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Synthesis and structural and electronic properties of the diacetylene- and ethylene-groups connected octaethylporphyrin(Ni) tetramer

Naoto Hayashi,[a] Azusa Naoe,[a] Keiko Miyabayashi,[b] Mami Yamada,[b]
Mikio Miyake[b] and Hiroyuki Higuchi[a,*]

[a]*Department of Chemistry, Faculty of Science, Toyama University, 3190 Gofuku, Toyama, Toyama 930-8555, Japan*
[b]*School of Material Science, JAIST (Hokuriku), 1-1 Asahi-dai, Tatsunokuchi, Noumi, Ishikawa 923-1292, Japan*

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Abstract—The tetramer of octaethylporphyrin nickel complex [OEP(Ni)], connected with diacetylene and ethylene linkages, was synthesized. Its structural and electronic properties were studied, proving that two constituents of the diacetylene-group connected OEP(Ni) dimer face to each other in s-*cis* conformation about the ethylene linkage but not so closely as to induce a transannular π-electronic interaction between them.

In case of the molecular design of new functional organic materials, it is very important to choose a particular one from various linkages, with which the optically active chromophores and pigments are connected purposively for the construction of assembly systems with well-defined and well-ordered structural features.[1] We have been engaged in the study of various octaethylporphyrin [OEP(Ni)] derivatives connected with the diacetylene linkage to investigate their electronic properties as the function unit of optoelectronic devices.[2] Among them, the diacetylene- and vinylene-groups connected OEP-(Ni) tetramer **1** exhibited the curious features, revealing that the compound **1** holds the electronic properties of the vinylene-group connected OEP(Ni) dimer **2** rather than those of the diacetylene-group connected OEP(Ni) dimer **3**.[3] Furthermore, the OEP(Ni) dimer **2** in *trans*-form is readily transformed into the corresponding *cis*-form isomer,[4a] while the compound **1** entirely resists the geometrical isomerization to *cis*-form. On the other hand, the ethylene linkage is simply useful for fixation of most π-electronic constituents without mutual affection between them through the linkage, because of no π-electronic bond in it.[5] However, some ethylene-group connected derivatives, in which the macrocyclic planar molecules such as porphyrin and phthalocyanine rings are directly combined, are known to exhibit the peculiar interactions between the constituent chromophores transannularly, depending on the nature of incorporated metals (M).[6] In the ethylene-group connected OEP(M) dimers **4**, the Zn complex exists in s-*cis* conformer (*syn*-form) due to the strong attractive interaction between the faced OEP(Zn) rings,[6b] while the Ni complex as well as its free-base exist in s-*trans* conformer (*anti*-form).[6a]

In our continuing investigations of oligomeric OEP(Ni) derivatives,[2,3] the OEP(Ni) tetramer **5** of a new type, in which the two diacetylene-group connected OEP(Ni) dimer constituents are connected with the ethylene linkage, was synthesized. Here, we wish to report the synthesis and structural peculiarity of **5** and to figure out a hybridism appearance between the OEP(Ni) dimer constituents **3** and **4** in **5**, as compared with those of the related compounds.

Synthesis of the title OEP(Ni) tetramer **5** was carried out by homo-coupling reaction of the diacetylene-group connected OEP(Ni) dimer alcohol **7**, according to the reported procedures by us[7] and others,[8] as shown in Scheme 1. The diacetylene linkage enhanced the reactivity of OEP(Ni) itself in Vilsmeier formylation. Thus, reaction of **3** with only 20 equiv Vilsmeier reagent

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Keywords: Octaethylporphyrin; Nickel complex; Diacetylene; Ethylene; Tetramer.

