



Synthesis and properties of unsymmetrically extended π -electronic conjugation system of octaethylporphyrin(Ni)–dihexyibithiophene–octaethylporphyrin(Pd) connected with diacetylene linkage

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This paper is dedicated to Emeritus Professor Soichi Misumi on the occasion of his 77th birthday

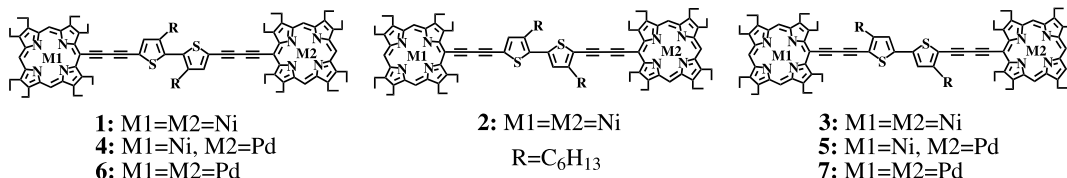
Abstract—Orientational isomers of the diacetylene-group connected dihexyibithiophene (DHBTh) derivatives have been synthesized, in which the different octaethylporphyrin (OEP(M); M=Ni or Pd) rings are attached at the ends. Reflecting the unsymmetrical structural feature, the peculiar electronic properties of the extended OEP(Ni)–DHBTh–OEP(Pd) system were observed.

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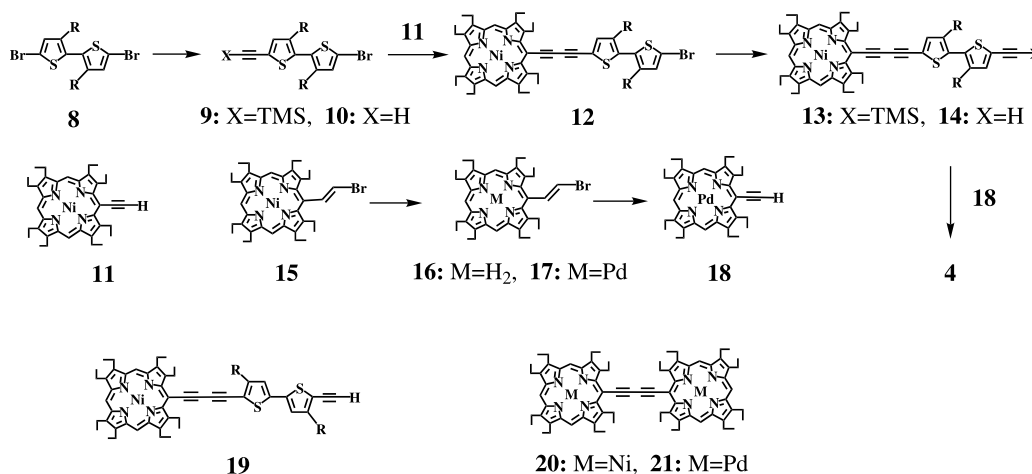
A wide variety of well-defined oligomers and arrays of the porphyrin nucleus has been vastly demonstrated for the sake of new organic materials with the purposive optoelectronic functionalities.¹ Previously, we reported the synthesis of orientational isomers **1**–**3** of the dihexyibithiophenes (DHBTh), in which the octaethylporphyrin (OEP) rings are connected with the diacetylene linkage at both terminal positions.² Spectral studies of this extended OEP(Ni)–DHBTh–OEP(Ni) π -electronic conjugation system proved that the electronic communication between the two terminal OEP(Ni) rings can be controlled by the central DHBTh constituents, exhibiting the split of Soret bands with the greater magnitudes in the order of orientation of DHBTh; head-to-head (HH) < head-to-tail (HT) < tail-to-tail (TT).³ As a next stage, in relation with such intensive researches on functional molecules,¹ unsymmetrization of the π -electronic conjugation system is necessary for achieving the efficient anisotropic electron- and/or energy-transfer channels. Thus, among a variety of principles, we first designed to

construct the unsymmetrically extended system (**4** and **5**), by introducing the different OEP rings into this system (**1** and **3**). Here, we wish to report the synthesis and structural properties of the OEP(Ni)–DHBTh–OEP(Pd) system and to figure out its hybridism appearance as a function unit for the optoelectronic devices, as compared with those of the symmetrical ones **1/3** and **6/7**.

