Available online at www.sciencedirect.com

SCIENCE DIRECT®

Tetrahedron Letters 46 (2005) 6961–6965

Tetrahedron Letters

Synthesis and structural and electronic properties of the octaethylporphyrin–dihexylbithiophene–fullerene derivatives (OEP–DHBTh–C_{60}) connected with diacetylene linkage

Naoto Hayashi,[a] Azusa Naoe,[a] Keiko Miyabayashi,[b] Mikio Miyake[b] and Hiroyuki Higuchi[a,*]

[a]*Department of Chemistry, Faculty of Science, Toyama University, 3190 Gofuku, Toyama, Toyama 930-8555, Japan*
[b]*School of Material Science, JAIST (Hokuriku), 1-1 Asahi-dai, Tatsunokuchi, Noumi, Ishikawa 923-1292, Japan*

Received 17 June 2005; revised 6 July 2005; accepted 15 July 2005

Abstract—Orientational isomers of the octaethylporphyrin–dihexylbithiophene–fullerene derivative (OEP–DHBTh–C_{60}) connected with the diacetylene linkage were synthesized. The electronic and electrochemical properties were studied, proving that the orientation of DHBTh affects not only the electronic structures of OEP–DHBTh–C_{60} but also their molecular motional behaviors evidently.

In recent years, the porphyrin derivatives bearing fullerene (C_{60}) connected with various linkages have been vastly demonstrated to develop the new organic functional materials such as artificial photosynthesis systems and photo-current convertible devices, by virtue of their high susceptibility to the opto-electronic stimulations.[1] We have been engaged in the studies of the electronic properties of the dinucleic octaethylporphyrin [OEP(M)] derivatives combined with dihexyl-2,2′-bithiophene (DHBTh) as a spacer constituent, revealing that the orientation of DHBTh dramatically affects the electronic communication between the two terminal OEP(M) rings.[2] Thus, the tail-to-tail (TT) orientation of the 3-hexylthiophene (HTh) rings in DHBTh elevates the HOMO and lowers the LUMO of the extended OEP(M) system efficiently, while the head-to-head (HH) orientation hardly does. On one hand, we recently reported a synthetic methodology for orientational isomers of the DHBTh derivative **1** attaching different OEP(M) rings at each terminal position.[3]

In connection with such an intensive research of the porphyrin–C_{60} derivatives, the isomeric DHBTh derivatives **2** and **3** were synthesized to examine and evaluate the orientation effect on their electronic properties, where one of the OEP(M) rings in **1** is replaced with the C_{60} moiety. In this letter, the peculiar feature in the structural and electronic properties of the derivatives **2** and **3**, described as OEP(Ni)-DHBTh-C_{60}, will be reported, as compared with the related compounds (Chart 1).

Synthesis of **2** and **3** was carried out through an azomethine ylide cycloaddition of the corresponding aldehydes to C_{60}, originally reported by Prato et al. (Scheme 1).[4] Thus, the DHBTh terminal acetylenes **4** and **5** were coupled with the OEP(Ni) acetylene **6**[5] to afford the key compounds OEP(Ni)–DHBTh(CHO) **7** and **8** in 55% and 60% yields, respectively.[6] The aldehydes **7** and **8** were admixed with C_{60} and heated in the presence of *N*-methylglycine to afford the desired compounds **2** and **3** in 20–25% yields, respectively. The OEP(Ni)–DHBTh–C_{60} derivatives **2** and **3** were both recrystallized from chloroform–methanol to form dark green microcrystallines.[6]

The structures of **2** and **3** were ascertained by means of MS, IR, and ^{1}H NMR spectral measurements. Our conventional techniques such as FAB and ESI-FT-ICR MS for such extended OEP(M) derivatives afforded no confirmable ion peaks ($M_W = 1747.784$ for $C_{123}H_{77}N_5S_2Ni$).[2,3] Only MALDI-TOF MS technique

---

Keywords: Octaethylporphyrin; Dihexylbithiophene; Fullerene; Diacetylene; Orientation.

