Synthesis and electronic properties of dinucleic octaethylporphyrin (OEP) derivatives spaced with \( p \)-phenylene group [OEP-(\( p \)-Phen)\(_n\)-OEP]. A comparative study with dihexylbithiophene (DHBTh) group-spaced OEP dimers [OEP-(DHBTh)\(_n\)-OEP]

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Dedicated to Emeritus Professor Philip Eaton on the occasion of his 70th birth year.

Abstract

The dinucleic octaethylporphyrin (OEP) derivatives described as OEP-(\( p \)-Phen)\(_n\)-OEP (\( n \) = 1–4) were synthesized, in each of which the porphyrin ring is spaced with \( p \)-phenylene group. Their electronic properties were studied, as compared with those of the corresponding dihexylbithiophene (DHBTh) derivatives with head-to-head (HH) and tail-to-tail (TT) orientations. It proves that OEP-(\( p \)-Phen)\(_n\)-OEP possesses an in-between feature of OEP-(HH-DHBTh)\(_n\)-OEP and OEP-(TT-DHBTh)\(_n\)-OEP in electronic properties.

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1. Introduction

In recent years, has been made for the construction of well-defined, well-ordered and well-functioning molecules based on the porphyrin (Por) nuclei [1]. Among them, the study of compound 1, a 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 (Chart 1) [2]. The OEP(Ni) dimer 1 is well known to possess the characteristic electronic structure due to the strong interaction between the two OEP(Ni) rings through the diacetylene linkage, affording a split Soret absorption band, in contrast with one symmetrical Soret band of OEP(Ni).

We have been engaged in the study of the 3,3'-dihexylbithiophene (DHBTh) derivatives of various types for enhancement of the particular properties of the material functions, by virtue of their high susceptibility to the outside electronic and optical stimulations, similar to the Por derivatives [3]. In order to evaluate the orientation effect of DHBTh as a spacer constituent on the electronic properties of 1, the extended \( \pi \)-electronic conjugation systems of the DHBTh derivatives 2\(_n\) (head-to-head isomer; HH) and 3\(_n\) (tail-to-tail isomer; TT) were previously constructed, and their electronic properties were studied (Chart 1) [4]. Based on the absorption spectral study of the OEP-(DHBTh)\(_n\)-OEP system, it was indicated...
that the electronic communication between two terminal OEP rings changes regularly with number n of the DHBTh constituents, reflecting their respective orientations [5].

In our continuing investigations of the diacetylene-group connected OEP(Ni) system, the p-phenylene group-spaced derivatives 4n have been synthesized, which are described as OEP-(p-Phen)n-OEP (n = 1-4) for convenience (Chart 1). Since the \( \pi \)-electronic conjugation extends at the p-positions of benzene (Bzn) ring, the whole molecule should have a completely one-dimensional straight molecular skeleton. Besides, Bzn ring is an aromatic component with 6\( \pi \)-electron conjugated cyclic system, similar to thiophene (Th) ring, and yet possesses ca. 1.75 times greater resonance energy than Th ring [6]. Therefore, it is curious to elucidate the electronic interaction between OEP rings through p-Phen ring as a spacer and to compare its transmission efficiency with the corresponding DHBTh constituents. Here, we wish to report the synthesis and electronic properties of 4n, as compared with the related compounds including 2n and 3n.

2. Experimental

Melting points (m.p.) of the new compounds were determined on a hot-stage apparatus and are uncorrected. IR spectra were measured on a Jasco FT/IR 7300 spectrophotometer as KBr disk; only significant absorptions are reported in \( \nu \) values (cm\(^{-1}\)). EI and FAB mass spectra were recorded with JEOL JMS-700 spectrometer. "\( \delta \)" NMR, 1\( \delta \) NMR, and \( \delta \) values (ppm) with TMS as an internal standard. Electronic absorption spectra were measured in CHCl\(_3\) solution on a Shimadzu UV-2200A spectrophotometer and were recorded in \( \lambda_{\text{max}} \) values (nm, sh = shoulder) and molar extinction coefficients (e), unless otherwise stated (Table 2). Both methanol and pyridine for the coupling reaction were distilled before use. The reactions were followed by TLC aluminum sheets precoated with Merck SiO\(_2\) F\(_{254}\) or with Merck Al\(_2\)O\(_3\) GF\(_{254}\). Organic extracts were dried over anhydrous sodium sulfate or magnesium sulfate prior to removal of the solvents.