Under the ordinary conditions for OEP(Ni),⁴ the denickelation from **1** and **3** to the corresponding free-bases OEP(H₂) was entirely unsuccessful, mostly to afford hardly soluble materials, or otherwise to exhibit poor reactivity. Therefore, in despair of persisting in a shortcut methodology for incorporation of the different metals into the OEP(H₂) rings of **1** and **3**, the multi-step but steady synthetic route was employed via the terminal acetylene **14** as a useful synthon (Scheme 1). For the synthesis of **4**, for example, Sonogashira treatment of dibromobithiophene **8**⁵ with one molar equivalent amount of trimethylsilylacetylene afforded the ethynyl



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Scheme 1.

product **9** in proper yield,⁶ which was readily suffered from alkaline hydrolysis to the terminal acetylene **10**. Cross coupling reaction of the ethynyl OEP(Ni) **11**⁷ with more than 5 molar equivalent amount of **10** under the Eglinton conditions gave the bromide **12** in moderate yield,⁸ together with a large quantity of the dimeric product from **10**. Then, according to a series of transformation procedures similarly for **10**, the terminal acetylene **14** describable as OEP(Ni)–DHBTh was smoothly obtained from **12**. On the other hand, the ethynyl OEP(Pd) **18** as a counterpart was led starting from the bromovinyl OEP(Ni) **15**,⁷ with which the tandem reactions of Ni extrusion (**16**) and Pd incorporation (**17**) were carried out, followed by dehydrobromination from **17** with NaH–DMSO. Finally, oxidative coupling reaction of the terminal acetylene **14** with more than 5 molar equivalent amount of **18** afforded the HH isomer **4** of the OEP(Ni)–DHBTh–OEP(Pd) system in 35% yield, together with the diacetylene-group connected OEP(Pd) dimer **21** (42%). The TT isomer **5** was also synthesized in a similar way, from **18** and TT isomeric OEP(Ni)–DHBTh **19**. Furthermore, the symmetrical OEP(Pd) derivatives **6** and **7** were synthesized from **18** and the respective DHBTh terminal bis(acetylene)s, through the previously reported procedures for the OEP(Ni) derivatives **1** and **3**.^{2,3}

Structures of all the new compounds were determined by means of MS and ¹H NMR spectra as well as elemental analyses. ¹H NMR spectrum of HH isomer **4**, for example, exhibited little difference in all the signals due to *meso*-protons of OEP (*meso*-H) and DHBTh protons (Th-H) from the corresponding ones of **1** and **6**, indicating retention of their respective structural features in the OEP(Ni)–DHBTh–OEP(Pd) system to a great extent (Table 1). In particular, since the respective chemical shifts due to *meso*-H are almost the same between **4**, **20**⁷ and **21**, it can be concluded that the structural reformation is not explicit enough to destroy the 18 π -electron ring system of OEP to form the new magnetic conjugation system by both extension through DHBTh and unsymmetrization of the conjugation system of this type. This was the same case for the TT

Table 1. Chemical shifts (δ /ppm) of the selected protons of OEP(M1)–DHBTh–OEP(M2) (400 MHz, CDCl₃)

Compounds	<i>meso</i> -H	Th-H
1	9.42, 9.40	7.33
3	9.42, 9.39	7.01
4	9.42, 9.40	7.33
	9.98, 9.94	7.39
5	9.43, 9.40	7.06
	10.00, 9.96	7.07
6	10.00, 9.95	7.41
7	10.02, 9.96	7.11
20	9.42, 9.39	
21	10.03, 9.96	

isomer **5**. Thus, on Th-H of **4** (**5**), the respective OEP(M) rings were found to exhibit their ring current effects (RCE) rather independently, with similar magnitudes to the corresponding RCE of **1/6** (**3/7**). This would lead to a consequence that the value of ca. 0.3 ppm in chemical shift changes is a common difference between HH and TT isomers in the present system, regardless of the incorporated metals, which should be attributed to different magnitudes of anisotropic effects on Th-H from the rigid linkage of diacetylene.

