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Synthesis and properties of the octaethylporphyrin–dihexylbithiophene–pyridine system (OEP–DHBTh–Py) connected with diacetylene linkage. Proton-mediated and heat-driven spectral changes

Naoto Hayashi,[a] Takuya Matsukihira,[a] Keiko Miyabayashi,[b] Mikio Miyake[b] and Hiroyuki Higuchi[a,*]

[a]*Graduate School of Science and Engineering, University of Toyama, 3190 Gofuku, 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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This paper is dedicated to Emeritus Professor Philip Eaton on the occasion of his 70th birthday

Abstract—Orientational isomers of the octaethylporphyrin–dihexylbithiophene–pyridine system (OEP–DHBTh–Py) connected with the diacetylene linkage were synthesized. The spectral measurements were performed under neutral and acidic conditions, clearly proving that the orientation of DHBTh affects not only the electronic structures of OEP–DHBTh–Py but also their proton-mediated spectral changes.

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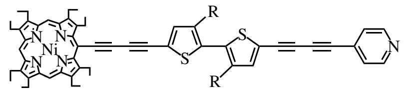
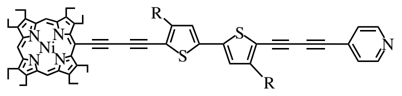
In recent years, we have been engaged in the studies of the diacetylene-group connected dihexyl-2,2′-bithiophene (DHBTh) derivatives bearing octaethylporphyrin [OEP(M)], experimentally proving that the orientation of DHBTh (head-to-head; HH, head-to-tail; HT, tail-to-tail; TT) plays an important role in a long-distant electronic communication between two terminal OEP(M) rings of OEP(M)–(DHBTh)$_n$–OEP(M).[1] Ever since this finding, according to a general synthetic methodology for unsymmetrical OEP(M1)–DHBTh–OEP(M2) system,[2] various derivatives of OEP(M)–DHBTh–[π-electronic system] have been constructed to examine the electronic interaction of OEP(M) with the opposite-side [π-electronic system] through the diacetylene-group connected DHBTh constituent.[3] From the study of the OEP–DHBTh–Fullerene system, for instance, it has been curiously shown that the orientation of DHBTh affects not only their electronic and electrochemical properties but also their molecular motional behaviors.[4]

In connection with intensive studies of a wide variety of derivatives carrying porphyrin and thiophene nuclei to develop the new organic functional materials,[5] a pair of derivatives **1** and **2** of OEP–DHBTh–[π-electronic system] was synthesized, in which [π-electronic system] was replaced with pyridine nucleus (Py) as a proton-acceptable site (Chart 1). The spectral behaviors of the OEP–DHBTh–Py system were observed under the



1: OEP-(HH)DHBTh-Py



2: OEP-(TT)DHBTh-Py

Chart 1.

Keywords: Porphyrin; Thiophene; Pyridine; Orientation; Protonation.

* Corresponding author. E-mail: higuchi@sci.u-toyama.ac.jp

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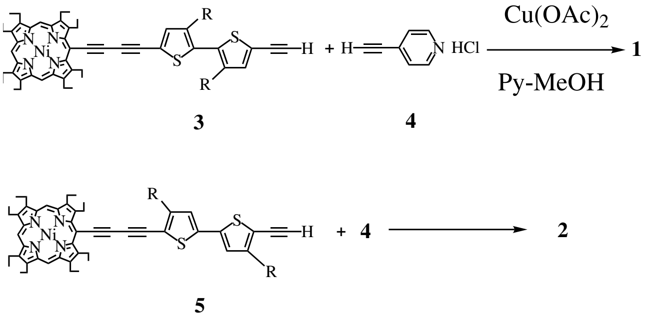

Scheme 1.

neutral and acidic media, in order to figure out the structural feature as a functional unit of the electronic devices. In this letter, the synthesis of **1** (HH isomer) and **2** (TT isomer) and the DHBTh effect on their proton-mediated spectral changes will be reported, as compared with those of the related compounds.