2.1. OEP-(p-Phen)\(_n\)-OEP (4n)

The mixture of acetylenes 7 (40 mg, 0.32 mmol) and 10 (670 mg, 1.1 mmol) in methanol and pyridine (60 cm\(^3\), 1:1) was added dropwise to the solution of copper(II) acetate (2 g, 11 mmol) in methanol and pyridine (150 cm\(^3\), 1:1) at 40–45 \(^\circ\)C over 5 h. The reaction mixture was stirred for additional 3 h. Poured into water, the mixture was extracted with CHCl\(_3\). The extracts were washed with water three times, shaken with 3 N HCl, washed with brine twice and then dried. The residue obtained after removal of the solvent was chromatographed on silica-gel (4 \times 70 cm) with hexane–CHCl\(_3\) (7:3) to afford 1 [2] (196 mg, 30%), \( 4_1 \) (75 mg), \( 4_2 \) (41 mg), \( 4_3 \) (26 mg) and \( 4_4 \) (5 mg) in order. \( 4_1 \) m.p. > 265 \(^\circ\)C (dec.); black-purple microcrystallines (hexane–CHCl\(_3\)); MS (FAB), \( m/z \) 1351 and 1352 (M\(^+\) and M\(^+\) + 1) for C\(_{263}\)H\(_{294}\)N\(_8\)Ni\(_2\); IR, \( \nu \) = 2961, 2927 and 2869 (CH), 2194 and 2133 (C=C;C); 1\( \delta \) NMR, \( \delta \) = 9.44 and 9.41 (4H and 2H, s, \( \text{meso-H} \)), 7.63 (4H, s, Phen-H), 4.16 (8H, q, \( J = 7.2 \text{ Hz, CH}_2 \)), 3.84–3.77 (24H, m, CH\(_2\)), 1.83 (12H, t, \( J = 7.2 \text{ Hz, CH}_3 \)), 1.78–1.73 (36H, m, CH\(_3\)). \( 4_2 \) m.p. > 265 \(^\circ\)C (dec.); black-purple microcrystallines (hexane–CHCl\(_3\)); MS (FAB), \( m/z \) 1475 and 1476 (M\(^+\) and M\(^+\) + 1) for C\(_{269}\)H\(_{304}\)N\(_8\)Ni\(_2\); IR, 2962, 2927 and 2869 (CH), 2194 and 2133 (C=C;C); 1\( \delta \) NMR, \( \delta \) = 9.43 and 9.40 (4H and 2H, s, \( \text{meso-H} \)), 7.58 (4H, d, \( J = 8.6 \text{ Hz, Phen-H} \)), 7.53 (4H, d, \( J = 8.6 \text{ Hz, Phen-H} \)), 4.13 (8H, q, \( J = 7.2 \text{ Hz, CH}_2 \)), 3.83–3.76 (24H, m, CH\(_2\)), 1.81 (12H, t, \( J = 7.2 \text{ Hz, CH}_3 \)), 1.76–1.72 (36H, m, CH\(_3\)).
microcrystallines (hexane–CHCl₃); MS (FAB), m/z 1599 and 1600 (M⁺ and M⁺ + 1) for C₁₁₀H₉₈N₈Ni₂; IR, v = 2960, 2922 and 2851 (CH), 2196 and 2134 (br, C=CH); ¹H NMR, δ = 9.42 and 9.40 (4H and 2H, s, meso-H), 7.59 (4H, d, J = 9.0 Hz, Phen-H), 7.53 (4H, d, J = 9.0 Hz, Phen-H), 7.51 (4H, s, Phen-H), 4.12 (8H, q, J = 7.2 Hz, CH₂), 3.82–3.78 (24H, m, CH₂), 1.81 (12H, t, J = 7.2 Hz, CH₃), 1.77–1.72 (36H, m, CH₃).