As contrasted with the high similarity in the skeletal feature between **1–7**, the close inspection by IR spectra with respect to the particular stretching vibrations due to the diacetylene linkage exhibited a suggestive feature of the π -electronic conjugation system, resulting in a low-energy shift for all the TT isomers as compared with the corresponding HH ones. This tendency was much pronounced for the Pd complexes to expand up to a difference of 10 cm⁻¹ between HH and TT isomers. This result indicates that the TT isomers induce a cumulated character into the diacetylene linkage much preferably, through which the efficient π -electronic interaction between the terminal OEP rings would take place particularly in the Pd complexes.

In the case of the symmetrical complexes (**1/3** and **6/7**), the electronic absorption spectra exhibit the characteristic features on reflection of orientation of the DHBTh constituents, leading to a simple conclusion that HH isomers afford almost one broad Soret bands, while TT isomers the splitting Soret bands into two main ones. Yet, the Pd complexes exhibited the slight hypsochromic shifts with their respective bands sharpening, as compared with the corresponding Ni complexes. On the other hand, the unsymmetrical complexes **4** and **5** also showed the spectral behavior the same as the symmetrical ones **1/6** and **3/7**, but rather possessed the features of the heavier metal Pd complexes in both HH and TT isomers (Fig. 1).

As it is implied from IR spectral analysis that other electronic stimulations bring out some differences in this system reflecting both orientation of DHBTh and incorporated metals, the unsymmetrical feature of **4** and **5** clearly appeared in a solvent effect on their spectra (Fig. 2). The HH isomer **4** was found to afford nearly the same spectra in both chloroform and hexane, while the TT isomer **5** the different spectra between them to afford the new band ($\lambda_{\text{max}}=630$ nm) with a long absorption tail in hexane. This is probably due to an elevation of HOMO level in a non-polar solvent, after being further free from the degenerated states of Q band by unsymmetrization of the conjugation system. In the case of the Ni complexes **1** and **3**, both HH and TT isomers did scarcely exhibit such a solvent effect on their spectra. The Pd complexes **6** and **7**, however, showed the same behavior as that for **4** and **5**, revealing that only the TT isomer **7** intensified the new absorption band ($\lambda_{\text{max}}=625$ nm) much further in hexane. Although it is premature to deduce a conclusion of the interaction origins of OEP nuclei in the system with solvents, all these results clearly indicate that the electronic communication takes place efficiently between the OEP(Ni) and OEP(Pd) rings in the unsymmetrical system of TT isomer **5** to give rise to a polarization action at the ground state.

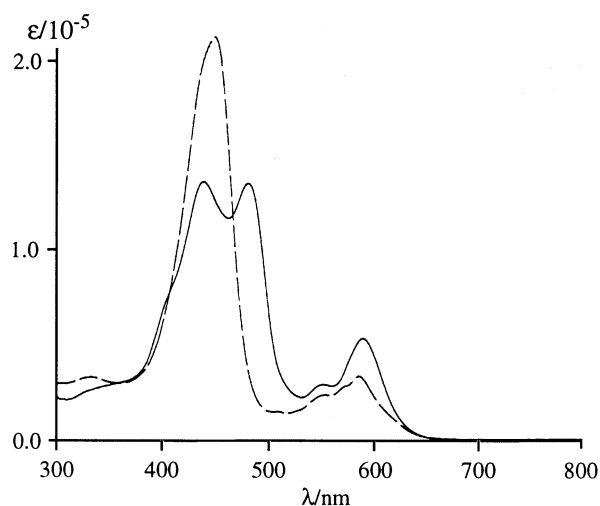


Figure 1. Electronic absorption spectra of **4** (---) and **5** (—) in chloroform.