The OEP–DHBTh–Py derivatives **1** and **2** were synthesized as shown in Scheme 1, utilizing an oxidative cross-coupling reaction of the OEP–DHBTh terminal acetylene **3**[2] or **5**[2] with 4-ethynylpyridine **4**[6] under the modified Eglinton conditions.[7] The Py terminal acetylene **4** is hard to exist in a free form for a long reaction period under such an oxidative atmosphere, spontaneously affording the diacetylene-group connected Py dimer **6**[8] (Chart 2). Therefore, the hydrochloride of **4** was employed for the coupling reaction as it was, with 50–60 times excessive amounts to **3** or **5**. In practice, the basic binary solvent system (pyridine–MeOH = 1:1) was found useful for gradual generation of the free acetylene **4**. The coupling reaction of **4** with the corresponding terminal acetylenes **3** and **5** smoothly took place to afford the desired products **1**[8] and **2**[8] in excellent yields, respectively, as stable dark purple microcrystallines (hexane–$CHCl_3$).

The structures of **1** and **2** were satisfactorily determined by means of MS, IR, and ^{1}H NMR spectral measurements. In ^{1}H NMR spectra, both **1** and **2** exhibited fairly simple features, affording two *meso*-protons (*meso*-H; Ha and Hb) at around 9.4 ppm and a set of pyridine-protons (Py-H; He and Hf) at around 8.6 and 7.4 ppm, respectively, as shown in Figure 1a for **1**. Other ethyl and hexyl substituents also afforded their corresponding protons at the very similar regions with the same splitting patterns between them. Only a particular difference between **1** and **2** appeared in the thiophene-protons (Th-H; Hc and Hd) of DHBTh, to resonate at around 7.3 ppm for **1** and at around 6.9 ppm for **2**, respectively, reflecting the greater anisotropic effect of the diacetylene linkage on Th-H of **1**. The spectra of **1** as well as **2**, however, showed that all chemical shifts due to *meso*-H, Th-H and Py-H are almost the same as those of the corresponding constituents **3**, **4**, and **5**. As a result, it is concluded that the OEP–DHBTh–Py derivatives **1** and **2** substantially possess the molecular skeletons of the OEP–DHBTh constituents **7** and **8**, simply combined with **4**, without particularly being affected by extension of their π-electronic conjugation with the Py ring (Chart 2).[3]

^{1}H NMR spectral changes of **1** were successively observed, as follows. Trifluoroacetic acid (TFA) was added drop by drop to a deuterated 1,1,2,2-tetrachloroethane ($CDCl_2CDCl_2$) solution of **1** (Fig. 1a), gradually changing its spectral appearance to afford a steady-state spectrum. As shown in Figure 1b, it is revealed that Th-H resonate at almost the same positions as those in $CDCl_2CDCl_2$, while Py-H shift to the low field by ca. 0.2 ppm and ca. 0.5 ppm, respectively. In addition, it is noted that not only *meso*-H but also methylene-H of the ethyl substituents enormously broadened with their chemical shifts unchanged or collapsed into a baseline (in $CDCl_3$–TFA). Finally, the original spectrum of **1** was entirely recovered by quenching TFA with triethylamine (NEt_3). These results explicitly indicate that protonation smoothly occurs at a terminal site of the Py ring to make Py-H shift to the lower fields and that the π-electronically basic diacetylene linkage is scarcely affected by TFA.

On one hand, from the signal broadening phenomenon for particular protons of **1** in an acidic medium (Fig. 1b), it is suggested that protonation to the Py ring brings some peculiar structural change into **1**. Under the same conditions, the signal broadening phenomena of *meso*-H and methylene-H in reference compounds **7** and **8** including OEP(Ni) were barely observed. Coalescence phenomenon between more than two conformational and/or geometrical isomers would not necessarily be taken into account here in the metalloporphyrins like **1**.[9] Face-to-face stacked aggregation of the OEP constituent is not the case, either, because no particular up-field shift of *meso*-H due to an anisotropic effect of the diamagnetic OEP(Ni) ring was observed in **1** (see Fig. 1a and b).[10] In a few cases of substituted porphyrin Ni(II) derivatives, it is known that paramagnetic complexes are formed upon addition of the fifth ligands such as piperidine and pyridine, resulting in the broad signals of *meso*-H together with their pronounced up-field shifts.[11] The formation of paramagnetic complex, however, seems to be uncertain in **1**, since a recognizable up-field shift of *meso*-H after protonation to it is not practically observed. Yet, addition of deuterated pyridine into $CDCl_2CDCl_2$ solution of **1** showed no particular spectral changes. As described below in the electronic