4c: m.p. > 265 °C (dec.); black-purple microcrystallines (hexane–CHCl₃); MS (FAB), m/z 1723 and 1724 (M⁺ and M⁺ + 1) for C₁₁₂H₁₀₂N₈Ni₂; IR, v = 2961, 2921 and 2850 (CH), 2195 and 2135 (br, C=CH); ¹H NMR, δ = 9.42 and 9.40 (4H and 2H, s, meso-H), 7.58 (4H, d, J = 8.4 Hz, Phen-H), 7.54 (4H, d, J = 8.4 Hz, Phen-H), 7.50 (8H, s, Phen-H), 4.13 (8H, q, J = 7.2 Hz, CH₂), 3.83–3.76 (24H, m, CH₂), 1.80 (12H, t, J = 7.2 Hz, CH₃), 1.77–1.71 (36H, m, CH₃).

3. Results and discussion

3.1. Synthesis

The synthesis of OEP-(p-Phen)ₜ-OEP 4n was carried out by an oxidative cross coupling reaction between the corresponding terminal acetylenes under the modified Eglinton conditions, similar to our conventional way for 2n and 3n (Scheme 1) [4,5]. Both acetylenes 7 [7] and 10 [2] were led from the corresponding aldehydes 5 and 8 in moderate yields, respectively, via bromovinylation followed by dehydrobromination, according to the reported procedures.

A mixture of 7 and 10 (2:7) in pyridine and methanol (1:1) was added to the solution of copper(II) acetate in pyridine–methanol (1:1), under a high dilution condition [8]. After usual work-up, the reaction mixture was separated by column chromatography on silica-gel. The eluted portions with hexane–chloroform (7:3) afforded 4n in order with increasing n of DHBTh (n = 1–4), together with 1 (n = 0, 30%) as the first eluted portion. It is curiously noted that the elution order of 4n was entirely reversed to the trend of 2n and 3n under the same condition, for which the reason is now uncertain. All the products were recrystallized from hexane–chloroform to form stable and black-purple microcrystallines.

3.2. Structural aspect

The structures of compounds 4n were determined mainly by mass and ¹H NMR spectral analyses, together with IR spectral measurement.

IR spectra of 4n were relatively simple, similar to 2n and 3n, but exhibited some characteristic features of these structures in stretching vibrations due to the diacetylene linkage. It was previously reported that the OEP-(HH-DHBTh)ₚ-OEP derivatives 2n afforded two medium peaks at around ν = 2130 and 2185 cm⁻¹, while the OEP-(TT-DHBTh)ₚ-OEP derivatives 3n exhibited these two peaks at the lower energy region from the corresponding peaks of 2n by 5–10 cm⁻¹ [5]. This result clearly indicates that TT series induce a cumulated character into the diacetylene linkage with greater extent, due to the higher molecular planarity of the (TT-DHBTh) constituent. Similarly, the OEP-(p-Phen)ₚ-OEP derivatives 4n afforded the two medium peaks, but reversely in the higher energy region, as compared with the corresponding derivatives 2n, at around 2135 and 2195 cm⁻¹. This result apparently indicates that the p-Phen spacer is not so sensitive to the external stimulation as the Th spacer, due to the greater resonance energy of Bzn ring than Th ring [6], and thus the diacetylene linkage of 4n does not take part in an extended conjugation system so intensively as that of 2n and 3n (vide infra).