* Corresponding author. Tel./fax: +81 076 445 6616; e-mail: higuchi@sci.toyama-u.ac.jp

0040-4039/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2005.07.168

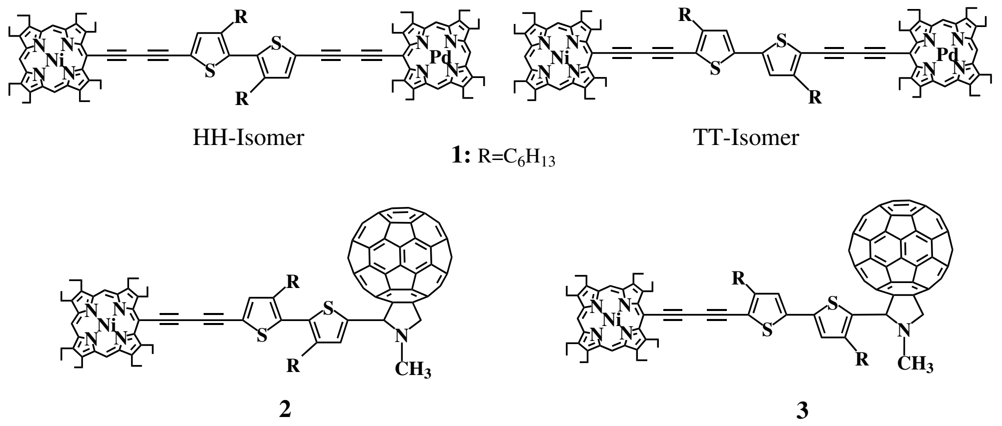
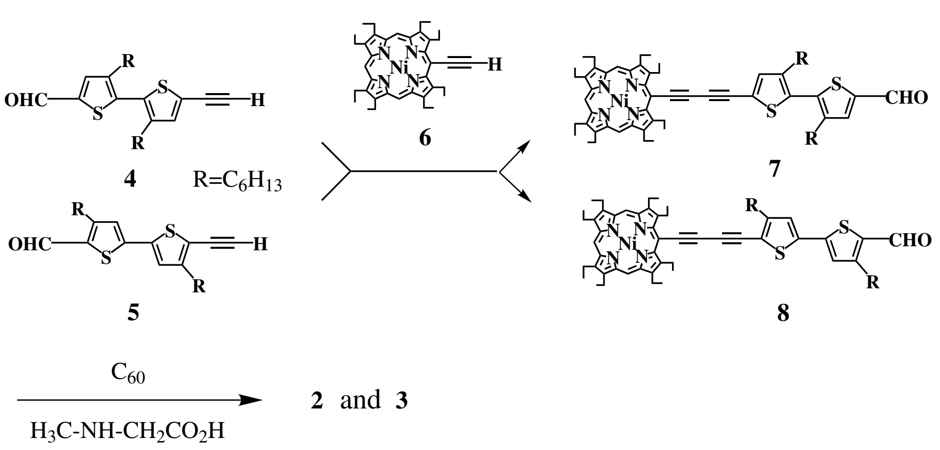


Chart 1.



Scheme 1.