* Corresponding author. Tel./fax: +81 76 445 6616; e-mail: higuchi@sci.toyama-u.ac.jp

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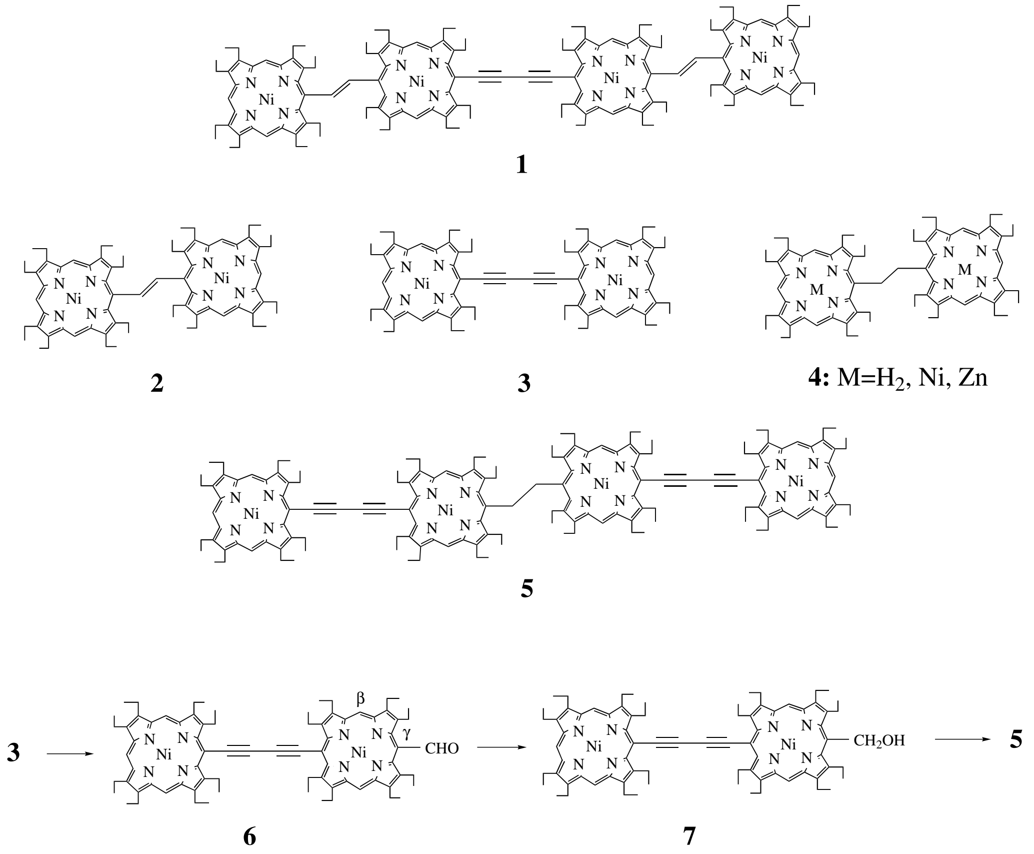


Scheme 1.

($POCl_3$–DMF) in $CHCl_3$ afforded a mixture of β- and γ-isomeric (**6**) aldehydes in 85% yield (approximately 1:1 based on ^1H NMR spectrum),[9] which is hardly separable by ordinary methods. However, as compared with the vinylene linkage, the diacetylene linkage was found to lower its efficiency in both reactivity and site-selectivity for **6**, from the fact that the formylation of **2** with 5–6 equiv Vilsmeier reagent afforded the corresponding mixture of β- and γ-isomeric aldehydes in a ratio of 1:3 (80%).[3] Reduction of these aldehydes with $NaBH_4$ in THF containing a few drops of H_2O gave a mixture of the corresponding methyl alcohols quantitatively, which could be separated to respective β- and γ-isomers by repeated column chromatography on SiO_2. Then, the treatment of the γ-alcohol **7** in DMF containing catalytic amount of concd H_2SO_4 afforded the desired compound **5** in 20% yield, which was recrystallized from $CHCl_3$–hexane to form black purple microcrystallines.

