Pergamon

Tetrahedron Letters 40 (1999) 9091–9095

TETRAHEDRON
LETTERS

Synthesis and properties of orientational isomers of hybridized dihexylbithiophene–octaethylporphyrin connected with 1,3-butadiyne linkages

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Received 1 September 1999; revised 7 October 1999; accepted 8 October 1999

Abstract

A new type of hybridized dihexylbithiophene–octaethylporphyrin derivative (DHBT–OEP) connected with the 1,3-butadiyne linkage was synthesized by oxidative cross-coupling of the corresponding terminal acetylenes. The absorption spectra and electrochemical properties of the DHBT–OEP hybrid were examined, clearly proving that the orientation of two 3-hexylthiophene rings of DHBT plays an important role in electronic communication between the two terminal OEP rings. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: dihexylbithiophene; octaethylporphyrin; coupling reactions; electronic spectra.

In recent years, a wide variety of structurally defined π-electronic conjugation systems composed of thiophene-based[1] and porphyrin-based[2] derivatives have received much attention as good candidates for electronic and opto-electronic devices, because of their higher optical and electronic susceptibilities and their more favorable processability for functional organic materials, as compared with benzene-based derivatives. Previously, we studied the absorption spectra and nonlinear optical (NLO) properties of the oligo(3-hexylthiophene) derivatives from the viewpoint of the π-electronic conjugation planarity and proved experimentally a structure–property relationship of the higher third-order NLO properties with the more extended π-electronic conjugation systems.[3] Furthermore, we have been engaged in studying the electronic and magnetic properties of the π-electronic conjugation systems of heterocyclic nuclei such as aza-annulene[4] and octaethylporphyrin (OEP) derivatives,[5] both of which carry the 1,3-butadiyne (diacetylene) linkage as a useful tool for making their π-electronic conjugation systems more rigid and extended.

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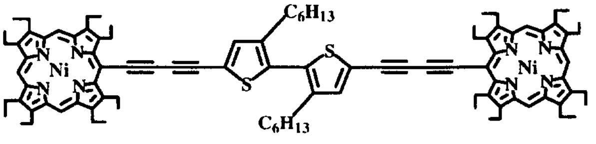
PII: S0040-4039(99)01929-2

In continuation of our investigations on the electronic properties of the new extended π-electronic conjugation system, a hybrid between dihexylbithiophene (DHBT) and OEP chromophores connected with the diacetylene linkage was synthesized. Here, we wish to report the synthesis of the title isomeric compounds **1** and **2** of the DHBT–OEP hybridized system, in which two 3-hexylthiophene rings of DHBT are linked with head-to-head (HH) and tail-to-tail (TT) orientations, and to discuss their electronic and electrochemical properties from the viewpoint of the π-electronic conjugation planarity.



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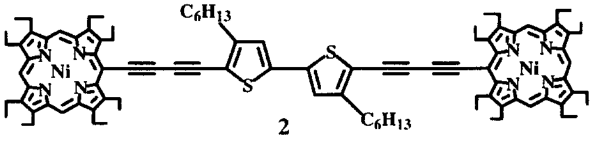