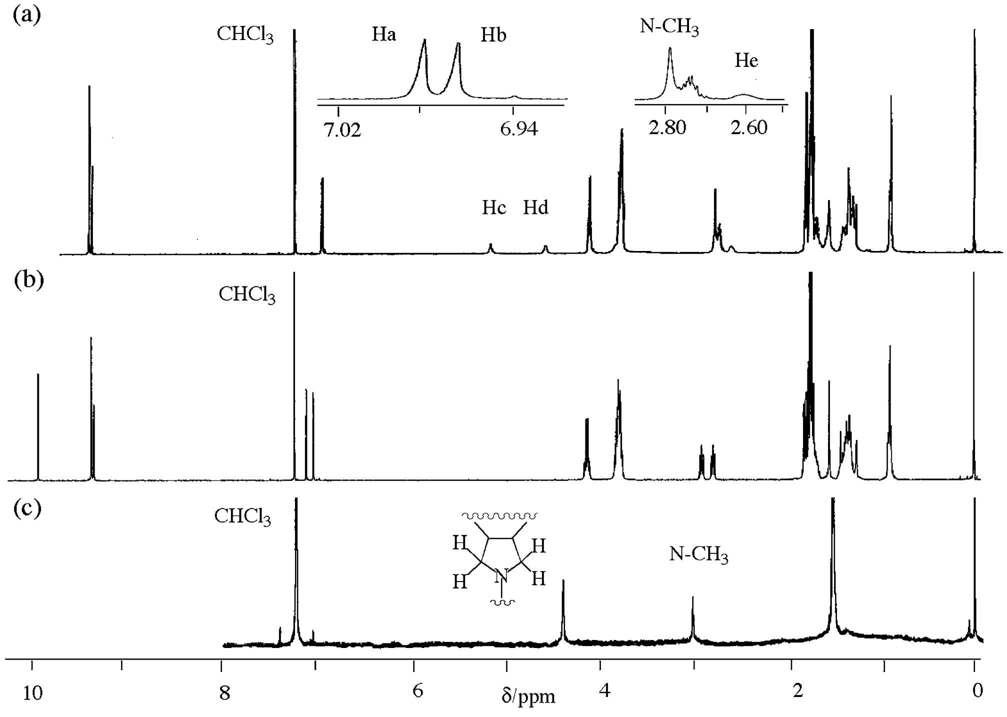
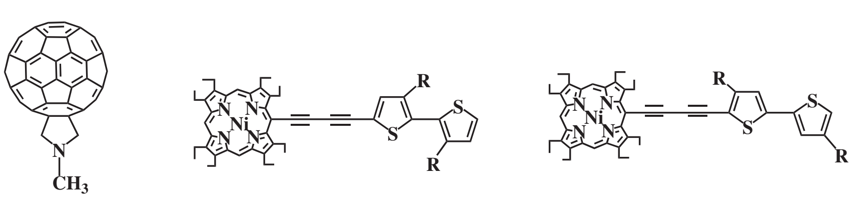


Figure 1. ^{1}H NMR spectra of (a) **3**, (b) **8** and (c) **9** (600 MHz, 25 °C). The former two spectra were measured in $CDCl_3$ and the last one was measured in $CDCl_3$–CS_2 (10:1).

based on 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) as a matrix was found useful for observation of the corresponding molecular ion peaks at around *m*/*z* 1745, of which the respective fragmentation patterns were completely consistent with the computer simulated ones. IR spectra reflected the orientation of DHBTh, characteristically showing a pair of weak and medium vibrational peaks due to the diacetylene linkage at 2177 and 2126 cm^{-1} for **2** and at 2170 and 2121 cm^{-1} for **3**, respectively. ^1H NMR spectra of **2** and **3** both exhibited the combined features of the respective OEP (Ni)-DHBTh constituents with the pyrrolidine C_{60} moiety, except for disappearance of the corresponding formyl protons of **7** and **8** after the coupling reaction (Fig. 1b). In case of the TT isomer **3** (Fig. 1a), the sharp signals due to both OEP(Ni) meso-protons (meso-H) and thiophene ring protons (Th-H; Ha and Hb) appeared at almost the same region as before the reaction of **8** with C_{60}. All the three protons (Hc–He) on the pyrrolidine moiety, however, enormously broadened and resonated in an outstandingly wide region (Hc: $\delta = 5.18$ ppm, Hd: $\delta = 4.60$ ppm, He: $\delta = 2.60$ ppm), as compared with those ($\delta = 4.38$ ppm) of the reference compound **9** (Chart 2 and Fig. 1c), in which Hd is coupled with He (HH COSY). This was also the case for the HH isomer **2** more or less, in addition to a notice of the very broad signal due to Hb as well (Fig. 2a). These results suggest that all Ha–He in **2** and **3** are individually placed in unusually restricted circumstances surrounded by the DHBTh and C_{60} constituents (vide infra).