¹H NMR spectra of 4₁ as well as 7 and 10 are shown in Fig. 1, as a typical example of 4n, and chemical shifts for the selected protons of 4n and related compounds are summarized in Table 1. The spectrum of 4₁ simply exhibits two singlet peaks due to meso-protons (meso-H) and one singlet peak due to p-Phen protons (Phen-H). Spectra also show that only one of the four sets for methylene-H of OEP resonates at the lower field separately due to the ring current effect of the nearby diacetylene linkage, clearly supporting the high symmetrical structure. It is also revealed that the spectrum of 4₁ basically holds the character of both structural features for 7 and 10, affording the corresponding peaks for all the protons, including alkyl substituent ones at almost the same positions, except for disappearance of the respective acetylenic-H peaks. This result indicates that the compound 4₁ possesses a simply connected structure between 1 and 1₁ (Fig. 2), without...
particular structure deformation by an extension of the conjugation system, though the Phen-H of 41 shows its peak at a slightly low field in consequence of forming the diacetylene linkage of OEP(Ni) dimer 1 from that (δ = 9.76) of OEP(Ni). Nevertheless, when the (p-Phen) constituents are incorporated into 1 to form 4n, meso-H for 4n are found almost unchanged from those of 1, all appearing at around δ = 9.40. This result indicates that the ring current effect of OEP(Ni) is reduced by the diacetylene linkage intensively, but not by the (p-Phen) constituents substantially. Therefore, it could be concluded that compounds 4n exist largely in the unique molecular structures where both OEP and (p-Phen) constituents are simply fixed with the rigid diacetylene linkage, with the OEP(Ni) ring current of 1 remaining in this molecular system to a great extent.

The OEP(Ni)-(p-Phen)n-OEP(Ni) derivatives 4n can also be regarded as a one-dimensionally extended system, in which all the (p-Phen) constituents have no abilities to perturb the ring current of OEP(Ni). This structural property suggests that the effective area of anisotropic effect from the OEP ring could be analyzed with high accuracy by searching the chemical shift behaviors of Phen-H, because each (p-Phen) constituent is fixed both independently and regularly with a rigid diacetylene linkage in one direction. From the molecular model examinations, for example, the compound 44 can be estimated to be ca. 55 Å in length between two center-to-center OEP(Ni) rings, since the molecules become longer by ca. 10 Å with increases of n. Although the chemical shift changes of Phen-H were not so large in magnitude, all the peaks appear regularly at respective positions, and were thus assigned to each Phen-H very easily, as shown in Fig. 2. In the case of 44, Ha and Hb resonate at around 7.58 and 7.53 ppm, respectively, while all the other Hc and Hd resonate at the position of 7.50 ppm, which is almost the same as the chemical shift for the corresponding Phen-H of 11. These results show us the following two important findings. One relates to information for the spherical location of Phen-H; all the Phen-H including those of the compound 44 exist somewhere within a deshielded region of the OEP ring, which results in their appearing at the lower field than an ordinary region for that of the referent compound 11. The other is information for the area of influence from the ring current of OEP(Ni); the anisotropic effect of OEP(Ni) along a rod direction of the OEP(Ni)-(p-Phen)n-OEP(Ni) system terminates at the third Hc for the OEP(Ni) complexes, which is placed at ca. 22 Å from the center of the OEP(Ni) ring.

From the chemical shift changes of the OEP(Ni)-(p-Phen)n-OEP(Ni) system, it is confirmed that the effectiveness of diamagnetic anisotropy from the OEP(Ni) ring in one-dimensionally extended system terminates at ca. 22 Å. This effective area of 22 Å is slightly shorter than that of 22 Å reported by searching the chemical shift behaviors of Phen-H in the OEP(Ni) ring current of 1 remaining in this molecular system to a great extent.

Fig. 1. 1H NMR spectra (600 MHz, CDCl3, 25 °C) for (a) 41, (b) 7, and (c) 10.

