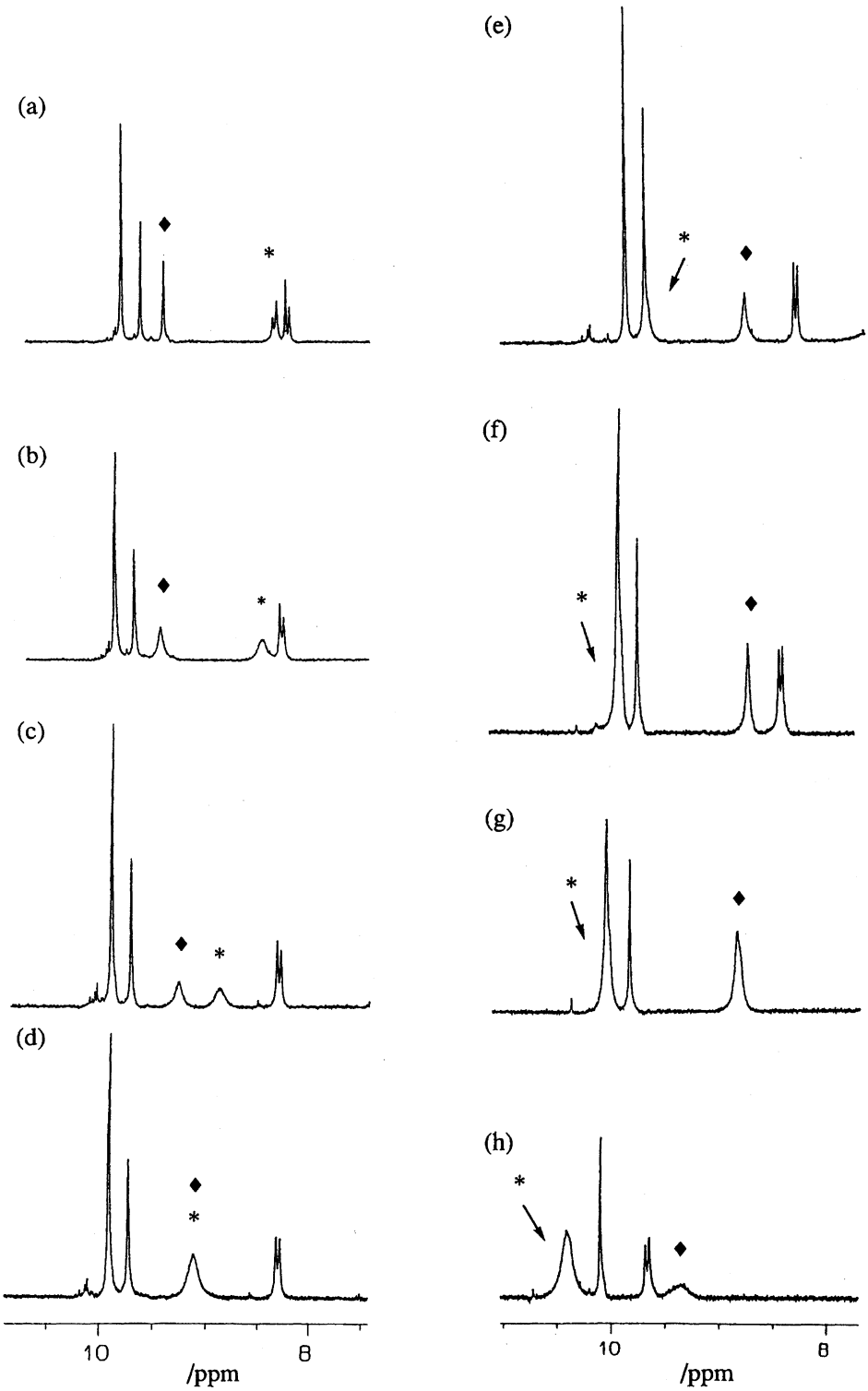


Fig. 5. ^{1}H NMR spectra of the meso and olefinic protons of **2-H$_2$** in $CDCl_3$ solution (0.38 mg in 430×10^{-3} cm^3) by addition of 10% v/v AcOH in $CDCl_3$ at 27 °C with 10 min interval; (a) 0 cm^3 (original), (b) 3×10^{-3} cm^3, (c) 15×10^{-3} cm^3, (d) 36×10^{-3} cm^3, (e) 54×10^{-3} cm^3, (f) 66—246×10^{-3} cm^3, (g) 288×10^{-3} cm^3, and (h) 375×10^{-3} cm^3.

tempted by ^{1}H NMR spectroscopy. The H–D exchange experiment was performed by shaking a $CDCl_3$ solution of **2-H$_2$** vigorously with an excess amount of D_2O for 15 s at 30 °C.

