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Synthesis and electronic properties of hexylthiophene–octaethylporphyrin derivatives (HTh–OEP) connected with diacetylene linkage: substituent effect on the electronic structure of the extended HTh–OEP conjugation system

Naoto Hayashi, Hiroki Nakashima, Yukari Takayama and Hiroyuki Higuchi*

Department of Chemistry, Faculty of Science, Toyama University, 3190 Gofuku, Toyama, Toyama 930-8555, Japan

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

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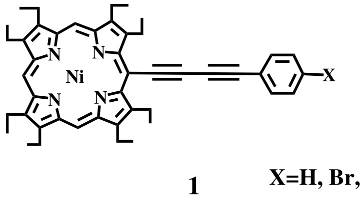
Abstract—Octaethylporphyrin (OEP) was combined with 2-substituted 3-hexylthiophenes (HTh) by diacetylene linkage to afford the highly extended conjugation system (HTh–OEP). Their absorption spectral properties were examined, proving that the electronic structure of OEP is affected by the more electron-withdrawing substituents through the diacetylene linkage more dramatically. The substituent effect on the HTh–OEP conjugation system is much outstanding, as compared with that on the corresponding benzene system (Bzn–OEP). © 2003 Elsevier Science Ltd. All rights reserved.

In connection with an intensive study of functional molecules, a variety of well-defined porphyrin-based conjugation systems has been demonstrated for the development of new organic materials such as optoelectronic and electrochemical devices, by virtue of their high susceptibilities to the light and electronic stimulations.[1] Previously, we reported the synthesis of the extended conjugation system between octaethylporphyrin (OEP) and *p*-substituted benzene (Bzn) rings, both chromophores of which are connected with the diacetylene linkage (**1**: Bzn–OEP).[2] From the absorption spectral studies, the intramolecular charge transfer (IaCT) interaction through the diacetylene linkage,[3] which would potentially open the door to various molecular functionalities such as non-linear optical (NLO) behaviors, was subtly observed only for the nitro derivative of the Bzn–OEP system. On the other hand, we have been engaged in the studies of various 3-hexylthiophene (HTh) derivatives, where the hexyl group is simply introduced for processability of the materials.[4] HTh itself also proved to interact with each other through the diacetylene linkage more intensively,[5] probably due to the smaller resonance energy (RE) of the Th ring, as compared with the corresponding Bzn derivatives.[6] Therefore, displacement of Bzn with HTh to construct the HTh–OEP system (**2**) would be expected to give rise to the more contribution of IaCT interaction in the extended conjugation system. Here we wish to report the synthesis of **2**, to describe their structural properties and to figure out the substituent effect on their electronic absorption spectra, as compared with the respective behaviors of **1**.

The first two derivatives of **2** (X = H and Br)[5c] were readily prepared by oxidative cross-coupling reactions between the corresponding terminal acetylenes, simi-



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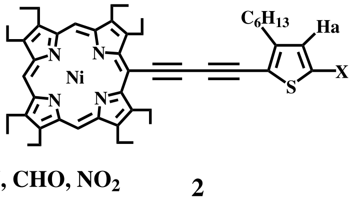
X=H, Br, CN, CHO, NO_2



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* Corresponding author.

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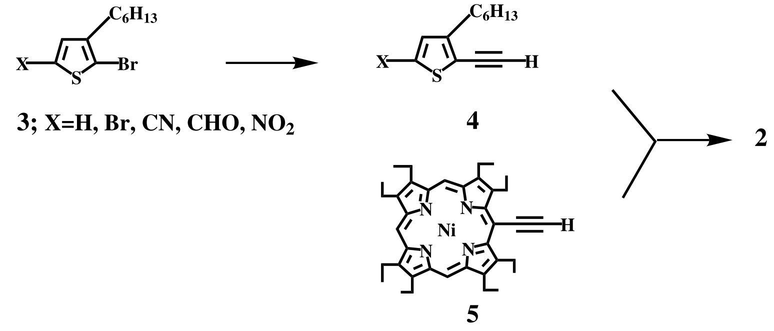
larly for the Bzn–OEP derivatives.[2] Since the lithiation at α-position of the Th nucleus is well known to proceed efficiently,[7] transformations of the lithiated species by electrophilic substitutions to the other derivatives of **2** (X = CN, CHO, NO_2) were initially examined. However, the attempts for transformation of those derivatives under various conditions; temperatures, bases and solvents,[8] were entirely unsuccessful to afford hardly soluble materials, or otherwise to exhibit poor reactivities to lithiation. Thus, as a result, synthesis of the other derivatives was also carried out by the coupling reactions of the terminal acetylenes **4**[8] and **5**,[9] as shown in Scheme 1. Reactions of **5** with more than 10 equiv. amount of **4** under the Eglinton conditions[10] afforded the HTh–OEP derivatives **2** (10–50%), together with the respective diacetylene-group connected HTh dimers from **4** in quantity. All the products of **2** are easily separated by column chromatography on silica gel and are stable reddish- to black-purple microcrystallines.[8]