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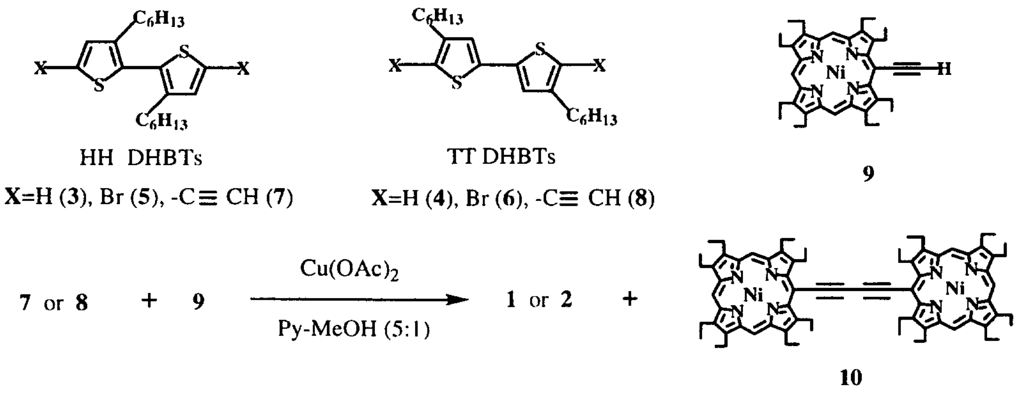
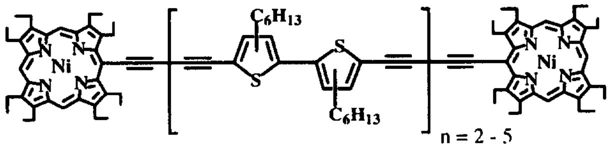
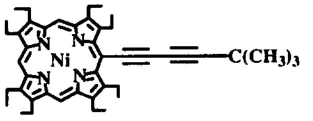
Similarly to the synthesis of a previously reported hybrid between OEP and *p*-substituted benzenes connected with a diacetylene linkage,[5] **1** and **2** were synthesized by an intermolecular oxidative cross-coupling of the corresponding terminal acetylene derivatives (Scheme 1). Starting from the DHBT isomers **3** and **4** according to our conventional methodology,[3,6] the acetylenes **7** and **8** were prepared in excellent yields by palladium-mediated coupling of the corresponding DHBT dibromides **5** and **6** with trimethylsilyl acetylene (HC:::CSiMe$_3$) under the Sonogashira conditions,[7] followed by alkaline hydrolysis. Reactions of **7** and **8** with 2.4 molar amounts of the OEP–Ni acetylene **9**[8] in the presence of anhydrous copper(II) acetate (Cu(OAc)$_2$) in a mixture of pyridine and methanol (Py:MeOH=5:1)[9] afforded the desired compounds **1** and **2** in 9% and 8% yields, respectively, together with a considerable amount (>20%) of the diacetylene-group connected OEP dimer **10**.[8] In both cases, the compounds of type **11**, which contain two, three, four, and five units of the DHBT α,α′-diethynyl component between two terminal OEP rings, were also obtained in 1–3% yields, respectively.[10] The hybridized products thus formed were separated by purification with repeated column chromatography on silica gel eluted with 30% v/v chloroform (CHCl$_3$) in hexane, all of which were recrystallized from CHCl$_3$–MeOH to afford black-purple colored fine needles (mp >300°C).



Scheme 1.



11 (HH or TT orientational DHBT)



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All the new compounds including **11** (n=2–5) were determined by means of MS (ESI-FT-ICR method),[10] IR, ^{1}H NMR and electronic absorption spectra, and elemental analyses. With the disappearance of the respective acetylenic protons (δ=3.38 ppm for **7**, 3.50 ppm for **8**, and 4.50 ppm for **9**) after the coupling reaction, the ^{1}H NMR spectrum of **1** exhibits two singlet signals (δ=9.42 ppm for 4H and 9.40 ppm for 2H) due to the OEP *meso* protons and a singlet signal (δ=7.33 ppm for 2H) due to the thienyl protons (ThH), apparently indicating its high molecular symmetry (Fig. 1). Except for the low-field shift of ThH of **1** by ca. 0.15 ppm from that of **7**, all the other protons, including those of the ethyl and hexyl substituents of **1**, appeared at almost the same positions as the corresponding protons of **7** and **9**. This was the same feature for the isomer **2** (δ=9.42, 9.39, and 7.00 ppm for 4H, 2H, and 2H).