As shown in Fig. 4, the signal due to NH^i proton in the inner OEP ring immediately disappeared, although the signal due to NH^o proton in the outer OEP rings remained almost unchanged (Fig. 4b). After the NH^i signal disappeared completely, the spectrum stayed unchanged for ca. 3 min. The NH^o signal, however, became gradually small (Fig. 4c) and then completely disappeared within 1.5 h.

These observations indicate that the NH^i proton of **2-H$_2$**

Table 1. Half-Wave Oxidation Potentials of **OEP-M**, **1-M**, **2-M**, and **3-M**

	OEP-M		1-M			2-M			3-M		
M	E^1	E^2	E^1	E^2	E^3	E^1	E^2	E^3	E^1	E^2	E^3
H_2	+0.94	+1.44	+0.59	+0.72	+1.49	+0.36	+0.56	+1.19	+0.50	+0.65	+1.15
Ni	+0.86	+1.32	+0.62	+0.70	+1.23	+0.49	+1.05	+1.25	+0.64	+1.13	+1.29

Oxidation potentials (E_{ox}/V) were measured by cyclic voltammetry in CH_2Cl_2 containing n-Bu_4NClO_4. GC (working E), Pt (counter E), and Ag/AgCl (reference E). Scan rate; 120 m V s^{-1}.

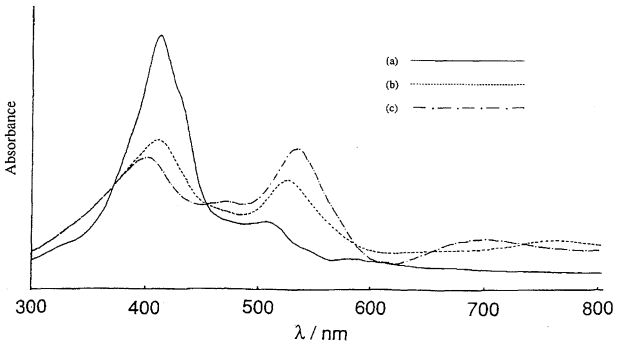


Fig. 6. Electronic absorption spectra of **2-H_2** in $CHCl_3$ solution (0.78×10^{-4} mol dm^{-3}, 3.0 cm^3) by addition of 10% v/v AcOH in $CHCl_3$ at 25 °C; (a) 0 cm^3 (original), (b) 18—54×10^{-3} cm^3, and (c) more then 162×10^{-3} cm^3.

exchanges with deuterium much faster than the NH° proton; in other words, the acidity of NH^i in **2-H_2** is higher than that of NH°. This indicates that the selective or stepwise metallation of the free-base tris(OEP) **2-H_2** would be possible, since deprotonation from **OEP-H_2** must occur at some stage for the synthesis of **OEP-M**.[12] Actually, it was observed that the metallation of **2-H_2** with Pd(II) acetate first took place in the inner OEP ring predominantly and then the inner metallated OEP ring enhanced the acidity of the outer free-base ring.[10]

Protonation Experiments. **OEP-H_2** accepts the proton H^+ to form the stable dications (**OEP-H_4**)$^{2+}$.[13] The two-step change were observed for the ^{1}H NMR spectra of the tris(OEP) **2-H_2** in acidic media as well as for its electronic spectra. Figure 5 shows the ^{1}H NMR spectral changes for the meso and olefinic proton signals of **2-H_2** in $CDCl_3$ solution. A $CDCl_3$ solution containing 10% v/v AcOH was added to the solution with 10 min intervals at 27 °C. In this experiment, we were unable to detect the signals due to the protonated NH$^+$ protons for **2-H_2**, because those signals disappeared immediately after addition of the acid, probably due to coalescence with the signals of the methyl protons or rapid exchange of NH protons with solvent. Therefore, the signal of the protonated NH$^+$ protons for **2-H_2** was detected in $CDCl_3$ containing 1% v/v TFA (see Experimental).[2,14]

As the acid was added, H^3 proton signals marked with ◆ shifted to the up-field and H^b proton signal marked with * to down-field with the broadening of the signals, but the signals of the other *meso* and olefinic protons stayed unchanged. When more acid was added, these two signals came close together (Fig. 5c) and coalesced (Fig. 5d). Then they shifted toward the opposite directions (Fig. 5e→Fig. 5f→Fig. 5g) and reached the final positions apart from each other in the spectrum of Fig. 5h. The spectrum of Fig. 5h was identical with that of **2-H_2** taken in the sole acetic acid (AcOH-d_4) or in a $CDCl_3$ solution containing 1% v/v TFA. The spectrum of Fig. 5f remained unchanged until the acid of more than 246×10^{-3} cm^3 was added, suggesting that the spectrum of Fig. 5f corresponds to the single protonated product.

