Tetrahedron Letters 55 (2014) 5164–5169

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Enormously extended π-electronic conjugation system of dimeric octaethylporphyrin transmitted with anthracene

Hideto Kempe [a], Natsuki Kuroda [b], Junro Yoshino [b], Naoto Hayashi [b], Hiroyuki Higuchi [a,b,*]

[a] Graduate School of Innovative Life Science, University of Toyama, 3190 Gofuku, Toyama, Toyama 930-8555, Japan
[b] Graduate School of Science and Engineering, University of Toyama, 3190 Gofuku, Toyama, Toyama 930-8555, Japan

ARTICLE INFO

Article history:
Received 30 May 2014
Revised 8 July 2014
Accepted 11 July 2014
Available online 27 July 2014

This Letter is dedicated to Emeritus Professor Philip E. Eaton (University of Chicago) for his 77th birth-year anniversary

Keywords:
Octaethylporphyrin
Anthracene
Dimer
π-Electronic system
Diacetylene
Phenylene

ABSTRACT

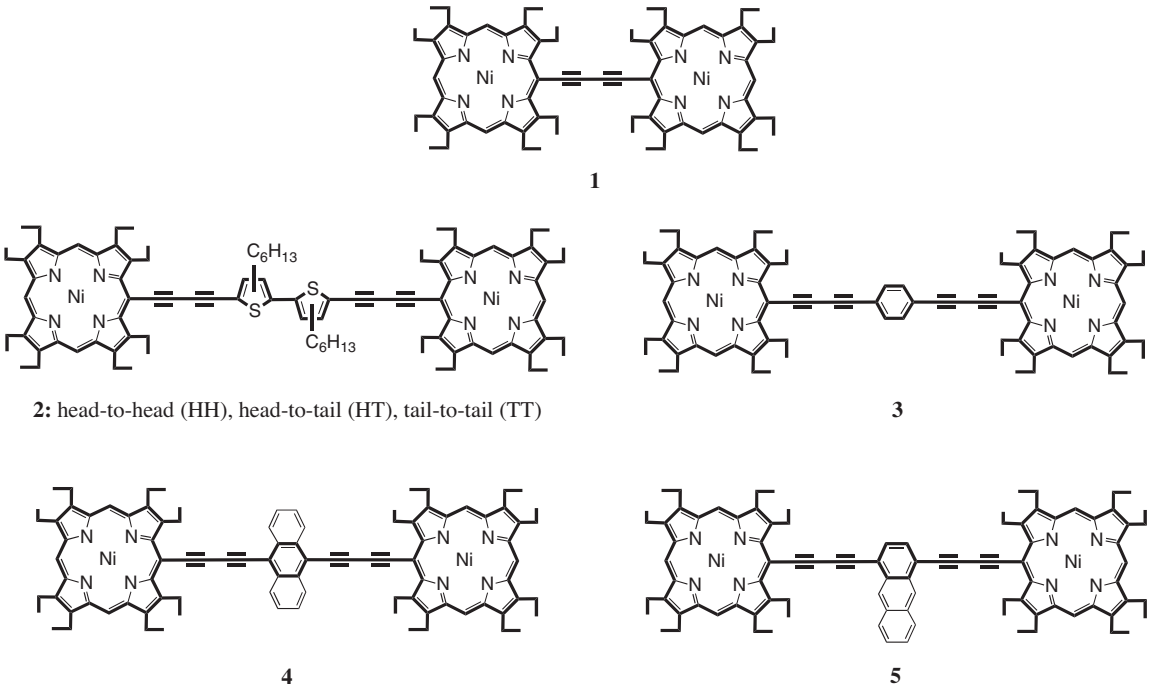
Based on the fact that anthracene (Anth) possesses much higher similarity in electron-releasing ability to porphyrin nucleus than the other polyacenes, the dimeric octaethylporphyrin (OEP) derivatives **4** and **5** (OEP–Anth–OEP) were synthesized and their structure–property relationships were examined, as compared with related OEP dimers **1**–**3**. Among them, the derivative **4** showed enormously high electronic communication between two terminal OEP rings, potentially providing a suitable unit of the electronic structure for molecular design of the OEP devices operating with less energy and with higher sensitivity to outside stimuli.

