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Synthesis and electronic properties of diacetylene- and vinylene-groups connected octaethylporphyrin tetramer

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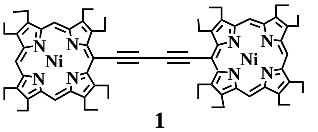
Abstract—The octaethylporphyrin (OEP) tetramer connected with both diacetylene and vinylene linkages was synthesized by an oxidative homo-coupling of the terminal acetylene of the vinylene-group connected OEP dimer. The electronic spectral and electrochemical studies were performed, proving that the hybridized OEP tetramer remains the characteristic properties of the vinylene-group connected OEP dimer more intensively as compared with the diacetylene-group connected OEP dimer. © 2002 Elsevier Science Ltd. All rights reserved.

In recent years, from various applicative viewpoints a great deal of effort has been made for the construction of well-defined, well-ordered and well-functioning molecules based on the porphyrin nuclei.[1] The compound **1**, dimer of octaethylporphyrin (OEP) connected with the diacetylene linkage, is of importance in terms of potential applicability to the function unit for opto-electronic communication systems.[2] The compound **2**, dimer of OEP connected with the vinylene linkage, is rather attractive as a model compound for the study of the special pair in a photosynthesis reaction center.[3] Each OEP dimer possesses the characteristic electronic structure due to the strong interaction between the two OEP rings through the respective linkages, coming to a simple conclusion that the diacetylene linkage affects Soret band more intensively, while the vinylene linkage does Q band preferably. We have also been engaged in the study of the one-dimensionally extended π-electronic conjugation system of OEP, proving that oligomerization of the OEP ring with particular linkages enhances their electron-releasing ability and optical susceptibility efficiently.[4] In connection with the peculiar features of these OEP dimers **1** and **2**, we designed the diacetylene- and vinylene-groups connected OEP tetramer **3** to examine and figure out the hybridism appearance of their properties as a function unit of the electronic devices. Here, we wish to report the synthesis of **3** and to describe its electronic properties, as compared with those of **1** and **2**.

The title compound **3** was synthesized by a homo-coupling of the terminal acetylene derived from the vinylene-group connected OEP dimer **2**, as shown in Scheme 1. Vilsmeier reaction of OEP is well known to proceed slowly to monoaldehyde even with 80–100 molar amounts of the reagent ($POCl_3$–DMF) at 50–55°C,[4,5] under the same conditions of which compound **2** was found to bring a fairly complicated mixture



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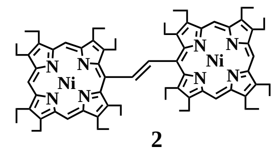

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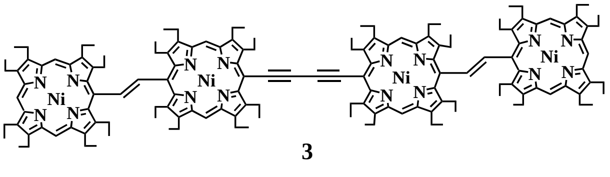

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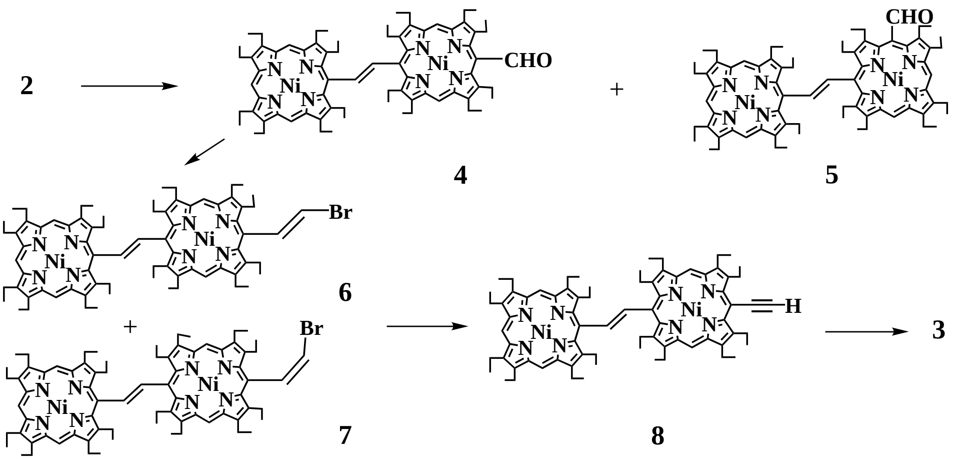

Scheme 1.