Table 1
Chemical shifts of the selected protons of OEP derivatives (600 MHz, CDCl3, δ (ppm))

| OEP(Ni) derivatives | meso-H         | Phen-H         |
|--------------------|---------------|----------------|
| 41                 | 9.44 (4H), 9.41 (2H) | 7.63 (4H)     |
| 42                 | 9.43 (4H), 9.40 (2H) | 7.58 (4H), 7.53 (4H) |
| 43                 | 9.42 (4H), 9.40 (2H) | 7.59 (4H), 7.53 (4H), 7.51 (4H) |
| 44                 | 9.42 (4H), 9.40 (2H) | 7.58 (4H), 7.54 (4H), 7.50 (8H) |
| OEP               | 9.76 (4H)     |                |
| 1                  | 9.42 (4H), 9.39 (2H) |              |

effect of OEP, and the chemical shift of Phen-H as a measure of anisotropic effect from the OEP ring [9]. It is apparent that the ring current effect of OEP weakens in consequence of the reformed conjugation system with the diacetylene linkage more or less, shifting meso-H to the high field by ca. 0.35 ppm for the diacetylene-group connected OEP(Ni) dimer 1 from that (δ = 9.76) of OEP(Ni). Nevertheless, when the (p-Phen) constituents are incorporated into 1 to form 4n, meso-H for 4n are found almost unchanged from those of 1, all appearing at around δ = 9.40. This result indicates that the ring current effect of OEP(Ni) is reduced by the diacetylene linkage intensively, but not by the (p-Phen) constituents substantially. Therefore, it could be concluded that compounds 4n exist largely in the unique molecular structures where both OEP and (p-Phen) constituents are simply fixed with the rigid diacetylene linkage, with the OEP(Ni) ring current of 1 remaining in this molecular system to a great extent.

The OEP(Ni)-(p-Phen)n-OEP(Ni) derivatives 4n can also be regarded as a one-dimensionally extended system, in which all the (p-Phen) constituents have no abilities to perturb the ring current of OEP(Ni). This structural property suggests that the effective area of anisotropic effect from the OEP ring could be analyzed with high accuracy by searching the chemical shift behaviors of Phen-H, because each (p-Phen) constituent is fixed both independently and regularly with a rigid diacetylene linkage in one direction. From the molecular model examinations, for example, the compound 44 can be estimated to be ca. 55 Å in length between two center-to-center OEP(Ni) rings, since the molecules become longer by ca. 10 Å with increases of n. Although the chemical shift changes of Phen-H were not so large in magnitude, all the peaks appear regularly at respective positions, and were thus assigned to each Phen-H very easily, as shown in Fig. 2. In the case of 44, Ha and Hb resonate at around 7.58 and 7.53 ppm, respectively, while all the other Hc and Hd resonate at the position of 7.50 ppm, which is almost the same as the chemical shift for the corresponding Phen-H of 11. These results show us the following two important findings. One relates to information for the spherical location of Phen-H; all the Phen-H including those of the compound 44 exist somewhere within a deshielded region of the OEP ring, which results in their appearing at the lower field than an ordinary region for that of the referent compound 11. The other is information for the area of influence from the ring current of OEP(Ni); the anisotropic effect of OEP(Ni) along a rod direction of the OEP(Ni)-(p-Phen)n-OEP(Ni) system terminates at the third Hc for the OEP(Ni) complexes, which is placed at ca. 22 Å from the center of the OEP(Ni) ring.

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| 42                 | 9.43 (4H), 9.40 (2H) | 7.58 (4H), 7.53 (4H) |
| 43                 | 9.42 (4H), 9.40 (2H) | 7.59 (4H), 7.53 (4H), 7.51 (4H) |
| 44                 | 9.42 (4H), 9.40 (2H) | 7.58 (4H), 7.54 (4H), 7.50 (8H) |
| OEP               | 9.76 (4H)     |                |
| 1                  | 9.42 (4H), 9.39 (2H) |              |
(ca. 25 Å) led from the OEP(Ni)-(DHBTh)-OEP(Ni) system, probably reflecting a difference of the local anisotropy from the spacer ring between Bzn and Th[5]. Nevertheless, these results may apparently indicate a potential applicability of the diacetylene-group connected OEP system as a molecular scale for analysis and prediction of the particular properties.