Electronic absorption spectra show that both **2** and **3** possess the simply combined spectral features between the pyrrolidine C_{60} derivative **9** and the respective OEP (Ni)–DHBTh(H) derivatives **10**[7] and **11**[7] (Chart 2), reflecting the orientation of DHBTh (Fig. 3). The HH isomer **2** exhibited one broad Soret band at around 445 nm and the TT isomer **3** exhibited the split Soret band with two clear maxima ($\lambda = 440$ and 467 nm), together with an intensive band at around 255 nm and



9 **10** **11**

Chart 2.

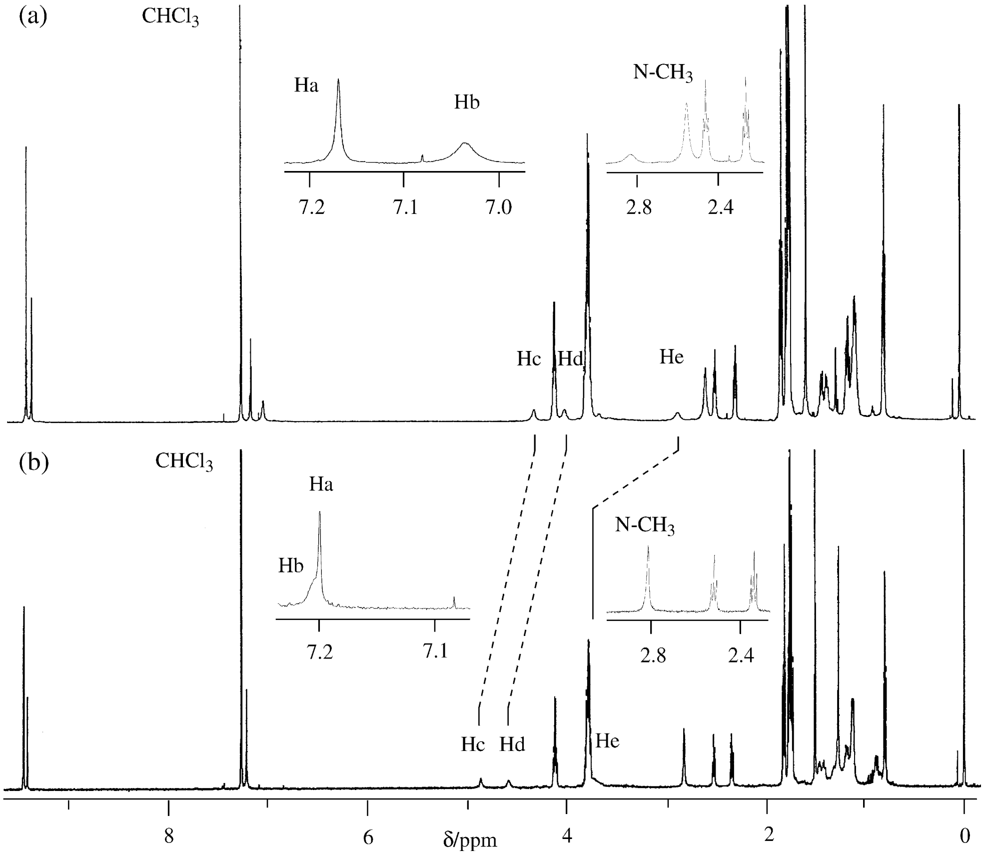


Figure 2. ^1H NMR spectra of **2** at (a) 25 °C and (b) 40 °C in $CDCl_3$.