The signals of the *meso* and olefinic protons of the protonated species at all stages exhibited a similar pattern to that in the initial spectrum of Fig. 5a without appearance of signals due to the new species. It is reported that the monocations of the porphyrins like (**OEP-H_3**)$^+$ exist only in the solution over a very limited pH range and are fairly unstable due to loss of the symmetry of the ring, which results in decrease of the resonance stabilization.[13b] Therefore, it may preclude formation of the monocationic species such as the monocationic inner OEP ring (**2-$H_{2,3,2}$**)$^{0,+,0}$, the bis(monocationic) outer OEP ones (**2-$H_{3,2,3}$**)$^{+,0,+}$, the tris-(monocationic) ones (**2-$H_{3,3,3}$**)$^{+,+,+}$, and the bis(dicationic) outer and monocationic inner ones (**2-$H_{4,3,4}$**)$^{2+,+,2+}$. Since the outer OEP rings are more basic than the inner one, as indicated from H–D exchange experiments, the spectrum of Fig. 5f at the first steady state probably corresponds to the bis(dicationic) species (**2-$H_{4,2,4}$**)$^{2+,0,2+}$ and the final spectrum of Fig. 5h to the tris(dicationic) species (**2-$H_{4,4,4}$**)$^{2+,2+,2+}$ (see below and Experimental). This may also be supported from the fact that all signals due to the *meso* and olefinic protons in the spectrum of Fig. 5f shifted to the somewhat lower field of the final positions in the spectrum of Fig. 5h by adding more acid.

The color of the $CHCl_3$ solution of **2-H_2** turned immediately from yellow to red by addition of the diluted AcOH solution. Accordingly, the electronic spectra greatly changed, as shown in Fig. 6. The initial spectrum of Fig. 6a for **2-H_2** in $CHCl_3$ solution gradually changed to afford the spectrum of Fig. 6b as the first steady state with two new bands at 520 and 770 nm, and then promptly changed to afford the spectrum of Fig. 6c with the longest wavelength absorption band at 940 nm tailing up to 1400 nm as the second steady state. The spectrum of Fig. 6c was exactly the same as that measured in the $CHCl_3$ solution containing 1% v/v TFA.[5a]

As has been observed in the ^{1}H NMR spectrum in $CDCl_3$ solution containing 1% v/v TFA, the electronic spectrum of Fig. 6c indicates the formation of the tris(dication) (**2-$H_{4,4,4}$**)$^{2+,2+,2+}$. The electronic spectrum of Fig. 6b arising from the protonated species of **2-H_2** at the first steady state should correspond to the ^{1}H NMR spectrum of Fig. 5f. The bis(OEP) **1-H_2** existing as (**1-$H_{4,4}$**)$^{2+,2+}$ in acidic media was reported to show the absorption spectrum of 'phlorin' type

(510 and 770 nm in $CHCl_3$ solution containing 1% v/v TFA).[14] The spectrum of 'phlorin' type was also observed in the spectrum of Fig. 6b for **2-H$_2$**, as mentioned above. Though it could not be verified whether the bis(dication)ic species (**2-H$_{4,2,4}$**)$^{2+,0,2+}$ at the first steady state undergoes fast isomerization to the 'phlorin' structure or not, the central OEP ring should be neutral, but should not be monocationic.

That both ^{1}H NMR and electronic spectral changes occur reversibly could be verified by adjusting the pH of the medium. Almost the same spectral changes were also observed for the α,β-isomer **3-H$_2$**. When the same amount of the acid as for the spectrum of Fig. 6b for **2-H$_2$** was added to **OEP-H$_2$** and **1-H$_2$**, the spectrum of **OEP-H$_2$** changed very little and the spectrum of **1-H$_2$** changed a little between before and after addition of the acid. However, in the case of α,β-tris(OEP) **3-H$_2$**, the similar spectral change to that of the α,γ-isomer **2-H$_2$** was observed by adding less than a third to a fourth of the amount of the acid necessary for **2-H$_2$**. These results indicate that the basicity of the OEP ring increases in the order of **OEP-H$_2$** < **1-H$_2$** < **2-H$_2$** < **3-H$_2$**.

Cyclic Voltammetry. Electrochemical oxidation, i.e., electron-releasing ability of the tris(OEP)s was examined by cyclic voltammetry. The half-wave oxidation potentials in dichloromethane for **2-M** and **3-M** as well as **1-M** and **OEP-M** are summarized in Table 1.

Both the tris(OEP)s **2** and **3** exhibited three oxidation waves, similarly to the case of the bis(OEP) **1**. With respect to the first oxidation potential as a measure of electron-releasing ability, the values are the lowest for the α,γ-tris(OEP) **2**, resulting in decrease with increase of the OEP ring in the order of **OEP-M** > **1-M** > **2-M**. However, the first oxidation potentials of the α,β-tris(OEP) **3-M** are higher than those of the α,γ-isomer **2-M** and rather close to those of the bis(OEP) **1-M**. It is also noted that **OEP-Ni** is oxidized at the lower potentials than the free-base **OEP-H$_2$**, while all Ni(II) complexes of the bis- and tris(OEP)s are oxidized at the higher potentials than the corresponding free-bases. Although it is premature to deduce any reasons for these observations, the results suggest that the OEP rings of the OEP oligomers interact with each other through the vinylene-linkage to raise up the HOMO level.