containing mono- and dialdehydes, on the basis of ^{1}H NMR and MS spectral analyses. After several examinations, the reaction of **2** only with 5–6 molar amounts of the reagent at 45°C was carried out to afford a mixture (3:1) of monoaldehydes **4**[6] and **5**[6] in ca. 80% yield, which is separated by repeated column chromatography on silica gel with hexane–chloroform. This result apparently indicates that the vinylene linkage accelerates not only the formylation of the OEP ring but also the directional preference toward the isomer **4**. Wittig reaction of **4** using $(CH_2Br)PPh_3{\cdot}Br$ with *n*-BuLi afforded a mixture (7–8:1) of the bromovinyl derivatives **6**[6] and **7**[6] in ca. 40% yield, together with a small amount of the vinyl compound.[7] Successively, without separation to each isomer, dehydrobromination of the mixture with NaH–DMSO was carried out to afford the acetylene derivative **8**[6] in ca. 20% yield. Then, the homo-coupling of **8** was carried out under the Eglinton conditions to afford **3** in ca. 75% yield as black–purple crystalline powder.[8]

The OEP tetramer **3** is fairly soluble in ordinary organic solvents, as compared with the diacetylene-group connected OEP dimer **1**. The structure of **3** was determined on the basis of MS and ^{1}H NMR spectra, as shown in Figs. 1 and 2. As is generally the case for nickel complexes, the MS spectrum by the ESI technique exhibited a fairly simple fragmentation pattern with peaks at around m/z 1280 assigned to the dicationic species of **3**, which is fully consistent with the computer simulated pattern of its sodium-associated species.[9] On the other hand, the ^{1}H NMR spectrum of **3** exhibited little changes for all the corresponding protons between before and after the coupling of **8**, except for the disappearance of the acetylenic proton (δ 4.51 ppm). Unexpectedly, it appears that compound **3** induces little structural reformation enough to perturb the OEP ring current due to an extension of the π-electronic conjugation, retaining the respective structural features of **1** and **2** to a great extent.[2–4] It was also noted that the vinylene linkage, which is thermodynamically susceptible to isomerization,[10] retains the *trans* configuration the same as that of **2** under Vilsmeier formylation and Eglinton coupling conditions.

The electronic absorption spectrum of **3** is shown in Fig. 3, together with those of **1** and **2**. It is well known that the Ni complex of OEP exhibits an absorption of Soret band at around 390 nm and two weak absorptions of Q band at 520–560 nm.[11] On the other hand, the diacetylene-group connected OEP dimer **1** splits the Soret band into three main absorptions at 430–490 nm together with a bathochromic shift of Q band.[2] In contrast with **1**, the vinylene-group connected OEP dimer **2** exhibits almost one broad absorption of Soret band at around 420 nm with a shoulder and gives rise to a long absorption tail of Q band over 800 nm.[3] Although both diacetylene and vinylene linkages would more or less display the characteristic effects on the OEP tetramer **3**, it shows that compound **3** remains the spectral feature of **2** rather predominantly over that of **1**, affording a broad Soret band at 400–440 nm and a very long absorption tail of Q band over 900 nm. This result seems to be compatible with the fact that the nickel complexes of the vinylene-group connected OEP oligomers are liable to hold the π-electronic conjugation planarities throughout the molecule even under the sterically and electronically perturbed circumstances, affording the long absorption tails up to the near infrared region.[12]

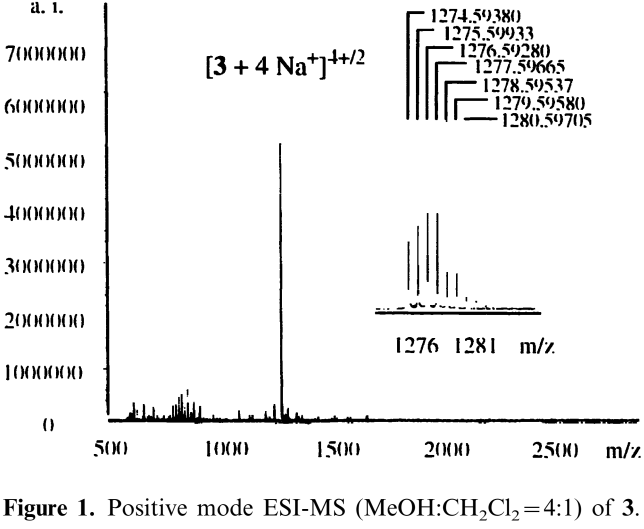

Figure 1. Positive mode ESI-MS ($MeOH{:}CH_2Cl_2=4{:}1$) of **3**.

