ORGANIC
LETTERS

2000
Vol. 2, No. 19
2963−2966

Control of Dihedral Angle of Meso–Meso Linked Diporphyrins by Introducing Dioxymethylene Straps of Various Length

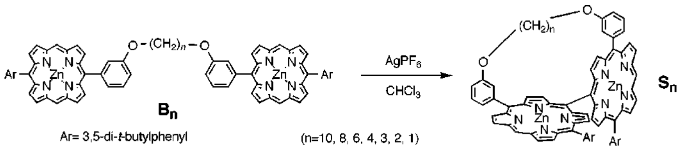
Naoya Yoshida and Atsuhiro Osuka*

Department of Chemistry, Graduate School of Science, Kyoto University,
Sakyo-ku, Kyoto 606-8502, Japan

osuka@kuchem.kyoto-u.ac.jp

Received June 16, 2000

ABSTRACT



Meso–meso linked strapped diporphyrins S_n ($n = 10, 8, 6, 4, 3, 2,$ and 1) were synthesized by intramolecular Ag(I)-promoted coupling of dioxymethylene-bridged diporphyrins B_n. With decrease of strap length, the absorption and fluorescence spectra and the one-electron oxidation potentials of S_n changed in a systematic manner, suggesting a progressive increase in electronic communication of two porphyrins.

Diporphyrins covalently bridged with a variety of linkers have been extensively studied for the investigation of intramolecular electron transfer and energy transfer,[1] the duplication of the charge separation function of photosynthetic reaction center,[2] and the development of photonic devices.[3] Control of electronic interactions between the donor and acceptor porphyrins is crucial for rational design of efficient diporphyrin models. Such control is possible by tuning geometrical parameters such as distance and orientation as well as the electronic properties of bridge. Studies of the orientation factor have, however, been rather limited so far.[4] Recently, we reported the synthesis of directly meso−meso linked diporphyrins by one-electron oxidation of 5,15-diaryl Zn(II)-porphyrins with Ag(I)-salt or anodic oxidation.[5,6] The close proximity of the two porphyrins in the array gives rise to large exciton coupling, while each porphyrin retains the monomer-like properties due to the almost orthogonal conformation which minimizes electronic conjugation of porphyrin π-systems.[7] Therefore, if the relative orientation of the two porphyrins in the meso−meso linked diporphyrin array can be changed in a systematic manner, it will constitute a nice set of models for a study of the effect of dihedral angle on the electronic coupling. The magnitude of the electronic coupling will influence the excitonic interactions and the rates of interporphyrin energy-transfer

---

[1] Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 435.

[2] Osuka, A.; Mataga, N.; Okada, T. *Pure Appl. Chem.* **1997**, *69*, 797.

[3] Chou, J.-H.; Nalwa, H. S.; Kosal, M. E.; Rakow, N. A.; Suslick, K. S. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds; Academic Press: San Diego, 2000; Vol. 6, Chapter 41.

[4] (a) Helms, A.; Heiler, D.; McLendon, G. *J. Am. Chem. Soc.* **1991**, *113*, 4325. (b) Sakata, Y.; Nakashima, S.; Goto, Y.; Tatemitsu, H.; Misumi, S.; Asahi, T.; Hagihara, M.; Nishikawa, S.; Okada, T.; Mataga, N. *J. Am. Chem. Soc.* **1989**, *111*, 8979. (c) Tsue, H.; Nakashima, S.; Goto, Y.; Tatemitsu, H.; Misumi, S.; Abraham, R. J.; Asahi, T.; Tanaka, Y.; Okada, T.; Mataga, N.; Sakata, Y. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 3067. (d) Osuka, A.; Shin, J.; Yoneshima, R.; Shiratori, H.; Ohno, T.; Nozaki, K.; Nishimura, Y.; Yamazaki, I.; Taniguchi, S.; Shimizu, T.; Okada, T. *J. Porphyrins Phthalocyanines* **1999**, *3*, 729.