The structure of **5** was chiefly determined by Mass, IR, and ^1H NMR spectra. ESI-FT-ICR mass spectrum was fairly simple to exhibit the doubly (*m*/*z* around 1240 for M^{2+}) and quadruply (*m*/*z* around 620 for M^{4+}) charged fragmentation groups (FG) intensively, with no peaks corresponding to the singly charged molecular ion (MW = 2485.9740 for $C_{154}H_{176}N_{16}Ni_4$) of **5**. Both FGs are completely consistent with the computer simulated patterns (Fig. 1). IR spectrum was also simple, characteristically showing a pair of weak and medium vibrational bands due to the diacetylene linkage at around 2180 and 2130 cm^{-1}, respectively, similarly to those of other diacetylene-group connected OEP(Ni) derivatives.[2] Furthermore, ^1H NMR spectra (Fig. 2) clearly supported the structure of **5** to afford three *meso*-protons (*meso*-H, 2:1:2) the same as those in the alcohol **7**, except for disappearance of the OH group and shift of the methanolic methylene protons to the fairly high field after the reaction.

The detailed analysis of ^1H NMR spectrum, however, revealed some curious features of **5**. Chemical shifts of *meso*-H can be regarded as a measure of the diamagnetic ring current of 18 π-electronic system; δ 9.76 for OEP-(Ni),[2,6] δ 9.42 and 9.39 for **3**[2] and δ 9.48 and 9.32 for **4** (M = Ni),[6a] clearly showing that introduction of the diacetylene and ethylene linkages into OEP(Ni) also weakens its ring current more or less. Therefore, the similar chemical shift tendency was observed in **5**. However, in addition to relatively high-field shift of all the three *meso*-H, one of them appeared at δ 8.60 ppm much separately from the other two, which corresponds to more than 1 ppm high-field shift from those of OEP(Ni). To the contrary, the ethylene linkage (δ 4.32) of **5** appeared in a fairly low field from that (δ 3.88)[6a] of **4** (M = Ni), which was unmistakably assigned by COSY NMR. Furthermore, the signals due to methylene protons of the ethyl substituents in **5** exhibited a very curious feature, similar to the case of the zinc complex in **4**, to resonate dispersedly and orderly in such a wide region from ordinary to high fields of 2.5–4.2 ppm.[6] Yet, their signal patterns suggested a multiplicity arising from prochirality of the molecular structure, where more than five methyl-

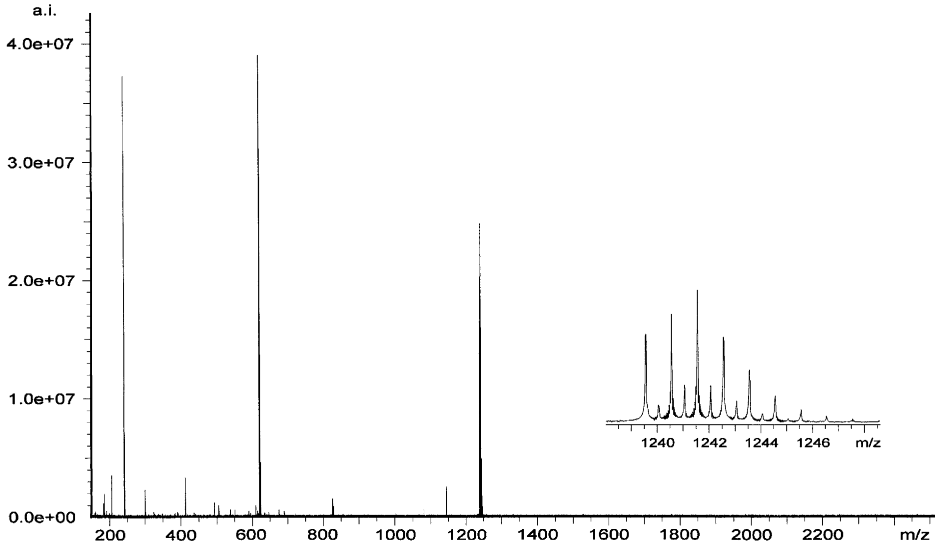


Figure 1. ESI-FT-ICR mass spectrum of **5** and the FG pattern at *m*/*z* around 1240 for M^{2+}.