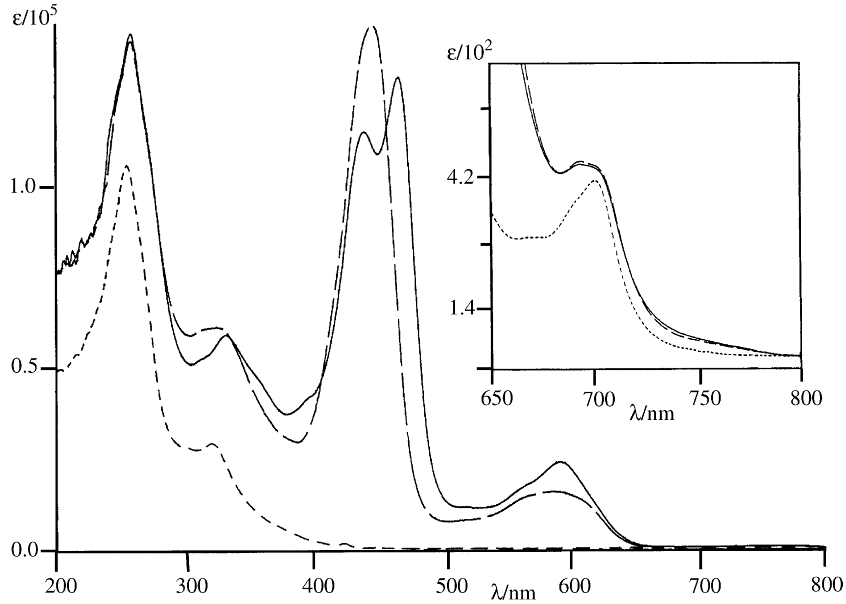


Figure 3. Electronic absorption spectra of **2** (broken), **3** (solid) and **9** (dotted) in the $CHCl_3$ solutions containing a few drops of CS_2 at room temperature.

Table 1. The first oxidation potentials ($E_{1/2}$ in mV) of the OEP(Ni)–DHBTh–C_{60} derivatives and related compounds

Compounds	20 °C	40 °C
2	1100	1200
3	940	1000
OEP(Ni)	1090	1100
10	1140	1150
11	980	990

Oxidation potentials were measured by cyclic voltammetry in $CHCl_3$ containing n-Bu_4NClO_4.GC (working E), Pt (counter E) and SCE (reference E). Scan rate; 120 mV/s.

an almost negligible band at around 700 nm due to the absorptions of **9**.[4] These results indicate no particular electronic reformation of the OEP(Ni)–DHBTh(H) constituent with the C_{60} moiety, in terms of their respective absorption maxima. However, it does not deny a possibility of the charge transfer interaction between them in this system, for verification of which electronically induced field studies such as solvent and substituent effects would be further necessary.[6] On the other hand, the electron-releasing abilities ($E^1_{1/2}$) of **2** and **3** at 20 °C ($CHCl_3$) were found to enhance slightly, as compared with the respective abilities of **10** and **11** (Table 1). This result may indicate that the C_{60} moiety plays a role to elevate the HOMO of the OEP(Ni) derivatives of this type somehow (vide infra).

In order to obtain the structural information of Ha–He in **2** and **3** under the particular circumstances, the temperature-dependent ^1H NMR spectral experiments were performed. In case of the HH isomer **2**, all meso-H remained almost unchanged, while not only Hc–He including N-methyl protons but also Th-H drastically changed to shift to the lower field as the temperature raised up. Particularly, Hb moved much swiftly toward Ha to fuse into one broad signal and He shifted by ca. 1 ppm at 40 °C, as compared with the respective ones at 25 °C (Fig. 2b). Surprisingly and unexpectedly, the TT isomer **3** did not exhibit such a temperature-dependent spectral change in practice.