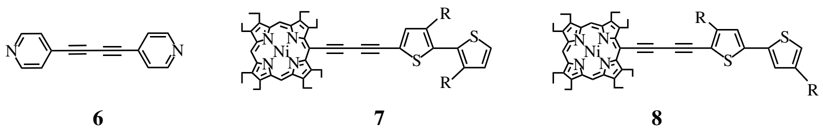

Chart 2.

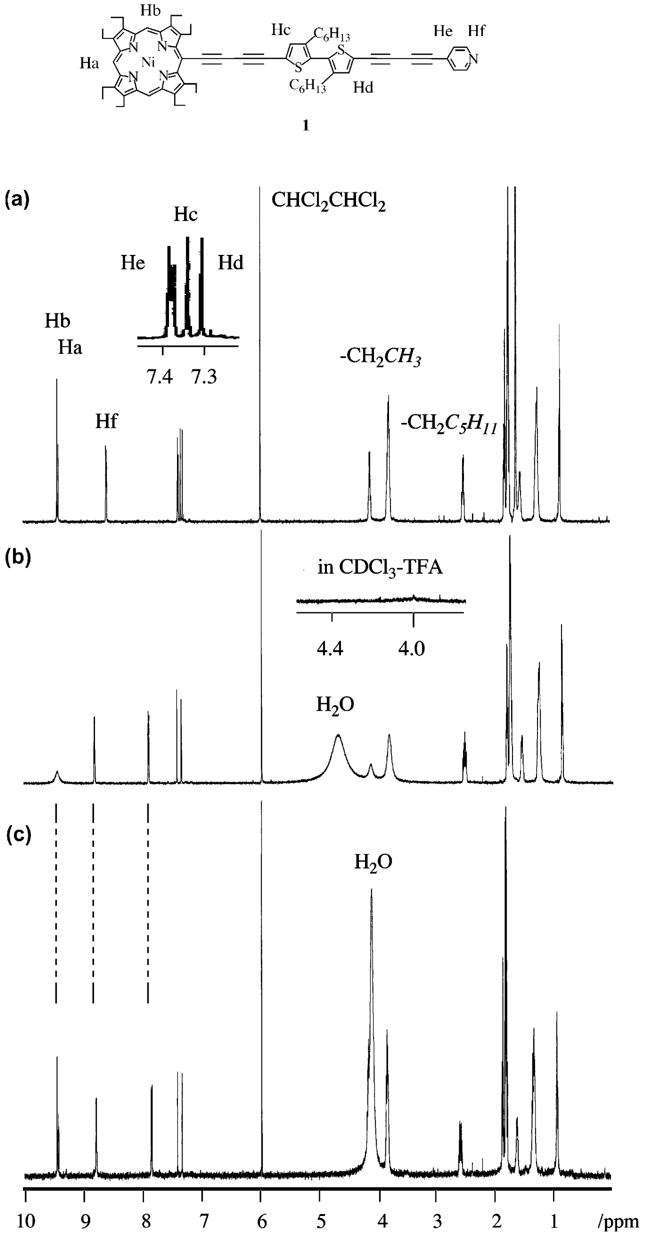

Figure 1. ^1H NMR spectral changes of **1** (600 MHz): (a) in $CDCl_2CDCl_2$ at 25 °C, (b) in $CDCl_2CDCl_2$ containing TFA at 25 °C and (c) in $CDCl_2CDCl_2$ containing TFA at 80 °C.