Conclusion

Examinations of ^{1}H NMR and electronic absorption spectra suggested that the tris(OEP)s α,γ-(**2**) and α,β-(**3**) have the similar conformational and configurational structures to the bis(OEP) **1**. The basicity of **3-H$_2$** proved to be greater than that of **2-H$_2$**, while the electron-releasing ability of **3** was found to be lower than that of **2**. In order to clarify the relationship between the electronic properties and the linked positions of the tris(OEP)s connected with the vinylene group in more detail, further investigations on various metal complexes of these compounds are underway.

Experimental

The melting points were determined on a hot-stage apparatus and are uncorrected. IR spectra were measured on a JASCO FT/IR 7300 spectrophotometer as KBr disks, unless otherwise stated; only significant absorptions are reported. Electronic spectra were determined in $CHCl_3$ solutions on a Shimadzu UV-2200A spectrophotometer (sh = shoulder). ^{1}H NMR spectra were taken in $CDCl_3$ solution on JEOL MAC-FX (90 MHz) or JEOL A400 (400 MHz) spectrometers, and were recorded in δ-values with TMS as an internal standard. Mass spectra were recorded with a JEOL JMS-D300 spectrometer operating at 75 eV in a direct inlet system and FAB mass spectra with a JEOL AX-505 spectrometer using *m*-nitrobenzyl alcohol as a matrix agent. Cyclic voltammetry was performed on a BAS CV-27. Silica gel (Daiso gel 1001W or Merck 60) and alumina (Merck, Act. II-III) were used for column chromatography. CH_2Cl_2 and $CHCl_3$ were distilled over calcium hydride and THF was distilled from sodium diphenylketyl under argon before use. The reactions were followed by TLC aluminum sheets precoated with Merck silica gel F_{254} or with Merck aluminum oxide GF_{254}. Organic extracts were dried over anhydrous sodium sulfate or magnesium sulfate prior to removal of the solvent.

5-Formyl-2,3,7,8,12,13,17,18-octaethylporphyrinatonickel(II) (5):[6] Phosphoryl chloride ($POCl_3$, 12.5 cm^3, 177mmol) was added to *N*,*N*-dimethylformamide (DMF; 13.7 cm^3, 134 mmol) over 1 h at 0—5 °C and the resulting mixture was stirred at ambient temperature for 30 min (Vilsmeier reagent). Then a solution of octaethylporphyrinatonickel(II) **4**[7] (1.0 g, 1.69 mmol) in 1,2-dichloroethane (500 cm^3) was added to Vilsmeier reagent over 15 min with stirring at 50—55 °C. After stirring for 1 h, saturated aq sodium acetate (500 cm^3) was added to the mixture. The solution was stirred for an additional 2 h at 60 °C and poured into water. The reaction mixture was extracted with CH_2Cl_2. The extracts were washed with brine and dried. The residue obtained after removal of the solvent was chromatographed on silica gel (5.2×11 cm) with benzene to afford **5** (931 mg, 89%) as reddish needles (from $CHCl_3$–MeOH): Mp 289—292 °C (decomp); Mass *m/z* 618 (M^+) and 620 (M^++2); IR (KBr) 2965, 2930, 2870 (CH), 1700, 1655 cm^{-1} (CO); ^{1}H NMR (90 MHz) δ = 11.88 (1H, s, CHO), 9.33 (1H, s, *meso* H), 9.29 (2H, s, *meso* H), 3.9—3.6 (16H, m, CH_2), 1.9—1.5 (24H, m, CH_3). Found: C, 71.66; H, 7.15; N, 8.99%. Calcd for $C_{37}H_{44}N_4ONi$: C, 71.72; H, 7.17; N, 9.05%.

5-Hydroxymethyl-2,3,7,8,12,13,17,18-octaethylporphyrinatonickel(II) (6)[6]**:** Sodium borohydride ($NaBH_4$; 144 mg, 3.81 mmol) was added to a solution of the carbaldehyde **5** (200 mg, 0.32 mmol) in THF (80 cm^3) containing a few drops of H_2O at room temperature and the mixture was stirred for 2 h. Then the mixture was poured into water and extracted with benzene. The extracts were washed with brine and dried. The residue obtained after removal of the solvent was chromatographed on alumina (4.2×5 cm) with benzene to afford **6** (192 mg, 96%) as dark purple columns (from $CHCl_3$–MeOH): Mp 295—299 °C (decomp); Mass *m/z* 620 (M^+); IR (KBr) 3430 (OH), 2960, 2930, 2870 cm^{-1} (CH); ^{1}H NMR (90 MHz) δ = 9.40 (3H, br s, *meso* H), 6.37 (2H, br s, CH_2O), 4.0—3.7 (16H, m, CH_2), 2.27 (1H, s, OH), 1.9—1.6 (24H, m, CH_3). Found: C, 71.78; H, 7.52; N, 8.99%. Calcd for $C_{37}H_{46}N_4ONi$: C, 71.49; H, 7.47; N, 9.02%.