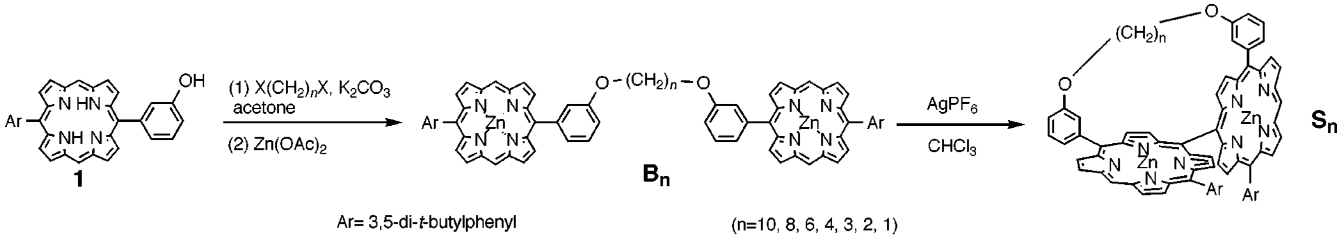
[5] (a) Osuka, A.; Shimidzu, H. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 135. (b) Ogawa, T.; Nishimoto, Y.; Yoshida, N.; Ono, N.; Osuka, A. *Chem. Commun.* **1998**, 337. (c) Ogawa, T.; Nishimoto, Y.; Yoshida, N.; Ono, N.; Osuka, A. *Angew. Chem., Int. Ed.* **1999**, *38*, 176. (d) Aratani, N.; Osuka, A.; Kim, Y. H.; Jeong, D. H.; Kim, D. *Angew. Chem., Int. Ed.* **2000**, *39*, 1458.

[6] Several groups reported independently the synthesis of meso−meso coupled diporphyrins. (a) Susumu, K.; Shimidzu, T.; Tanaka, K.; Segawa, H. *Tetrahedron Lett.* **1996**, *37*, 8399. (b) Khoury, R. G.; Jaquinod, L.; Smith, K. M. *Chem. Commun.* **1997**, 1057. (c) Senge, M. O.; Feng, X. *Tetrahedron Lett.* **1999**, *40*, 4165. (d) Shi, X.; Liebeskind, L. S. *J. Org. Chem.* **2000**, *65*, 1665.

[7] Cho, H. S.; Song, N. W.; Kim, Y. H.; Jeoung, S. C.; Hahn, S.; Kim, D.; Kim, S. K.; Yoshida, N.; Aratani, N.; Osuka, A. *J. Phys. Chem. A* **2000**, *104*, 3287

10.1021/ol006216n CCC: $19.00

Scheme 1



and electron-transfer reactions. In this paper, we report the synthesis of a series of strapped meso–meso linked diporphyrins with straps of various length.

Initially, bridged diporphyrins **B**$_n$ were prepared as shown in Scheme 1. Decamethylene-1,10-dioxy-bridged diporphyrin **B**$_{10}$ was obtained by Williamson reaction of hydroxyphenylporphyrin **1** with 1,10-dibromodecane (K_2CO_3, acetone) followed by zinc insertion in 86% yield. Similar reactions of **1** with longer dihaloalkanes ($n = 10-4$) gave their bridged dimers **B**$_8$–**B**$_4$ in good yields (82–92%), while the reactions with shorter dihaloalkanes ($n = 3$, 2, and 1) gave bridged dimers **B**$_3$–**B**$_1$ in poor yields. Elimination side products were formed in the reactions of **B**$_3$ and **B**$_2$, and the reaction of **B**$_1$ was quite slow in acetone. Solubilities of **B**$_n$ become poorer with the decrease of strap length, which caused another difficulty in the preparation of shorter-strap bridged diporphyrins **B**$_3$–**B**$_1$. In the meanwhile, however, we found that use of more dipolar DMF as the solvent led to improved yields of **B**$_3$–**B**$_1$ (Table 1).