absorption spectral study, it was indicated that protonation to the Py ring by TFA simultaneously causes coordination of the TFA counter anion as the fifth ligand onto the OEP ring of **1**. This ligandation of the TFA anion might affect the free motional behavior of the OEP(Ni) constituent in such a long one-dimensional system somehow, resulting in an outstanding prolongation of the relaxation times only for most protons directly attaching to the OEP ring. However, the TFA counter anion produced after protonation to the Py ring seems to coordinate very weakly onto the OEP(Ni) ring of **1**. It was evidently ascertained that the temperature elevation gradually changes its spectral appearance to recover the very high resolution for all signals above 60 °C, with their chemical shifts almost unchanged (Fig. 1c). This result suggests a migration of the TFA anion from the OEP(Ni) ring backward to the cationic site of the Py constituent.

Although a rational interpretation responsible for the signal broadening phenomenon in **1** should wait for further studies,[12] the present extended OEP(Ni) derivative **1** can be regarded as a reversible system to show proton-mediated and heat-driven spectral changes, as summarized in Figure 2. The TT isomer **2** also showed almost the same spectral change as **1**, in which the kinetic difference between them obviously reflects the conjugation planarity of DHBTh.[13]

The electronic absorption spectra of **1** and **2** were similarly observed in the neutral and acidic media (Fig. 3). In $CHCl_3$ solution, reflecting the orientation of DHBTh, HH isomer **1** exhibited one symmetrical curve of Soret band at $\lambda_{max} = 450$ nm (Fig. 3a), while TT isomer **2** did the broadly distorted Soret band at $\lambda_{max} = 475$ nm with two shoulder bands in a shorter wavelength region (Fig. 3b). Derivatives **1** and **2** showed the corresponding Q bands with slightly different shapes from each other, seemingly trapezoidal for **1** and triangular for **2**, but both isomers afforded almost the same absorption maximum at around $\lambda_{max} = 600$ nm. These results are highly in accordance with the contrastive roles of the terminal 3-hexylthiophene ring (HTh) of DHBTh in **7** and **8**.[3] Thus, it could be simply concluded that HH isomer **1** exhibits a combined electronic structure between two components; OEP and Py interacted with HTh through the diacetylene linkage, describable as [OEP–HTh]–[HTh–Py], while TT isomer **2** extends π-electronic conjugation throughout the molecule due to the higher conjugation planarity of DHBTh.

In connection with ^1H NMR spectral changes, addition of TFA to the $CHCl_3$ solutions of **1** and **2** also induced

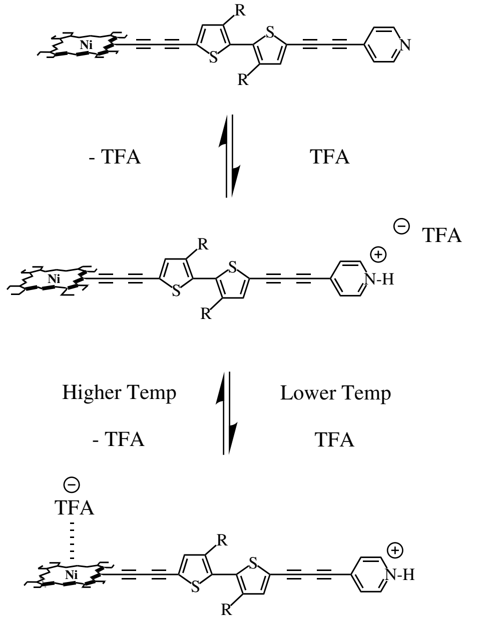

Figure 2. Proton-mediated and heat-driven structural changes of the OEP–DHBTh–Py derivative (**1**).