5,15-Diformyl-2,3,7,8,12,13,17,18-octaethylporphyrinatonickel(II) (8) and 5,10-Diformyl-2,3,7,8,12,13,17,18-octaethylporphyrinatonickel(II) (9): $POCl_3$ (86.0 cm^3, 923 mmol) was added to DMF (129 cm^3, 1.67 mol) over 3 h at 0 °C and the mixture was stirred at ambient temperature for 30 min. A solution of **4**[7] (1.0 g, 1.69 mmol) in 1,2-dichloroethane (215 cm^3) was added to the Vilsmeier reagent during 15 min with stirring at 50 °C. After stirring for 5h, saturated aq sodium acetate (700 cm^3) was added to the mixture, keeping the temperature at 20—30 °C. The mixture

was stirred for an additional 3 h at 60 °C. Then the mixture was poured into water and extracted with CH_2Cl_2. The extracts were washed with brine and dried. The residue obtained after removal of the solvent was chromatographed on silica gel (4×20 cm) with hexane–benzene (1 : 1) to afford the α,γ-dicarbaldehyde **8** (R_f 0.16, 390 mg, 36%) from the initial fractions and the α,β-dicarbaldehyde **9** (R_f 0.15, 370 mg, 35%) from the following fractions.

8: Reddish purple needles (from $CHCl_3$–MeOH); Mp 286—287 °C (decomp); Mass *m/z* 646 (M^+); IR (KBr) 2965, 2930, 2870 (CH), 1705, 1655 cm^{-1} (CO); ^1H NMR (90 MHz) δ = 11.86 (2H, s, CHO), 9.06 (2H, s, *meso* 10-H and 20-H), 3.8—3.4 (16H, m, CH_2), 1.8—1.4 (24H, m, CH_3); UV-vis λ_{max} 431 (73700), 650 nm (8980). Found: C, 70.55; H, 6.79; N, 8.66%. Calcd for $C_{38}H_{44}N_4O_2Ni$: C, 70.48; H, 6.86; N, 8.65%.

9: Dark reddish purple needles (from hexane–benzene); Mp 270—277 °C (decomp); Mass *m/z* 646 (M^+); IR (KBr) 2965, 2930, 2860 (CH), 1710, 1665 cm^{-1} (CO); ^1H NMR (90 MHz) δ = 11.90 (2H, s, CHO), 9.09 (2H, s, *meso* 15-H and 20-H), 3.78—3.58 (16H, m, CH_2), 1.76—1.55 (24H, m, CH_3); UV-vis λ_{max} 342 (10000), 428 (64000), 535 (sh, 2800), 570 (sh, 3800), 651 nm (7500). Found: C, 70.36; H, 6.45; N, 8.40%. Calcd for $C_{38}H_{44}N_4O_2Ni$: C, 70.48; H, 6.86; N, 8.65%.

5, 15- Bis(hydroxymethyl)- 2, 3, 7, 8, 12, 13, 17, 18- octaethylporphyrinatonickel(II) (10): $NaBH_4$ (138 mg, 3.66 mmol) was added to a solution of the dicarbaldehyde **8** (100 mg, 0.16 mmol) in THF (40 cm^3) containing a few drops of H_2O at room temperature and the mixture was stirred for 3 h. Then the mixture was poured into water and extracted with benzene. The extracts were washed with brine and dried. The residue obtained after removal of the solvent was chromatographed on alumina (4.2×5 cm) with benzene to afford **10** (95 mg, 95%) as dark purple columns (from hexane–benzene): Mp 225—230 °C (decomp); Mass *m/z* 650 (M^+); IR (KBr) 3415 (OH), 2960, 2930, 2870 cm^{-1} (CH); ^1H NMR (400 MHz) δ = 9.13 (2H, s, *meso* 10-H and 20-H), 6.17 (4H, d, J = 5 Hz, CH_2O), 3.93—3.57 (16H, m, CH_2), 1.9—1.5 (24H, m, CH_3), 1.25 (2H, t, J = 5 Hz, OH); UV-vis λ_{max} 315 (10700), 357 (15600), 420 (135000), 552 (9030), 592 nm (13000). Found: C, 70.22; H, 7.36; N, 8.30%. Calcd for $C_{38}H_{48}N_4O_2Ni$: C, 70.04; H, 7.44; N, 8.60%.