Structures of all the new compounds were determined on the basis of MS, IR and ^{1}H NMR spectra as well as elemental analyses. ^{1}H NMR spectra of **2** exhibited little changes for all the corresponding protons between before and after the coupling of **4** and **5**, except for disappearance of acetylenic protons (C:::CH). It appears that the skeletal reformation in the HTh–OEP system is not particularly caused by extension of conjugation system, nor by introduction of substituents X, retaining the respective structural features of **4** and **5** to a great extent. Thus, as contrasted with apparent low-field shift of HTh protons (Ha) due to the nearby substituents of X from $\delta = 6.91$ ppm (X = H) to $\delta = 7.74$ ppm (X = NO_2), all the *meso*-protons of OEP (*meso*-H) resonated at around $\delta = 9.4$ ppm the same region as for **5**. This is exactly the same case for the Bzn–OEP system **1**,[2] clearly indicating that the substituent effect of X on both of **1** and **2** is not so intensive enough to destruct the 18 π-electron ring system of OEP to form the new magnetic conjugation system. On the other hand, IR spectral analysis with respect to the particular absorptions due to C:::C–C:::C stretching vibrations exhibited a very suggestive feature of the π-electronic conjugation system **2**, resulting in a low-energy shift by ca. 20 cm^{-1} from the corresponding Bzn–OEP derivatives and yet in a perceptible substituent dependence from $\nu = 2185$ cm^{-1} (X = H) to $\nu = 2175$ cm^{-1} (X = NO_2). These observations conclude that the substituents X of **2** could perturb the electronic structure of OEP through the diacetylene linkage more intensively without deforming the main skeleton so crucially, as compared with those of **1**.

In spite of the high similarity in the skeletal feature between **1** and **2**, the electronic absorption spectra of **2** proved to be very susceptible to the substituent properties of X and to the polarities of solvents. With respect to the Soret bands, the derivatives of **2** bearing X = H, Br and CN exhibited one broad symmetrical curves, similar to those of **1**, but shifted their maxima as much as more than 10 nm to the longer wavelengths from those of **1**. This result suggests that in accord with various indices from theoretical and/or empirical criteria of aromaticity between Th and Bzn nuclei,[11] the HTh ring could play a role much easier for an extension of π-electronic conjugation and thus the substituent effect of X would be transmitted through the diacetylene linkage to the OEP chromophore more efficiently. In particular, Soret bands of **2** dramatically changed with the electron-withdrawing abilities of X, resulting in the apparent splittings for the formyl ($\Delta\lambda = 22$ nm) and nitro ($\Delta\lambda = 52$ nm) derivatives, among which the longer wavelength bands (IaCT) were found much sensitive to the solvent polarities (Fig. 1).[2]

The solvent effect on the IaCT bands was outstanding, changing their maxima over 30 nm from $\lambda = 483$ (hexane) to $\lambda = 453$ (sh) nm (acetonitrile) for the nitro derivative of **2**, which proved to correspond to 3.9 kcal/mol and to be twice as great in solvatochromism than that of **1** (Fig. 2).

According to Rao,[12] the maxima due to IaCT bands in the donor–acceptor Bzn system such as *p*-substituted anilines and anisoles are well known to correlate linearly with Hammett's substituent constants (σ). Simply applying Rao's equation to IaCT bands of **1** and **2** in view of the same molecular skeletons, their maxima were found to exhibit non-linear correlations with σ values in both cases (Fig. 3). Yet, it is rather noted that the difference of absorption maxima for IaCT bands between **1** and **2** ($\Delta\lambda$ equal to ΔE), as a measure of transmission efficiency of the substituent effect, enlarges with increases of the electron-withdrawing abilities of substituents; X = H (9 nm, 1.3 kcal/mol), X = Br (10 nm, 1.5 kcal/mol), X = CN (14 nm, 2.0 kcal/mol), X =



Scheme 1.