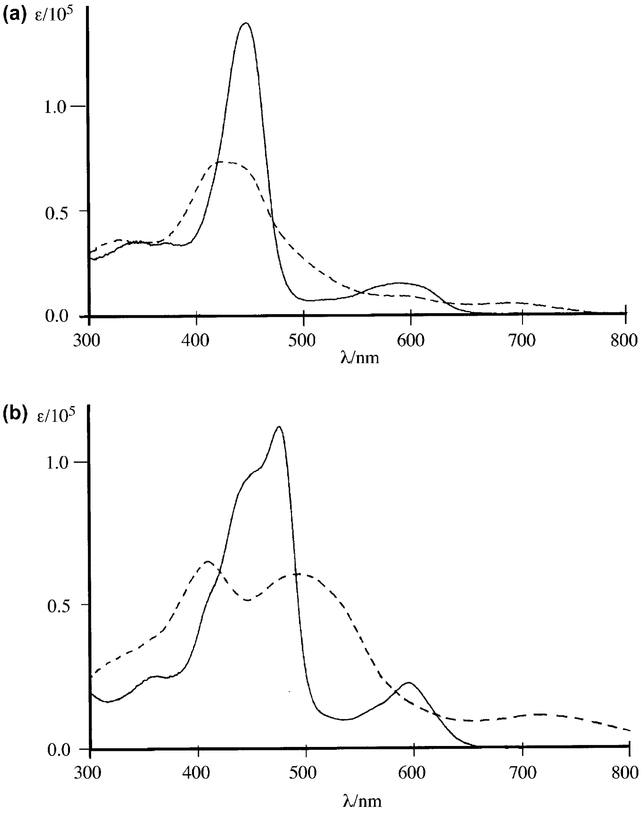

Figure 3. Electronic absorption spectra in $CHCl_3$ solution (solid line) and in TFA-added $CHCl_3$ solution (broken line) at 25 °C: (a) for **1** and (b) for **2**.

the unique behaviors of their Soret and Q bands, respectively. Thus, in the steady state, HH isomer **1** largely broadened Soret band and decreased its intensity with a small hypsochromic shift. On the other hand, TT isomer **2** dramatically changed Soret band to split into two main bands, showing hypsochromic ($\lambda_{max} = 405$ nm) and bathochromic ($\lambda_{max} = 495$ nm) shifts, respectively. Furthermore, in both cases, the initial Q bands in $CHCl_3$ decreased and inversely the new bands increased in a 100–130 nm longer wavelength region, to appear at around $\lambda_{max} = 690$ nm for **1** and at around $\lambda_{max} = 725$ nm for **2**, respectively. This result indicates an additional axial coordination by the TFA counter anion on the OEP(Ni) ring, which weakens the back-donation interaction from Ni(II) to the 18π-electronic conjugation system of OEP to pull down its LUMO, resulting in a considerable bathochromic shift of Q band.[14] Finally, quenching of TFA with NEt_3 recovered their original spectra perfectly, in accordance with ^1H NMR experiments.

These spectral changes apparently indicate that the present system is transformable between two electronic structures of marked individuality by TFA as a mediator. In other words, a positive-charge introduction into one terminal site reforms the electronic structure of another terminal OEP site efficiently to perturb its $\pi \rightarrow \pi^*$ transition through the DHBTh constituents. Yet, it is proved that the conjugated base, TFA anion, weakly coordinates from the axial site onto the OEP(Ni) ring of **1** but efficiently affects its $n \rightarrow \pi^*$ transition, too, reflecting their conjugation planarity of DHBTh.

The present structural and spectral conclusions evidently come from the characteristic nature of the OEP–DHBTh–Py derivative, in which each constituent is connected with the straight and rigid linkage of diacetylene. Further investigations of protonation to **1** and **2** under various acidic conditions are now in progress.[13]

Acknowledgments

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dd, $J = 6.1$ and 1.3 Hz). Other physical properties of the new compounds will be reported somewhere in detail.

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12. The signal broadening phenomenon of *meso*-H in ^{1}H NMR spectra could be induced not only due to the complexed OEP(Ni) paramagnetism with the fifth ligand but also due to the kinetic motion of the OEP(Ni) constituent around the molecular axis. Further studies for the present phenomenon are underway.
13. In addition to proton-mediated and temperature-dependent spectral changes, solvent- and pK_a-dependent spectral changes of **1** and **2** were also observed. The results from quantitative analyses of their spectral changes will be reported in detail, together with the DHBTh effect on their electrochemical properties.
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