5, 10- Bis(hydroxymethyl)- 2, 3, 7, 8, 12, 13, 17, 18- octaethylporphyrinatonickel(II) (11): $NaBH_4$ (750 mg, 19.7 mmol) was added to a solution of the dicarbaldehyde **9** (500 mg, 0.16 mmol) in THF (200 cm^3) containing a few drops of H_2O at room temperature and the mixture was stirred for 3 h. Then the mixture was poured into water and extracted with CH_2Cl_2. The extracts were washed with brine and dried. The residue obtained after removal of the solvent was chromatographed on alumina (4×20 cm) with a mixture of CH_2Cl_2 and EtOH (1 : 1) to afford **11** (433 mg, 87%) as deep purple needles (from hexane–CH_2Cl_2): Mp 225—229 °C (decomp); Mass *m/z* 650 (M^+); IR (KBr) 3429 (OH), 2960, 2930, 2870 cm^{-1} (CH); ^1H NMR (400 MHz) δ = 9.15 (2H, s, *meso* 15-H and 20-H), 6.21 (4H, d, J = 5 Hz, CH_2O), 3.95—3.55 (16H, m, CH_2), 1.80—1.55 (24H, m, CH_3), 1.25 (2H, t, J = 5 Hz, OH); UV-vis λ_{max} 314 (16200), 357 (22000), 417 (174000), 552 (10000), 595 nm (13500). Found: C, 69.86; H, 7.45; N, 8.40%. Calcd for $C_{38}H_{48}N_4O_2Ni$: C, 70.04; H, 7.44; N, 8.60%.

α,γ-Tris(OEP) Nickel(II) Complexes (12): Method A: A solution of the methanol **6** (384 mg, 0.62 mmol) in DMF (100 cm^3) and a solution of the α,γ-bis(methanol) **10** (100 mg, 0.16 mmol) in DMF (50 cm^3) were added simultaneously to the solution of concd H_2SO_4 (0.15 cm^3, 2.79 mmol) in DMF (100 cm^3) over 1 h at 140 °C. The resulting mixture was stirred for an additional 5 h. Then the mixture was poured into water and extracted with CH_2Cl_2. The extracts were washed successively with aq $NaHCO_3$ and brine, and dried. The residue obtained after removal of the solvent was chromatographed on silica gel (4.2×7 cm) with hexane–CH_2Cl_2 (4 : 1) to afford the OEP nickel(II) complex **4**[7] (22 mg) from the initial fractions and the bis(OEP) nickel(II) complex **7-Ni**[6] (83 mg) from the following fractions. The mixture of the ethylene- and vinylene-connected α,γ-tris(OEP) nickel(II) complexes **12-Ni** (14 mg, ca. 5% yield based on the methanol **10**) was obtained from the later fractions.

Method B: A solution of concd H_2SO_4 (0.15 cm^3, 2.79 mmol) in DMF (10 cm^3) was added to the mixture of the methanols **6** (384 mg, 0.62 mmol) and **10** (100 mg, 0.16 mmol) in DMF (120 cm^3) over 1 h at 150 °C. The resulting mixture was stirred for an additional 2 h. Then the mixture was poured into water and extracted with CH_2Cl_2. The extracts were washed successively with aq $NaHCO_3$ and brine, and dried. The residue obtained after removal of the solvent was chromatographed on silica gel (4.4×10 cm) with hexane–CH_2Cl_2 (4 : 1) to afford **4**[7] (20 mg) from the initial fractions and **7-Ni**[6] (67 mg) from the following fractions. The tris(OEP) nickel(II) complexes **12-Ni** (42 mg; ca. 15% yield) were obtained from the later fractions. The later fractions was found to contain **2-Ni** as one of the products by analysis of the ^1H NMR spectrum (the underlined chemical shifts show the signals due to the *meso* protons of **2-Ni**); ^1H NMR (400 MHz) δ = 9.49, 9.47, 9.44, 9.40, 9.38, 9.36, 9.30, 9.27, 7.70—7.52 (m), 7.58—7.52 (m), 4.0—2.8 (m), 2.1—1.5 (m), 1.3—0.8 (m) (also see below).

5,15-Bis[2-(2,3,7,8,12,13,17,18-octaethyl-5-porphyrinyl)vinyl]-2,3,7,8,12,13,17,18-octaethylporphyrin (2-H_2): The mixture of the ethylene- and vinylene-connected α,γ-tris(OEP) nickel(II) complexes **12-Ni** (50 mg) in concd H_2SO_4 (10 cm^3) was stirred for 5 h at ambient temperature. Then the mixture was poured into ice water and neutralized by addition of solid Na_2CO_3. The mixture was poured into ice water and neutralized by addition of solid Na_2CO_3. The mixture was extracted with CH_2Cl_2, and the extracts were washed with brine and dried. The residue obtained after removal of the solvent was chromatographed on silica gel (3.6×4 cm) with CH_2Cl_2–ethyl acetate (7 : 3) to afford the crude product (43 mg) of the corresponding free-based tris(OEP)s **12-H_2**.