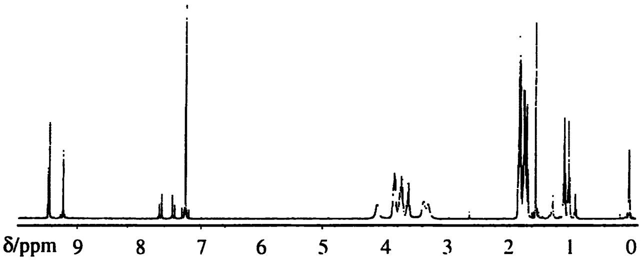

Figure 2. ^{1}H NMR spectrum of **3** (400 MHz, CDCl$_3$, 25°C).

Cyclic voltammetry was performed to measure the oxidation potentials of **3**, affording the reversible voltammogram with three redox waves (Table 1). The tetramer **3** was initially oxidized at 0.58 V as a measure of the electron-releasing ability, which is almost comparable to that of the vinylene-group connected OEP dimer **2**.[4a] As has been deduced from the electronic absorption spectral behavior,[4,12] the longer absorption tail of Q band can be regarded as a sign of the higher electron-releasing ability. In this respect, it is concluded that the diacetylene linkage of **3** plays a role mostly in holding the molecular geometry definitely with a slight affection on the higher HOMO level of the vinylene-group connected OEP dimer **2**.

From the viewpoint of structure–property relationship, further investigations of the OEP tetramer **3** are in progress.

Table 1. Half-wave oxidation potentials of **1**, **2**, and **3** under the conditions of GC working electrode versus SCE at a scan rate of 120 mV/s in dichloromethane

	$E^1_{1/2}$ (V)	$E^2_{1/2}$ (V)	$E^3_{1/2}$ (V)
1	0.86	1.01	1.35
2	0.62	0.70	1.23
3	0.58	0.74	1.30

References

1. (a) Burble, A. K.; Officer, D. L.; Playgoer, P. G.; Rid, D. C. W. *Chem. Rev.* **2001**, *101*, 2751–2796; (b) Aratani, N.; Osuka, A. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 1361–1379.
2. Arnold, D. P.; Johnson, A. W.; Mahendran, M. *J. Chem. Soc., Perkin Trans. 1* **1978**, 366–370.
3. Ponomarev, G. V.; Shul'ga, A. M. *Khim. Geterotskil. Soedin.* **1986**, 278–279.
4. (a) Higuchi, H.; Shimizu, K.; Ojima, J.; Sugiura, K.; Sakata, Y. *Tetrahedron Lett.* **1995**, *36*, 5359–5362; (b) Higuchi, H.; Shinbo, M.; Usuki, M.; Takeuchi, M.; Tani, K.; Yamamoto, K. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 1259–1275; (c) Higuchi, H.; Ishikura, T.; Miyabayashi, K.; Miyake, M.; Yamamoto, K. *Tetrahedron Lett.* **1999**, *40*, 9091–9095; (d) Higuchi, H.; Ishikura, T.; Mori, K.; Takayama, Y.; Yamamoto, K.; Tani, K.; Miyabayashi, K.; Miyake, M. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 889–906.
5. Arnold, D. P.; Johnson, A. W.; Winter, M. *J. Chem. Soc., Perkin Trans. 1* **1977**, 1643–1647.
6. ^{1}H NMR spectral data (400 MHz, CDCl$_3$, δ/ppm) are given. Compound **4**: 11.66 (1H, s, CHO), 9.44 (1H, s, *meso*-H), 9.42 (2H, s, *meso*-H), 9.04 (2H, s, *meso*-H), 7.75 and 7.34 (1H each, d, J=15.2 Hz, CH=CH), 3.88–3.22 (32H, m, CH$_2$), 1.82–1.62 (36H, m, CH$_3$), 1.10 (6H, t, J=7.2 Hz, CH$_3$), 0.98 (6H, t, J=7.2 Hz, CH$_3$). Compound **5**: 11.70 (1H, s, CHO), 9.45 (1H, s, *meso*-H), 9.43 (2H, s, *meso*-H), 9.10 (1H, s, *meso*-H), 9.08 (1H, s, *meso*-H), 7.71 and 7.31 (1H each, d, J=15.2 Hz, CH=CH), 3.87–3.21 (32H, m, CH$_2$), 1.83–1.64 (36H, m, CH$_3$), 1.12 (6H, t, J=7.2 Hz, CH$_3$), 0.98 (3H, t, J=7.2 Hz, CH$_3$), 0.91 (3H, t, J=7.2 Hz, CH$_3$). Compound **6**: 9.46 (1H, s, *meso*-H), 9.44 (2H, s, *meso*-H), 9.34 (1H, d, J=14.0 Hz, C$\underline{\text{H}}$=CHBr), 9.26 (2H, s, *meso*-H), 7.67 and 7.48 (1H each, d, J=15.6 Hz, CH=CH), 5.66 (1H, d, J=14.0 Hz, CH=C$\underline{\text{H}}$Br), 3.88–3.30 (32H, m, CH$_2$), 1.84–1.68 (36H, m, CH$_3$), 1.08 (6H, t, J=7.6 Hz, CH$_3$), 0.99 (6H, t, J=7.2 Hz, CH$_3$). Compound **7**: 9.53 (1H, d, J=8.0 Hz, C$\underline{\text{H}}$=CHBr), 9.47 (1H, s, *meso*-H), 9.46 (2H, s, *meso*-H), 9.25 (2H, s, *meso*-H), 7.76 and 7.51 (1H each, d, J=15.6 Hz, CH=CH), 6.95 (1H, d, J=8.0 Hz, CH=C$\underline{\text{H}}$Br), 3.89–3.14 (32H, m, CH$_2$), 1.84–1.64 (36H, m, CH$_3$), 1.12 (6H, t, J=7.6 Hz, CH$_3$), 0.97 (6H, m,