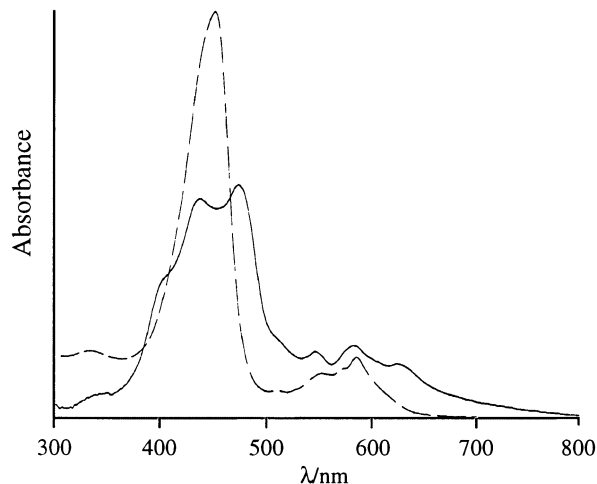


Figure 2. Electronic absorption spectra of **4** (---) and **5** (—) in hexane.

It is evidently demonstrated that concurrently with orientation of the DHBTh constituent, unsymmetrization by introducing the different metal complexes of OEP is also essentially effective for the energy and/or electron transfer functionality from one to the other in the present π -electronic conjugation system.⁹ Yet, it is noted that the synthetic success of the terminal acetylenes **14** and **19** would impel the present research forward onto the next stage, aiming at the applications of the extended π -electronic conjugation systems with these simply- and well-defined straight molecular skeletons.¹⁰

Acknowledgements

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References

- For recent reviews of the functional molecules of porphyrins, see: (a) Osuka, A.; Fujikane, D.; Shinmori, H.; Kobatake, S.; Irie, M. *J. Org. Chem.* **2001**, *66*, 3913; (b) Lukas, A. S.; Bushard, P. J.; Wasielewski, M. R. *J. Phys. Chem. A* **2002**, *106*, 2074; (c) Kodis, G.; Liddell, P. A.; Garza, D. L.; Clausen, P. C.; Lindsey, J. S.; Moore, A. L.; Moore, T. A.; Gust, D. *J. Phys. Chem. A* **2002**, *106*, 2036; (d) Harth, E. M.; Hecht, S.; Helms, B.; Malmstrom, E. E.; Frechet, J. M. J.; Hawker, C. J. *J. Am. Chem. Soc.* **2002**, *124*, 3926; (e) Choi, M. S.; Aida, T.; Yamazaki, T.; Yamazaki, I. *Chem. -A Euro. J.* **2002**, *8*, 2668; (f) Odobel, F.; Suresh, S.; Blart, E.; Nicolas, Y.; Quintard, J. P.; Janvier, P.; LeQuestel, J. Y.; Illien, B.; Rondeau, D.; Richomme, P.; Haupl, T.; Wallin, S.; Hammarstrom, L. *Chem. -A Euro. J.* **2002**, *8*, 3027.

2. Higuchi, H.; Ishikura, T.; Miyabayashi, K.; Miyake, M.; Yamamoto, K. *Tetrahedron Lett.* **1999**, 40, 9091.
3. Higuchi, H.; Ishikura, T.; Mori, K.; Takayama, Y.; Yamamoto, K.; Tani, K.; Miyabayashi, K.; Miyake, M. *Bull. Chem. Soc. Jpn.* **2001**, 74, 889.
4. (a) Arnold, D. P.; Nitschinsk, L. J. *Tetrahedron Lett.* **1992**, 33, 8781; (b) Buchler, J. W. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. I, pp. 390–483.
5. (a) Higuchi, H.; Nakayama, T.; Koyama, H.; Ojima, J.; Wada, T.; Sasabe, H. *Bull. Chem. Soc. Jpn.* **1995**, 68, 2363; (b) Higuchi, H.; Yoshida, S.; Uraki, Y.; Ojima, J. *Bull. Chem. Soc. Jpn.* **1998**, 71, 2229.
6. Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 16, 4467.
7. Arnold, D. P.; Johnson, A. W.; Mahendran, M. *J. Chem. Soc., Perkin Trans. 1* **1978**, 366.
8. Eglinton, G.; Galbraith, A. R. *Chem. Ind.* **1956**, 737.
9. The time-resolved spectroscopic measurements of **1–7** and their related compounds are now under investigations, the results from which will be reported elsewhere properly.
10. The system describable as OEP(M)–DHBTh–(π -system), in which the (π -system) constituents are benzoquinone, pyrene and so forth, has been successfully synthesized in a similar way. Their electronic properties are now under investigations.