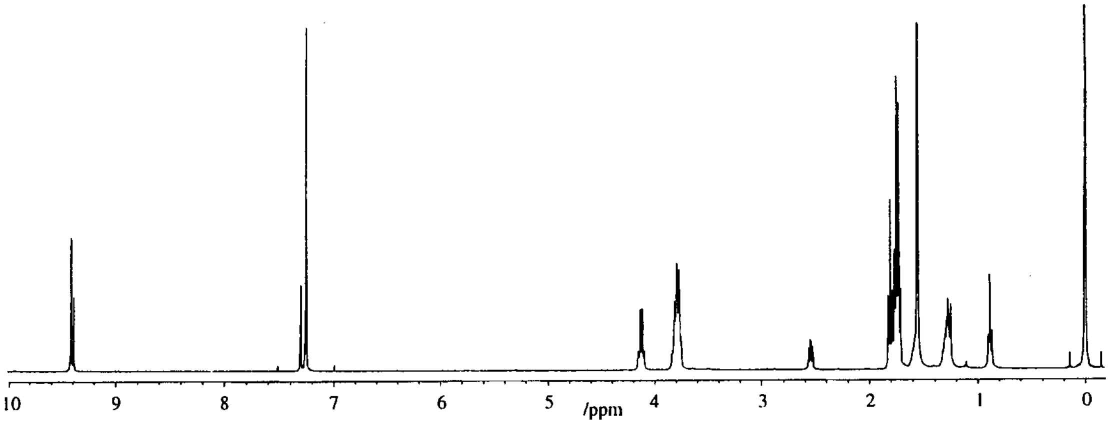

Figure 1. ^{1}H NMR spectrum of the HH orientational isomer (**1**) of DHBT–OEP (400 MHz, $CDCl_3$)

In contrast with the high similarity in ^{1}H NMR spectral behavior between two DHBT–OEP isomers, the electronic absorption spectra of **1** and **2** exhibited their characteristic features, as shown in Fig. 2. The HH orientational DHBT–OEP **1** afforded a fairly intensive Soret band at 454 nm (ε 190000) and a very broad Q band at 562 nm (ε 24500, sh) and 593 nm (ε 28000), which is rather comparable to the spectrum of **12** [λ_{max}=428 (ε 182000), 556 (ε 7000), and 598 nm (ε 10000)].[5a] On the other hand, the TT isomer **2** afforded a clear splitting of the Soret band with absorption maxima of 440 nm (ε 134000) and 484 nm (ε 143000) and the Q band at 601 nm with an increased intensity (ε 52000), which is highly comparable to the spectrum of **10** [λ_{max}=427 (ε 112800), 457 (ε 114400), 484 (ε 130600), and 618 nm (ε 57300)].[8] These results indicate that the orientation of DHBT plays an important role in achieving molecular planarity and that the π-electronic interaction between two terminal OEP rings occurs in the TT isomer **2** as effectively as that in the directly combined OEP dimer **10**.

Electrochemical oxidations of **1** and **2** were found to proceed via three stages to the final products, similarly to that of **10**, reflecting the extended structure composed of two OEP rings. However, the first two oxidation waves for the HH isomer **1** were very close, while all the three waves for the TT isomer **2** were clearly separated (Fig. 3). The first half-wave oxidation potentials ($E_1^{1/2}$), measure of