FAB MS spectrum of the free-base tris(OEP)s mixture **12-H_2** showed fragment peaks of *m/z* 1652 and 1653 corresponding to the mass number of the molecular weight of **2-H_2**, in addition to those of *m/z* 1654, 1655, 1656, and 1657 corresponding to the mass number of the molecular weight of the free-bases of the ethylene- and/or vinylene-connected tris(OEP)s. The ^1H NMR spectrum of the crude **12-H_2** indicated that it contains **2-H_2** (see below).

The crude product (43 mg) of the free-base tris(OEP)s **12-H_2** was dissolved in AcOH (100 cm^3) and was stirred at 65 °C for 1 h. After being neutralized with $NaHCO_3$ and then diluted with water, the reaction mixture was extracted with CH_2Cl_2. The extracts were washed with brine and dried. The residue obtained after removal of the solvent was chromatographed on silica gel (3.6×3 cm) with CH_2Cl_2–diethyl ether (7 : 3) to afford the vinylene connected α,γ-tris(OEP) **2-H_2**[5a] (42 mg) as black fine needles (from hexane–CH_2Cl_2): Mp > 300 °C; Mass (FAB) *m/z* 1653.3 (M^++1); IR (KBr) 3300 (NH), 2960, 2930, 2870 cm^{-1} (CH); ^1H NMR (400 MHz) δ = 10.07 (4H, s, H^1), 9.89 (2H, s, H^2), 9.68 (2H, br s, H^3), 8.57 (2H, br d, J = 15 Hz, H^b), 8.48 (2H, d J = 15 Hz, H^a), 4.1—3.6 (48H, m, CH_2), 2.0—1.8 (48H, m, CH_3), 1.2—1.0 (24H, m, CH_3), −1.25 (2H, br s, NH^i), −2.54 (4H, br s, NH^o); ^1H NMR (400 MHz, $CDCl_3$ containing 1% v/v TFA) δ = 10.20 (6H, br s, H^1 and H^b), 9.91 (2H, s, H^2), 9.79 (2H, d, J = 15 Hz, H^a), 9.15 (2H, br s, H^3), 4.1—2.9 (48H, m, CH_2), 1.9—0.5 (72H, m, CH_3), −0.15 (4H,

s, NH^i), −1.81 (8H, s, NH^o); UV-vis λ_{max} 330 (sh, 42400), 375 (sh, 116000), 414 (267000), 430 (sh, 209000), 507 (67800), 541 (67800), 580 (25400), 633 nm (18300), and the weak bands up to 1100 nm; UV-vis ($CHCl_3$ containing 1% v/v TFA)[5a] λ_{max} 350 (sh), 405, 480, 530, 675, 830 (sh), 940 nm with the tail up to 1400 nm. Found: C, 81.22; H, 8.15; N, 9.98%. Calcd for $C_{112}H_{138}N_{12}$: C, 81.45; H, 8.36; N, 10.19%.

Trinickel(II) Complex of 5,15-Bis[2-(2,3,7,8,12,13,17,18-octaethyl-5-porphyrinyl)vinyl]-2,3,7,8,12,13,17,18-octaethylporphyrin (2-Ni): The mixture of the free-base α,γ-tris(OEP) **2-H$_2$** (20 mg, 0.012 mmol) and $Ni(OAc)_2 \cdot 4H_2O$ (400 mg, 1.61 mmol) in DMF (30 cm^3) was stirred at 105—110 °C for 5 h. The mixture was poured into water and extracted with CH_2Cl_2. The extracts were washed with brine and dried. The residue obtained after removal of the solvent was chromatographed on silica gel (3.8×5 cm) with benzene to afford **2-Ni**[5a] (21 mg, 98%) as fine black needles (from hexane–CH_2Cl_2): Mp > 300 °C; Mass (FAB) no particular ion peak was observed; IR (KBr) 2960, 2930, 2870 cm^{-1} (CH); ^{1}H NMR (400 MHz) δ = 9.49 (2H, s, H^2), 9.44 (4H, s, H^1), 9.30 (2H, br s, H^3), 7.64 (2H, br d, J = 15 Hz, H^b), 7.53 (2H, d, J = 15 Hz, H^a), 3.9—3.0 (48H, m, CH_2), 1.9—1.6 (48H, m, CH_3), 1.1—0.9 (24H, m, CH_3); UV-vis λ_{max} 353 (16300), 408 (261000), 421(sh, 214000), 491 (sh, 60900), 516 (sh, 53100), 564 nm (43400), and the weak bands up to 1000 nm. Found: C, 73.56; H, 7.29; N, 9.13%. Calcd for $C_{112}H_{132}N_{12}Ni_3$: C, 73.85; H, 7.25; N, 9.23%.