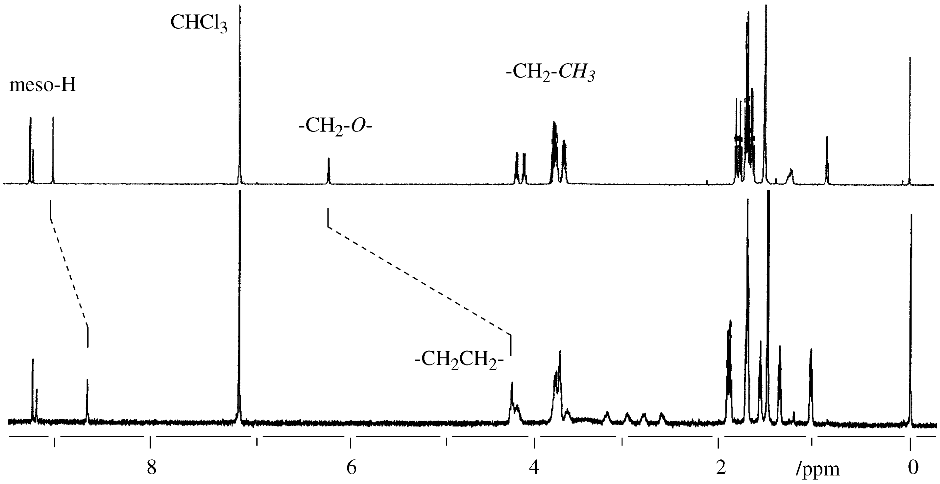


Figure 2. ^{1}H NMR spectra of **5** (lower) and **7** (upper) (400MHz, $CDCl_3$).

ene-proton groups are splitted into sextets.[4a,6a] These phenomena reasonably show that the substituent geometry about the ethylene linkage behaves in *syn*-form and thus two constituents of the diacetylene-group connected OEP(Ni) dimer in **5** face to each other. This consequence is completely opposite to the geometry of the two OEP(Ni) constituents in **4**.

On the other hand, electronic absorption spectrum of **5** did not exhibit a particular difference from that of **3**, but broadened slightly (Fig. 3). Still, an enhanced intensity and a little bathochromic shift of the respective absorption bands were simply observed for **5**, as compared with those of **3**. These results indicate that two constituents of the diacetylene-group connected OEP(Ni) dimer (**3**) in **5** do not stack each other so closely as to induce a transannular π-electronic interaction between them. Supposing a $sp^3C–sp^3C$ bond situation about the ethylene linkage simply normal, the conformational feature of these two rigid constituents in **5** could be naturally pictured as a hinge structure with a dihedral angle of more than 39°. This supposition in **5** is evidently consistent with a distance-dependent appearance of anisotropic effect from the diamagnetic ring current of OEP(Ni) both on the oppositely faced constituents and on the more deshielded ethylene linkage. As another evidence, the OEP(Ni) tetramer **5** exhibited the first oxidation potential (E_1) of 830mV, regardable as a measure of electron-releasing ability of the molecule, which is rather comparable to that of **3** ($E_1 = 860\,mV$)[2c,3] prior to **4** ($M = Ni$; $E_1 = 720\,mV$).[10] These results support no existence of particular π-electronic interaction between the face-to-face diacetylene-group connected OEP(Ni) dimers in **5**, proving that the derivative **5** possesses an isolated dimeric feature of **3**.

It is well known that the intramolecular polarization of the Zn complex is fairly large, on the basis of the fact that the net electron population (ep: 0.40) of zinc is greater on the OEP ring system[11] but the electronegativity (en: 1.6) of zinc is smaller,[12] as compared with those of the Ni complex (ep: 0.30, en: 1.8). Resultingly, the