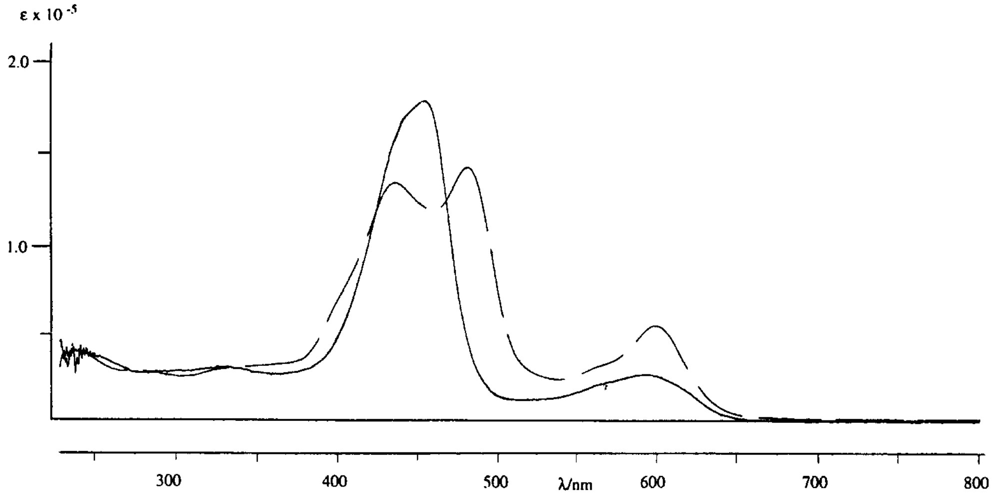

Figure 2. Electronic absorption spectra of **1** (—) and **2** (- - - -) in $CHCl_3$

electron releasing ability, were analyzed to be 0.88 V for **1** and 0.82 V for **2**, resulting in the lower electron-releasing ability of **1** and the higher electron-releasing ability of **2**, as compared with that of **10** ($E_1^{1/2}$=0.86 V). These results indicate that the TT DHBT with a higher molecular plane stabilizes the respective oxidation products from the DHBT–OEP hybrid more efficiently.

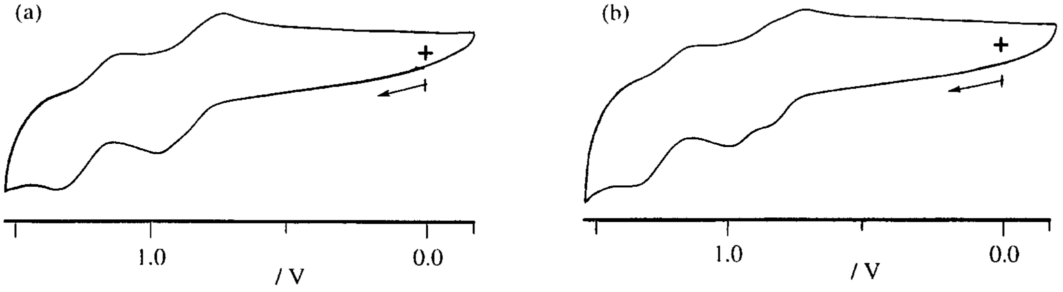

Figure 3. Cyclic voltammograms for oxidation of DHBT–OEP: (a) for **1** and (b) for **2** under the conditions of GC working electrode vs SCE at a scan rate of 120 mV/s in CH_2Cl_2

In consequence, it is proved that DHBT–OEP hybrid **1** and **2** exist in a highly extended π-electronic conjugation system reflecting the magnitude of the molecular planarity of DHBT, in which the electronic interaction between two terminal OEP rings through the diacetylene linkage is much larger for the TT isomer **2** to push up the HOMO level more effectively.

Further comparative studies on the electronic properties such as NLO response of these orientational isomers of the DHBT–OEP hybrid are now in progress.

Acknowledgements

Financial support by grant-in-aid no. 11640528 for Scientific Research from the Ministry of Education, Science, Sports and Culture is gratefully acknowledged.

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10. Each compound of type **11** was definitely ascertained by ESI-FT-ICR method, in which molecular ion peaks (M^+) of the HH isomeric series were observed as m/2z 993.93665 for n=2, m/2z 1183.99047 for n=3, m/3z 916.08107 for n=4, and m/3z 1042.77929 for n=5. See review for ESI-FT-ICR MS; Marshall, A. G.; Hendrickson, C. L.; Jackson, G. S. *Mass Spectrom. Rev.* **1998**, *17*, 1–35. Physical properties of all the new compounds including **11** will be reported in detail elsewhere.