Taking molecular model examinations into consideration, it is reasonably deduced that the HH isomer **2** orients Hb toward the C_{60} spherical body and He onto the HTh ring plane at the lower temperature, as depicted in Figure 4a, probably due to an attractive interaction between a donor part of HTh and an acceptor part of C_{60} in consequence. Yet, the N-methyl substituent exists apart from the DHBTh moiety to avoid a steric repulsion with each other and thus the five-membered pyrrolidine ring flips very slow. In particular, Hb and He are tightly fixed in a crowded and shielded environment so that these protons resonate at the fairly high field with broadening. Under such an unusually hindered structural situation, at the higher temperature where the pyrrolidine ring flips easier, Hb changes its position to be deshielded apart from the C_{60} moiety and He moves in a region freer from anisotropic effect of the HTh ring. On the other hand, in case of the TT isomer **3**, the steric repulsion between hexyl substituent and C_{60} moiety induces DHBTh to behave in a different form from that of **2**, where S-atom of the HTh ring orients toward the C_{60} sphere with retaining its TT orientation (Fig. 4b). This structural situation in **3** naturally leads to a conclusion that an additional steric repulsion between hexyl and N-methyl substituents is too severe to flip the pyrrolidine ring freely, resulting in no particular spectral changes between 25 and 40 °C.

The temperature-dependent ^1H NMR spectral changes imply that the π-electronic conjugation planarity of the DHBTh constituent recovers toward the inherent dihedral angle between two HTh rings in DHBTh more or less,[7,8] because of more reduction of a sterically hindered

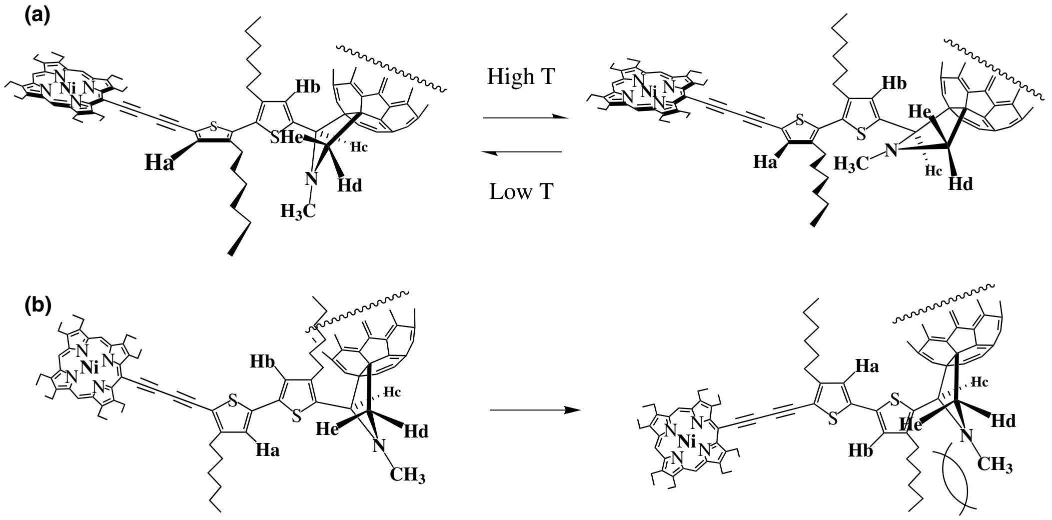


Figure 4. A plausible feature of the structural behavior of (a) HH isomer **2** and (b) TT isomer **3**, based on the spectral change results.

situation at the higher temperature. Such a trivial conformational change of the DHBTh constituent, however, did not clearly reflect on the electronic spectra of **2** and **3**. Nevertheless, the electron-releasing abilities were found susceptible even to such a small thermal stimulation evidently. At the higher temperature, the reference compounds scarcely changed their $E^1_{1/2}$ values, while the HH and TT isomers apparently lowered their electron-releasing ability, with reflecting the orientation of DHBTh (Table 1). Presumably through the recovered π-electronic conjugation planarity of the DHBTh constituent in the molecule, the electron-withdrawing property of the C_{60} moiety transfers to the terminal OEP(Ni) ring to lower its HOMO efficiently.