3.3. Electronic absorption spectra

Electronic absorption spectral measurements of the diacetylene-group connected OEP derivatives 1–4 were performed in CHCl₃ at room temperature. Their spectral data as well as those of related compounds, are summarized in Table 2.

It is known that OEP(Ni) affords the well-characterized absorption bands in CHCl₃, at 370 nm (ε 27,500, sh) and 393 nm (ε 234,400) for Soret band (π–π transition) and at 516 nm (ε 11,500) and 552 nm (ε 37,000) for Q band (n–π* transition)[10]. As shown in Table 2, introduction of the diacetylene linkage into OEP(Ni) at the meso-position (14: Chart 3) induces considerable changes in both absorption maxima and curves; Soret band at 428 nm (182,000) and Q band at 556 nm (7000) and 598 nm (10,000). This result indicates that the electronic reconstruction takes place between OEP(Ni) and diacetylene linkage efficiently to form an extended π-electronic conjugation system. However, it is interesting to note that derivative 14 affords a quite simple spectrum, similar to OEP(Ni), in spite of the loss of a high molecular symmetry D₄h element of OEP(Ni). Furthermore, combination of the 3-hexylthiophene ring (HTh) with 14, i.e., 15 and 16 (Chart 3), did not affect the electronic structure of 14 so intensively as to change its absorption curve, only shifting the respective bands to the longer wavelength regions very slightly. This result suggests that HTh ring in this system behaves itself like an electron-donating substituent, similar to the t-butyl group in 14, simply causing an elevation of HOMO level of 14. It is also obvious that the substitution position of the hexyl group has no influence on their electronic properties at all.

In contrast with the spectral behavior of 14, the diacetylene-group connected OEP(Ni) dimer 1 exhibits an impressive spectrum characteristic of the strong interaction between two OEP(Ni) rings through the diacetylene linkage, in which the Soret band splits into three bands at maxima of 427, 457 and 484 nm, and the Q band fairly increases its intensity[2]. Curiously, it may be noted that an introduction of the vinylene linkage in place of the diacetylene linkage into 1, i.e., 17 (Chart 3), scarcely
affects the Soret band, with respect to the spectrum of OEP(Ni), but rather affects the Q band intensively, to afford some characteristic weak bands up to 800 nm [11].

So far, various DHBTh derivatives have shown some curious properties reflecting the orientation of DHBTh, which are sometimes hard to predict from the properties of HTh itself. In fact, 2n and 3n also showed the peculiar feature in their electronic structures. As shown in Fig. 3, the spectrum (a) for HH isomer 21 simply exhibited two bands characteristic of the OEP(Ni)-HTh system 15 and 16, affording the slightly broad Soret band at around 450 nm and the Q band at around 600 nm. On the other hand, the spectrum (b) for TT isomer 31 exhibited mainly three bands, as a consequence of the Soret band splitting into two bands at 440 and 484 nm. Although the Q band of 31 appeared at almost the same maximum as that of 21, the intensity of Q band for 31 was much greater than that for 21. These results suggest that the electronic interaction between two OEP(Ni) rings takes place through the diacetylene-group connected DHBTh constituent, with reflection of the extension magnitudes in the π-electronic conjugation depending on the respective orientations of DHBTh. In other words, the electronic interactions between two OEP(Ni) rings, probably via exciton coupling mechanism [12], strengthen regularly in order of the molecular planarity for π-electronic conjugation, also causing an enhancement of their transition probability for Q band in the same order.