Introduction

The dimeric octaethylporphyrin (OEP) derivative **1** is well known to possess a unique electronic structure due to the efficient interaction between two OEP rings through the rigid but π-electronically mobile linkage of 1,3-butadiyne (diacetylene), in which the Soret-Band characteristic of porphyrin nucleus splits and shifts intensively toward the lower-energy region (Chart 1).[1] In recent years, similar to such a simple OEP system carrying an individual electronic structure like **1**, a variety of porphyrin-based π-electronic conjugation systems with well-defined skeleton have been receiving much attention as good candidates for opt-electronic and electrochemical devices, because of their higher electronic susceptibility and their more favorable processibility for functional organic materials, in comparison with the benzene-based derivatives.[2] In relation with such a drastic development of organic functional materials science based on porphyrin nuclei, we previously demonstrated our original system of octaethylporphyrin–dihexylbithiophene–octaethylporphyrin (**2**: OEP–DHBTh–OEP, Chart 1), in which the three components are connected with the diacetylene linkage as well.[3] The absorption spectra and electrochemical properties of **2** were comparatively examined, proving that the orientation mode of two 3-hexylthiophene (3-HTh) rings in DHBTh (head-to-head; HH, head-to-tail; HT, tail-to-tail; TT) plays an important role in π-electronic communication between two OEP rings. In contrast with the high similarity in molecular skeletal feature between these HH-, HT-, and TT-DHBTh orientational isomers, a transmissible efficiency in π-electronic conjugation was much different between them. The HH-isomer $\mathbf{2_{HH}}$ just slightly broadened the Soret-Band to afford almost one absorption band similar to that of OEP, while the TT-isomer $\mathbf{2_{TT}}$ clearly split the Soret-Band into two main bands similar to that of **1**. Yet, $\mathbf{2_{HH}}$ was electrochemically oxidized via two two-electron transfer processes toward the final bis(dicationic) OEP product, while $\mathbf{2_{TT}}$ was steadily oxidized via three one-, one-, and two-electrons transfer processes to afford the corresponding bis(dicationic) OEP product.[4] These results apparently indicate that not only particular electronic structure but also thermal stabilization of the reactive intermediates produced in this system could be achieved purposively by choosing an orientation of two 3-HTh rings, that is, by tuning a conjugation planarity of DHBTh as a spacer.[5] Successively, the electronic properties of corresponding 1,4-phenylene derivative **3** (OEP–Phen–OEP, Chart 1),[6] a more

* Corresponding author. Tel./fax: +81 (0)76 445 6616.
E-mail address: higuchi@sci.u-toyama.ac.jp (H. Higuchi).

http://dx.doi.org/10.1016/j.tetlet.2014.07.045
0040-4039/



1

2: head-to-head (HH), head-to-tail (HT), tail-to-tail (TT)

3

4

5

Chart 1.

compact molecular skeleton than **2**, were preliminarily examined in order to evaluate the transmissible efficiency of the DHBTh and Phen spacers in π-electronic communication between two terminal OEP rings. To be short, Phen proved to possess an in-between ability of HH- and TT-DHBTh spacers in this system (vide infra).