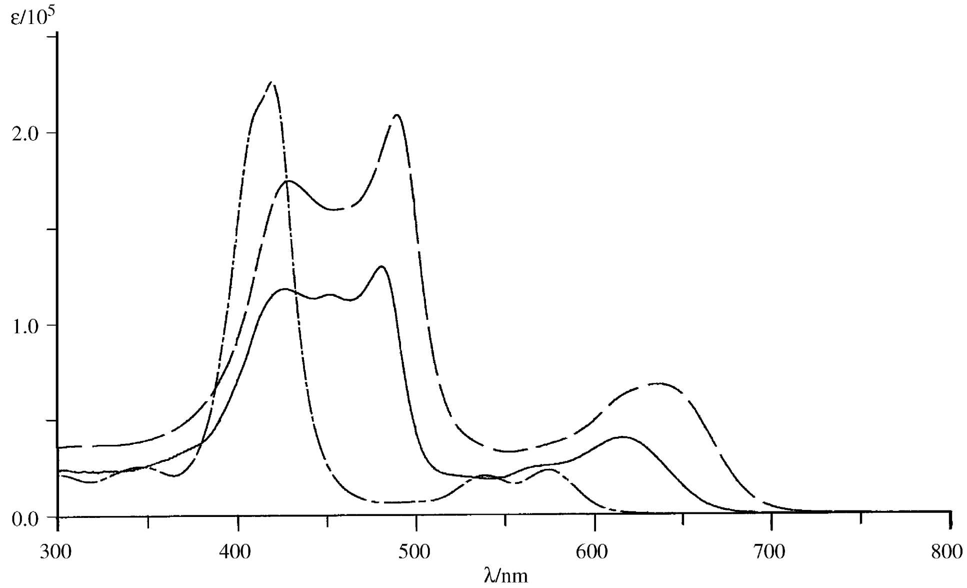
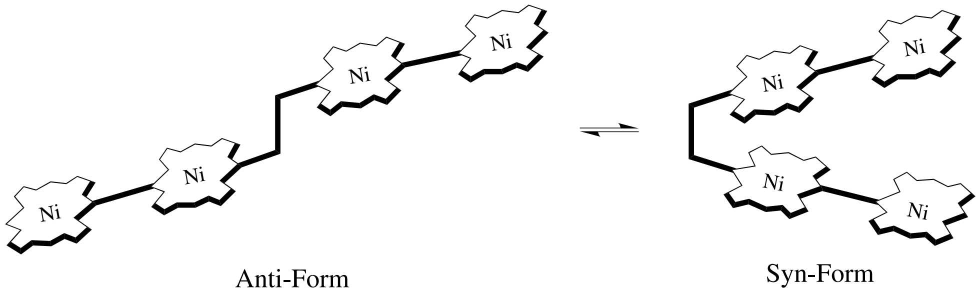
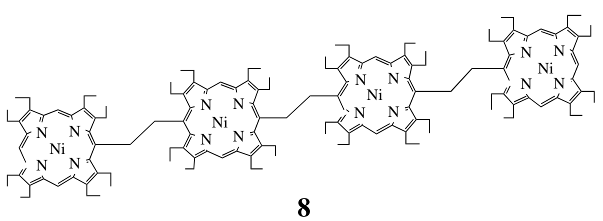


Figure 3. Electronic absorption spectra of **3** (—), **4** (M = Ni,– · –), and **5** (–––) in $CHCl_3$.

attractive dipole–dipole interaction arises in the Zn complex of **4** intensively enough to overcome the steric repulsive interaction to exist in *syn*-form, while the corresponding Ni complex and free-base are not the case, existing in *anti*-form preferably. On the other hand, such a force-balance situation for the Ni complex in **4** is entirely reversed in **5**, resulting in *syn*-form predominantly. As a consequence, a critical feature that the attractive force between the two diacetylene-group connected OEP(Ni) dimeric constituents in **5** is intensive enough to be comparable to the dipole–dipole interaction of the Zn complex in **4** should be derived from the structural informations of **5**. Such an excessive energy gain in attractive force would be brought from the greater van der Waals interaction due to the larger π-electronic area of **3**,[13] even though the steric repulsive interaction between them in *syn*-form increases as well. It can be concluded that the present finding is also a peculiar phenomenon from the nature of the straight and rigid linkage of diacetylene, since all the constituents in another OEP(Ni) tetramer **8**, simply connected only with the ethylene linkage, do not exist in such a sterically unfavorable *syn*-form in solution, similar to the nickel complex in **4**.[14]





8

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