As compared with the spectral behaviors of the related compounds, it might be concluded that HH isomer 21 possesses a very similar electronic structure to 15 (or 16), which is identical to the dimeric character of 15 (or 16). In this case, the (HH-DHBTh) constituent can not participate efficiently in the π-electronic conjugation with OEP(Ni) through the diacetylene linkage, because the two HTh rings are twisted about the pinch bond of DHBTh so much as to interrupt the conjugation due to the steric hindrance between the hexyl group and the sulfur atom belonging to an opposite HTh ring [5b,13]. On the other hand, the electronic structure of TT isomer 31 is rather comparable to that of 1, in which the central DHBTh component participates in the π-electronic conjugation throughout the whole molecule due to its highly planar conformation. It can be also concluded that such characteristic features of the DHBTh constituents, where the HH isomer behaves itself as a dimeric character of HTh, while the TT isomer exists in the extended system hybridized between two HTh rings, appear in the electronic properties of the OEP-DHBTh-OEP system, as they are.

These findings indicate that DHBTh would play an important role in the electronic communication and function transmittance between two terminal chromophores regardable as the functional sites. By controlling the conformational planarity of the spacer constituents, all the wide-ranging efficiencies of the particular electronic properties would be tuned at the molecular level, for example, by choosing not only the orientations of DHBTh

### Table 2

| OEP(Ni) derivatives | Soret bands | Q bands |
|---------------------|-------------|---------|
| **OEP(Ni)**         |             |         |
| 1                   | 427 (112,800) | 566 (35,000, sh) |
|                     | 457 (114,400) | 593 (57,300) |
|                     | 484 (130,600) |         |
| 14                  | 428 (182,000) | 556 (7000) |
|                     |              | 598 (10,000) |
| 15                  | 443 (149,000) | 574 (12,000, sh) |
|                     |              | 603 (12,500) |
| 16                  | 446 (182,000) | 572 (12,200, sh) |
|                     |              | 602 (12,300) |
| 18                  | 440 (146,500) | 564 (26,000, sh) |
|                     | 471 (133,000, sh) | 599 (43,500) |

**Chart 3.**
but also other alkyl substituents, including the hexyl group on the bithiophene ring (abbreviated as DABTh).

In case of the more extended OEP-(DHBTh)$_n$-OEP system $2n$, with an increase of $n$, spectra of the HH orientational series became much broader at around 440 nm and their absorption maxima shifted slightly to the shorter wavelengths (Fig. 3a) [5]. On the other hand, the TT isomeric series $3n$ exhibited a different behavior from $2n$, in which two split maxima of Soret band at 440 and 484 nm for $3_1$ gathered gradually and fused into the longer wavelength band at around 480 nm, with an increase of $n$ (Fig. 3b). These results could also be ascribed to a difference of the conformational planarity between HH and TT DHBTh constituents. As a result, the electronic structures of HH series gradually separate into two main characteristic features with increases of $n$; one arises from the diacetylene-group connected OEP-HTh component like $15$ (or $16$) and another arises from the remaining HTh-(DHBTh)$_{n-2}$-HTh components, affording their combined broad spectra (Fig. 4a). On the other hand, the TT series extends its electronic conjugation system between OEP(Ni) and DHBTh through the diacetylene linkage with increases of $n$, which may result in some reduction of the HOMO–LUMO energy differences. However, an extension of the $\pi$-electronic conjugation of this type would simultaneously weaken the electronic interaction between two terminal OEP(Ni) rings gradually, because the two terminal OEP(Ni) rings move in the opposite direction and locate apart from each other by ca. 13 Å with every one increment of $n$. It is likely that such a regular extension of the $\pi$-electronic conjugation induces a gradual recovery of the structurally unsymmetrical but electronically degenerated structures for the TT series as well. Thus, it could be proposed that the TT series converges with increases of $n$ into the hybridized electronic structure between the diacetylene-group connected OEP-(TT-DHBTh) component and the remaining (TT-DHBTh)$_{n-2}$ component (Fig. 4b).

Fig. 3. Serial electronic absorption spectra of OEP-(DHBTh)$_n$-OEP (CHCl$_3$, 25 $^\circ$C) for (a) $2n$ and (b) $3n$.