In our continuous investigations of the extended π-electronic OEP conjugation system **1**–**3**, the derivatives **4** and **5** have been synthesized, for enhancement of the transmissible efficiency in the π-electronic communication between two OEP rings, aiming at the functional OEP devices driven by the weaker energy stimuli (Chart 1). A linear series of polyacenes are well known to increase their response to electrochemical stimuli in order with the number of cumulated benzene ring; $E^{ox}_{1/2}$ 2.30 V (benzene), 1.54 V (naphthalene), 1.09 V (anthracene), 0.77 V (tetracene), in accordance with their ionization potentials.[7d] Among them, anthracene can be expected to interact with the nickel complexes of porphyrins including OEP ($E^{ox}_{1/2}$ 0.95–1.05 V)[7a–c] more efficiently than the other polyacene. Therefore, the further extended π-electronic OEP conjugation system with the higher sensitivity to outside stimuli than **3** could be brought into **4** and **5** (OEP–Anth–OEP), both of which are also very compact the same as **3** in molecular skeletal length. And, in relation with the Phen spacer in **3**, there are two primitive modes of the Phen moiety in Anth, describable as the dibenzo-Phen moiety for **4** and as the naphtho-Phen moiety for **5**. Thus, it is also of interest to evaluate the transmissible efficiency brought from the linking-position effect on the diacetylene-group connected π-electronic OEP conjugation system of this type. Here, we wish to report the synthesis of **4** and **5** and their electronic and electrochemical properties, as compared with related compounds including **1**–**3**.

Synthesis of title compounds 4, 5, 13, and 15

In a similar way to the synthesis of **3**,[6] the diacetylene-group connected OEP dimers **4** and **5** were synthesized by an oxidative cross coupling reaction of the OEP terminal acetylene **6**[1] with the Anth diethynyl compound **7**[8] or **8**[9] under our modified Eglinton conditions (Schemes 1 and 2).[3–5,10] Usual work-up afforded the desired compounds **4**[11] and **5**[11] in 12% and 19% yields, respectively, as bluish purple microcrystallines. The corresponding OEP–(Anth)$_{n-1}$–Anth–OEP derivatives (**9** and **10**: $n \geqslant 2$, Chart 2)[12] could be also isolated in small amount (Chart 2), together with a quantity of **1**. Similarly, the coupling reaction of 6 with **11**[13] or **12**[14] gave the related compounds **13**[11] and **15**[11] in 32% and 30% yields, respectively, together with the homo-coupling products **1**, **14**,[12] and **16**.[12] The structures of **4**, **5**, **13**, and **15** were ascertained by MS, IR, and ^{1}H NMR spectral measurements. Similar to **3**, the Anth derivatives **4**, **5**, **13**, and **15** are fairly stable even under the visible light at ambient temperature.

Molecular skeletal feature of title and related compounds 4, 5, 13, and 15 from ^{1}H NMR spectral measurements

The spectra of **5** as well as corresponding terminal acetylenic reactants **6** and **8**, for example, are shown in Figure 1. Reflecting the symmetrical structural feature, the spectrum of **5** is fairly simple, similar to that of **4**. It proved that all the protons belonging to OEP of both **4** and **5** appeared in almost the same region, affording *meso*-protons (*meso*-H) at around 9.45 ppm and ethyl-protons (ethyl-H) at 4.30–3.76 and 1.98–1.73 ppm. On the other hand, the protons due to Anth constituent (Anth-H) all shifted to the lower field more or less (∼ca. 0.3 ppm) from the corresponding protons in each reactant, by being connected with the diacetylenic OEP. Anth-H$_{(1)}$ in **4** appeared at 8.73 ppm and Anth-H$_{(2)}$ at 7.74 ppm, while Anth-H$_{(9)}$ in **5** appeared at 9.09 ppm, Anth-H$_{(5)}$ at 8.16 ppm, Anth-H$_{(2)}$ at 7.88 ppm, and Anth-H$_{(6)}$ at 7.61 ppm. The protons of unsymmetrical compounds **13** and **15** were also perturbed slightly by a diamagnetic ring current effect of the diacetylenic OEP, but showed a similar spectral behavior to those of **4** and **5**, substantially holding respective skeletal features of **6**, **11**, and **12**. Thus, these results conclude that since all the components in these derivatives **4**, **5**, **13**, and **15** are simply connected with the rigid and straight linkage of diacetylene, the molecular skeletons are preferably well-defined for analysis and modification of the electronic properties. This skeletal feature is exactly important and useful for evaluation of their functionality.