Table 1. Isolated Yields of **B**$_n$ from **1**

product	X(CH$_2$)$_n$X	solvent	yield, %
B$_{10}$	$Br(CH_2)_{10}Br$	acetone	86
B$_8$	$I(CH_2)_8I$	acetone	82
B$_6$	$I(CH_2)_6I$	acetone	83
B$_4$	$Br(CH_2)_4Br$	acetone	92
B$_3$	$I(CH_2)_3I$	acetone	27
B$_3$	$Br(CH_2)_3Br$	acetone	61
B$_2$	$I(CH_2)_2I$	acetone	
B$_2$	$Br(CH_2)_2Br$	acetone	13
B$_2$	$Br(CH_2)_2Br$	DMF	40
B$_1$	$BrCH_2Br$	acetone	12
B$_1$	$BrCH_2Br$	DMF	84

With a set of **B**$_n$ ($n = 10$, 8, 6, 4, 3, 2, and 1) in hands, we examined their Ag(I)-promoted meso–meso coupling reaction. Intermolecular Ag(I)-promoted meso–meso coupling reaction was effective for Zn(II) 5,15-diarylporphyrins at ca. 2×10^{-3} M but the isolated yields of meso–meso coupled diporphyrins were normally in a range of 20–30% mostly because of formation of meso–meso coupled higher oligomers.[5a] Such oligomerization was easily enhanced upon addition of a small amount of *N*,*N*-dimethylacetoamide and by heating.[8] Since the intramolecular coupling reaction of **B**$_n$ must be preferable in dilute conditions, the reaction of **B**$_{10}$ was attempted at 9×10^{-5} M, which led to isolation of **S**$_{10}$ in 68% yields along with the recovery of **B**$_{10}$ (17%) and higher oligomers (ca. 10%) after preparative GPC and silica gel column chromatography. In an analogous manner, the reactions of **B**$_8$, **B**$_6$, and **B**$_4$ afforded **S**$_8$, **S**$_6$, and **S**$_4$ constantly in 60–65% yields. However, the yields of **S**$_3$–**S**$_1$ were moderate regardless of these dilute conditions (Table 2).

Table 2. Isolated Yields of S$_n$ from B$_n$

substrate	concentrated (mM)	product	yield, %
B$_{10}$	0.09	**S**$_{10}$	68
B$_8$	0.14	**S**$_8$	65
B$_6$	0.14	**S**$_6$	60
B$_4$	0.10	**S**$_4$	63
B$_3$	0.10	**S**$_3$	38
B$_2$	0.08	**S**$_2$	35
B$_1$	0.04	**S**$_1$	20

These strapped diporphyrins were characterized by ^1H NMR, FAB mass, steady-state absorption and fluorescence spectra, and differential pulse voltammetry. Under the standard conditions, most of the strapped diporphyrins were stable except **S**$_1$ whose absorption spectrum changed slowly, implying its unstable property. Therefore, all the characterizations of **S**$_1$ were carried out with the fresh sample.

MM2 calculations suggested a decrease in the dihedral angle with shortening of the strap as expected. In addition,

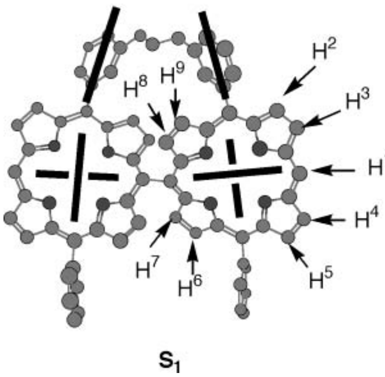
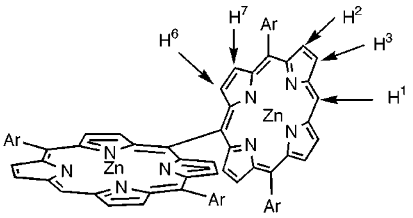


Figure 1. Minimized structure of **S**$_1$. Protons and *tert*-butyl groups are omitted for clarity.

such calculations also suggested the gradual distortion of the porphyrin rings for diporphyrins with short straps. The MM2-minimized structure of $\mathbf{S}_1$ is shown in Figure 1, in which the designations of the peripheral protons are indicated.