Fig. 4. The main electronic structural aspects of OEP-(DHBTh)$_n$-OEP for (a) $2n$ and (b) $3n$. 
Similarly, in case of the OEP(Ni)-(p-Phen)$_n$-OEP(Ni)$^-$ system 4$_n$, it is obvious that the Q band of 4$_1$ was very similar in shape and maximum ($\lambda_{\text{max}} = 596$ nm) to that of 2$_1$, while its Soret band ($\lambda_{\text{max}} = 463$ nm) was undoubtedly unsymmetrical in shape with a clear shoulder ($\lambda = 435$ nm), different from one broad Soret band of 2$_1$ (Fig. 5). As compared with the spectrum of 3$_1$, the Q band of 4$_1$ appeared at the same region but was fairly broad and less intensive, while the Soret band was much sharper. In this respect, the spectral feature of 4$_1$ is exactly the same as that of the unsymmetrical OEP-(HT-DHBTh)-

OEP derivative 18 (Chart 3), with a little hypsochromic shift. However, the intensity ratios of the Soret band and its shoulder band are entirely reversed.
between 4₁ and 18. Yet, it is noted that all the Soret bands for 2₁, 4₁, 18 and 3₁ started from the same position at around 400 nm and regularly split into two bands, affording the new bands at the longer wavelength region in this order. This result clearly indicates that the spacer mobility for π-electronic conjugation between two terminal OEP rings in each molecule increases in order of 2₁<4₁<18<3₁.

In contrast with the broadening of spectral changes for 2n with increases of n, the spectral changes of the extended OEP-(p-Phen)ₙ-OEP system 4n became rather sharper and more symmetric, and intensified with their absorption maxima shifted slightly to the shorter wavelengths at around 450 nm (Fig. 6). This phenomenon could also be ascribed to a gradual recovery of the structurally unsymmetrical but electronically degenerated structure of the OEP-(p-Phen) system 19 (Fig. 7), similar to the trend of the OEP-(TT-DHBTh)ₙ-OEP derivatives 3n, converging toward a combined spectrum between 19 and the remaining (p-Phen)ₙ₋₂ groups.

4. Conclusion

The extended conjugation OEP-(p-Phen)ₙ-OEP system 4n was successfully constructed by an oxidative cross coupling reaction between the corresponding terminal acetylenes, similarly as for the systems 2n and 3n of OEP-(DHBTh)ₙ-OEP. From the results of IR spectral measurements, the diacetylene linkage of 4n did not take part in an extended conjugation system so intensively as those of 2n and 3n, and thus the p-Phen spacer of 4n proved to be not so sensitive to the external stimulation as the Th spacer due to the greater resonance energy of Bnz ring than Th ring. Furthermore, based on ¹H NMR spectral study, the derivative 4₁ revealed to possess a simply combined skeletal feature of the diacetylene-group connected dinucleic moieties 1 and 11. Yet, it is clearly indicated that the diacetylene-group connected OEP system of this type possesses some potential applicability as one-dimensional molecular scale.

In contrast with a high similarity in the molecular skeletal feature, the π-electronic interaction between two terminal OEP rings through those spacer components increased intensively in order of 2₁<4₁<18<3₁. This result indicates that the OEP-(p-Phen)-OEP derivative 4₁ possesses an in-between electronic property of the OEP-(HH-DHBTh)ₙ-OEP and OEP-(TT-DHBTh)ₙ-OEP derivatives, reflecting a slightly tighter conjugation system than 18. With increases of the p-Phen constituents in the OEP-(p-Phen)ₙ-OEP system, the Soret bands regularly changed and became sharper at around 450 nm, shifting slightly to the shorter wavelengths, proving that the electronic structure of 4n converges toward a combined feature between 19 and the remaining (p-Phen)ₙ₋₂ group. In conclusion, the OEP-(p-Phen)ₙ-OEP system of 4n is also substantially an analogous one to the one-dimensionally extended OEP-(DHBTh)ₙ-OEP system and possesses an in-between electronic structure of 2n and 3n.

Further investigation on the electronic properties of 4n, including electrochemical property, is now in progress.

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