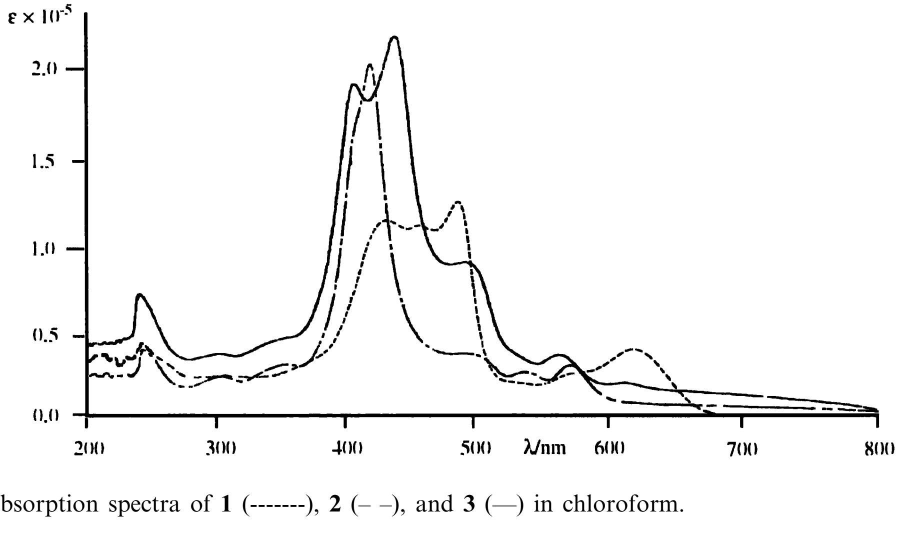

Figure 3. Electronic absorption spectra of **1** (-------), **2** (– –), and **3** (—) in chloroform.

CH_3). Compound **8**: 9.46 (1H, s, *meso*-H), 9.44 (2H, s, *meso*-H), 9.22 (2H, s, *meso*-H), 7.67 and 7.46 (1H each, $J=15.6$ Hz, CH=CH), 4.51 (1H, s, C:::CH), 4.18–4.09 (4H, br m, CH_2), 3.87–3.60 (20H, M, CH_2), 3.42–3.26 (8H, br m, CH_2), 1.83–1.66 (36H, m, CH_3), 1.07 (6H, t, $J=7.6$ Hz, CH_3), 0.99 (6H, t, $J=7.0$ Hz, CH_3). The other spectral and physical properties will be reported elsewhere.

7. Arnold, D. P.; Nitschinsk, L. J. *Tetrahedron* **1992**, 8781–8792.
8. Eglinton, G.; Galbraith, A. R. *Chem. Ind.* **1956**, 737–738.
9. Marshall, A. G.; Hendrickson, C. L.; Jackson, G. S. *Mass Spectrom. Rev.* **1998**, *17*, 1–35.
10. (a) Ponomarev, G. V.; Borovkov, V. V.; Sugiura, K.; Sakata, Y.; Shul'ga, A. M. *Tetrahedron Lett.* **1993**, *34*, 2153–2156; (b) See Ref. 4b.
11. (a) Buchler, J. W.; Puppe, L. *Justus Liebigs Ann. Chem.* **1970**, *740*, 142–163; (b) Buchler, J. W. In *Porphyrins And Metalloporphyrins*; Smith, K. M., Ed.; Elsevier Scientific Publishing Co.: New York, 1975; pp. 157–231.
12. Higuchi, H.; Shinbo, M.; Usuki, M.; Takeuchi, M.; Hasegawa, Y.; Tani, K.; Ojima, J. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 1887–1898.