Further investigations of the optical and electronic properties of the OEP(M)-DHBTh-C_{60} derivatives are now in progress.[9]

Acknowledgements

Financial support by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports, Culture and Technology, is gratefully acknowledged. H.H. is also grateful to VBL Research Center and to Center of Instrumental Analyses at Toyama University for their supporting measurements of physical properties of the new compounds.

References and notes

1. Only a few articles of the porphyrin–fullerene derivatives are shown: (a) Liddell, P. A.; Kodis, G.; Andreasson, J.; DelaGarza, L.; Bandyopadhyay, S.; Mitchell, R. H.; Moore, T. A.; Moore, A. L.; Gust, D. *J. Am. Chem. Soc.* **2004**, *126*, 4803; (b) Schuster, D. I.; Cheng, P.; Jarowski, P. D.; Guldi, D. M.; Luo, C. P.; Echegoyen, L.; Pyo, S.; Holzwarth, A. R.; Braslavsky, S. E.; Williams, R. M.; Klihm, G. *J. Am. Chem. Soc.* **2004**, *126*, 7257; (c) Sutton, L. R.; Scheloske, M.; Pirner, K. S.; Hirsch, A.; Guldi, D. M.; Gisselbrecht, J. P. *J. Am. Chem. Soc.* **2004**, *126*, 10370; (d) Guldi, D. M.; Imahori, H.; Tamaki, K.; Kashiwagi, Y.; Yamada, H.; Sakata, Y.; Fukuzumi, S. *J. Phys. Chem. A* **2004**, *108*, 541; (e) Imahori, H. *J. Phys. Chem. B* **2004**, *108*, 6130; (f) Kodis, G.; Liddell, P. A.; Moore, A. L.; Moore, T. A.; Gust, D. *J. Phys. Org. Chem.* **2004**, *17*, 724; (g) Vali, S. A.; Tome, J. P. C.; Krawczuk, P. J.; Dourandin, A.; Shafirovich, V.; Cavaleiro, J. A. S.; Schuster, D. I. *J. Phys. Org. Chem.* **2004**, *17*, 814.
2. (a) Higuchi, H.; Ishikura, T.; Miyabayashi, K.; Miyake, M.; Yamamoto, K. *Tetrahedron Lett.* **1999**, *40*, 9091; (b) Higuchi, H.; Ishikura, T.; Mori, K.; Takayama, Y.; Yamamoto, K.; Tani, K.; Miyabayashi, K.; Miyake, M. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 889.
3. Hayashi, N.; Matsuda, A.; Chikamatsu, E.; Mori, K.; Higuchi, H. *Tetrahedron Lett.* **2003**, *44*, 7155.
4. Maggini, M.; Scorrano, G.; Prato, M. *J. Am. Chem. Soc.* **1993**, *115*, 9798.
5. Arnold, D. P.; Johnson, A. W.; Mahendran, M. *J. Chem. Soc., Perkin Trans. 1* **1978**, 366.
6. All the new compounds in this study were fully confirmed by means of spectral measurements, together with elemental analyses. The detailed results including all the other physical and structural properties will be reported elsewhere.
7. Hayashi, N.; Murayama, M.; Mori, K.; Matsuda, A.; Chikamatsu, E.; Tani, K.; Miyabayashi, K.; Miyake, M.; Higuchi, H. *Tetrahedron* **2004**, *60*, 6363.
8. Hayashi, N.; Nishi, H.; Morizumi, K.; Kobayashi, I.; Sakai, H.; Akaike, R.; Tani, K.; Higuchi, H. In *Recent Research Developments in Organic Chemistry*; Pandalai, S. G., Ed.; Transworld Research Network: Kerala, 2004; Vol. 8, pp 401–424.
9. Orientation effect of DHBTh not only on the electrochemical property but also on the fluorescence behavior in various types of OEP derivatives including the demetalated compounds from **2** and **3** will conclusively be reported.