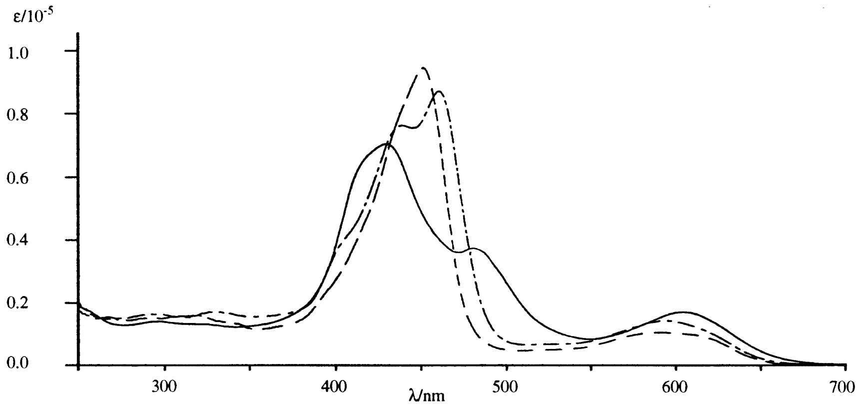


Figure 1. Electronic absorption spectra of **2**; X=CN (- - - -), X=CHO (—·—) and X=NO_2 (——) in chloroform.

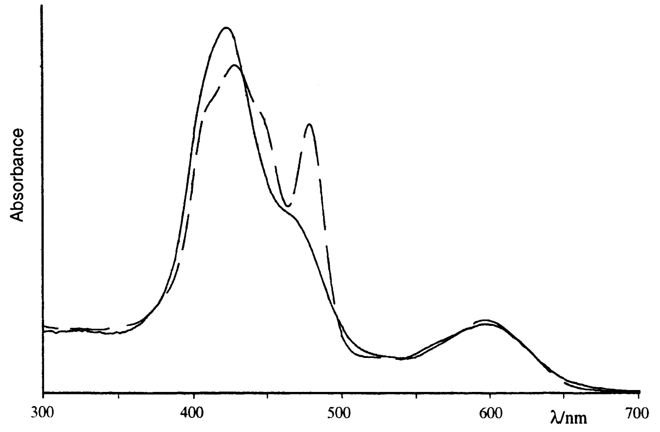


Figure 2. Electronic absorption spectra of the nitro derivative of **2** in hexane (- - - - - -) and acetonitrile (——).

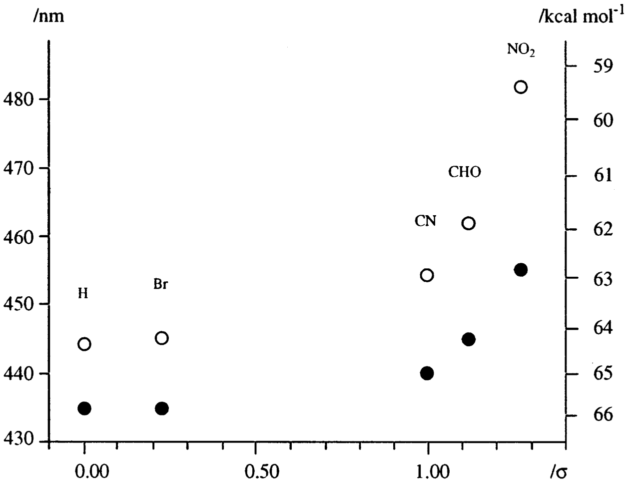


Figure 3. Absorption maxima changes of IaCT bands of **1** (●) and **2** (○) in chloroform.

CHO (17 nm, 2.4 kcal/mol) and X=NO_2 (28 nm, 3.6 kcal/mol).

These results conclude that the HTh ring polarizes the π-electronic conjugation system of **2** concurrently with the electron-withdrawing substituents further efficiently, providing an essential feature for enhancement of the particular electronic properties such as NLO properties.[3,13] Further comparative studies on the electrochemical properties of **1** and **2** are now in progress, as well as on the theoretical analysis of their absorption spectra.

Acknowledgements

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