***α,β*-Tris(OEP) Nickel(II) Complexes (13-Ni):** The cross coupling reaction of **6** with **11** was carried out according to Method B. A solution of concd H_2SO_4 (0.3 cm^3, 5.58 mmol) in DMF (20 cm^3) was added to the mixture of the methanols **6** (815 mg, 1.31 mmol) and **11** (200 mg, 0.31 mmol) in DMF (220 cm^3) over 1 h at 150 °C. The mixture was stirred for an additional 2 h. Then the mixture was poured into water and extracted with CH_2Cl_2. The extracts were washed successively with aq $NaHCO_3$ and brine, and dried. The residue obtained after removal of the solvent was chromatographed on silica gel (2.8×36 cm) with hexane–benzene (4 : 1) to afford **4**[7] (85 mg) from the initial fractions, **7-Ni**[6] (235 mg) from the following fractions, and the crude **OEP** α,β-tris(OEP)s **13-Ni** (38 mg) from the later fractions.

5,10-Bis[2-(2,3,7,8,12,13,17,18-octaethyl-5-porphyrinyl)vinyl]-2,3,7,8,12,13,17,18-octaethylporphyrin (3-H$_2$): The mixture of the ethylene- and vinylene-connected α,β-tris(OEP) nickel(II) complexes **13-Ni** (38 mg) in concd H_2SO_4 (10 cm^3) was stirred for 8 h at ambient temperature. The mixture was poured into ice water and was neutralized by addition of solid Na_2CO_3. The mixture was extracted with CH_2Cl_2. The extracts were washed with brine and dried. The residue obtained after removal of the solvent was chromatographed on silica gel (4×18 cm) with CH_2Cl_2–ethyl acetate (4 : 1) to afford the corresponding free-base tris(OEP)s **13-H$_2$** (32 mg). The mixture was dissolved in AcOH (100 cm^3) and was stirred at 65 °C for 1 h. After being neutralized with $NaHCO_3$ and then diluted with water, the reaction mixture was extracted with CH_2Cl_2. The extracts were washed with brine and dried. The residue obtained after removal of the solvent was chromatographed on silica gel (2×18 cm) with benzene–CH_2Cl_2 (7 : 3) to afford **3-H$_2$** (26 mg) as black needles (from hexane–CH_2Cl_2): Mp > 300 °C; Mass (FAB) *m/z* 1653.1 (M^+ + 1); IR (KBr) 3300 (NH), 2950, 2950, 2860 cm^{-1} (CH); ^{1}H NMR (400 MHz) δ = 10.00 (4H, s, H^1), 9.82 (2H, s, H^2) 9.62 (2H, br s, H^3), 8.49 (2H, br d, J = 15 Hz, H^b), 8.41 (2H, d, J = 15 Hz, H^a), 4.1—3.5 (48H, m, CH_2), 1.9—1.7 (48H, m, CH_3), 1.3—1.2 (12H, m, CH_3), 1.1—1.0 (12H, m, CH_3), −1.31 (2H, br s, NH^i), −2.61 (4H, br s, NH^o); UV-vis λ_{max} 330 (sh, 42000), 378 (sh, 115000), 414 (283000), 437 (sh, 189000), 509 (69000), 550 (sh, 31000), 578 (25500), 631 (16500), 671 nm (16000), and the weak bands up to 1100 nm. Found: C, 81.32; H, 8.22; N, 9.91%. Calcd for $C_{112}H_{138}N_{12}$: C, 81.45; H, 8.36; N, 10.19%.

Trinickel(II) Complex of 5,10-Bis[2-(2,3,7,8,12,13,17,18-octaethyl-5-porphyrinyl)vinyl]-2,3,7,8,12,13,17,18-octaethylporphyrin (3-Ni): The mixture of the free-base α,β-tris(OEP)s **3-H$_2$** (18 mg, 0.011 mmol) and $Ni(OAc)_2 \cdot 4H_2O$ (390 mg, 1.59 mmol) in DMF (30 cm^3) was stirred for 5 h at 105—110 °C. The mixture was poured into water and extracted with CH_2Cl_2. The extracts were washed with brine and dried. The residue obtained after removal of the solvent was chromatographed on silica gel (3.8×5 cm) with benzene to afford **3-Ni** (18 mg, 91%) as black needles (from hexane–CH_2Cl_2): Mp > 300 °C; Mass (FAB) no particular ion peak was observed; IR (KBr) 2960, 2945, 2850 cm^{-1} (CH); ^{1}H NMR (400 MHz) δ = 9.41 (2H, s, H^2), 9.35 (4H, s, H^1), 9.18 (2H, br s, H^3), 7.77 (2H, br d J = 15 Hz, H^b), 7.48 (2H, d, J = 15 Hz, H^a) 3.8—3.0 (48H, m, CH_2), 2.0—1.5 (48H, m, CH_3), 1.2—1.0 (12H, m, CH_3), 1.1—1.0 (12H, m, CH_3); UV-vis λ_{max} 358 (17500), 405 (268000), 421 (sh, 220000), 490 (sh, 60000), 520 (sh, 53500), 565 nm (42000), and the weak bands up to 1000 nm. Found: C, 74.06; H, 7.54; N, 9.48%. Calcd for $C_{112}H_{132}N_{12}Ni_3$: C, 73.85; H, 7.25; N, 9.23%.

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