The ^{1}H NMR spectrum of **2** (Figure 2) shows signals due to a meso-H (H^1) and four kinds of beta-H (H^2, H^3, H,^{6} and H^7). The outer beta-Hs (H^2 and H^3) appeared at almost the same positions as those of a monomer, but the inner beta-Hs showed high field shift owing to a ring current effect of the adjacent porphyrin. The^{1}H NMR spectra of the strapped diporphyrins commonly showed signals due to a meso-H (H^1) and eight kinds of beta-H (H^2—H^9). The outer beta-Hs (H^2—H^5) and meso-H (H^1) were less affected by the change of the chain length. On the other hand, the inner beta-Hs showed contrasting shifts. With shortening of strap, beta-Hs of the strap side (H^8 and H^9) are shifted to high field and those of opposite side (H^6 and H^7) are shifted to low field. Therefore, these facts suggest the decrease of dihedral angle between two porphyrins and tilting of the porphyrin axis perpendicular to the meso—meso bond toward the strap side with shortening of strap as shown in Figure 1. The fact that the meso-H and the outer beta-H appeared at the similar chemical shifts for all $\mathbf{S}_n$ indicates that porphyrin ring current is not seriously affected and the distortion of porphyrin ring seems relatively small even in $\mathbf{S}_1$ with the shortest strap.



2

Ar= 3,5-di-*t*-butylphenyl

Figure 2.

The absorption spectra of the strapped diporphyrins are shown in Figure 3. As reported previously,[5] nonstrapped meso—meso coupled diporphyrin **2** exhibited a split Soret band at 415 and 447 nm and weakly perturbed Q-band at 553 nm, which have been interpreted in terms of exciton coupling of the two transition dipole moments along the meso—meso bond axis. Averaged perpendicular conformation of **2** has been inferred from a systematic analysis of the absorption spectra of a series of meso—meso coupled porphyrin arrays.[5d,7] The absorption spectra of $\mathbf{S}_{10}$, $\mathbf{S}_8$, and $\mathbf{S}_6$ were close to that of **2**. Therefore, we may consider that relatively long straps have no significant influence on the dihedral angle between monomers. The absorption spectral changes at the Soret-band region with a change in the strap length were more prominent for $\mathbf{S}_4$, $\mathbf{S}_3$, $\mathbf{S}_2$, and $\mathbf{S}_1$, in that the shoulder at the high energy side of the Soret band gained increasing intensity at 397 nm in $\mathbf{S}_2$ and 395 nm in $\mathbf{S}_1$, the unperturbed Soret band around 413 nm was gradually red-shifted from 419 nm in $\mathbf{S}_{10}$ and $\mathbf{S}_4$ to 424 nm both in $\mathbf{S}_2$ and $\mathbf{S}_1$, and the low energy Soret bands were increasingly red-shifted and intensified, giving rise to 469 nm in $\mathbf{S}_3$ and 478 nm in $\mathbf{S}_2$ and $\mathbf{S}_1$. The broad and nearly single band shape of the Q-band of **2**, $\mathbf{S}_{10}$, $\mathbf{S}_8$, and $\mathbf{S}_6$ displayed a systematic change to distinct two-band-shaped Q-bands with the gradual red-shift of the low-energy Q-bands. Although we do not have quantitative explanation of these spectral changes that are outside of the present work, these changes strongly indicate the increasingly enhanced electronic communication between the porphyrins.

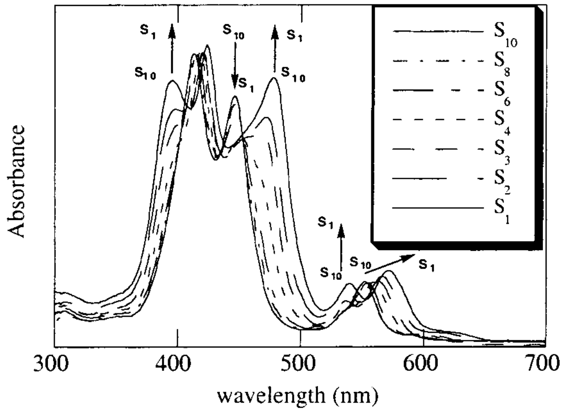


Figure 3. UV—vis absorption spectra of $\mathbf{S}_n$ in CH_2Cl_2.

Figure 4 shows the fluorescence spectra of selected $\mathbf{S}_n$ that showed a steady red-shift with a loss of shoulders with the decrease of the strap length, roughly reflecting the red-shift of the respective absorption Q-bands. These changes also imply enhanced communication between the two porphyrin rings.

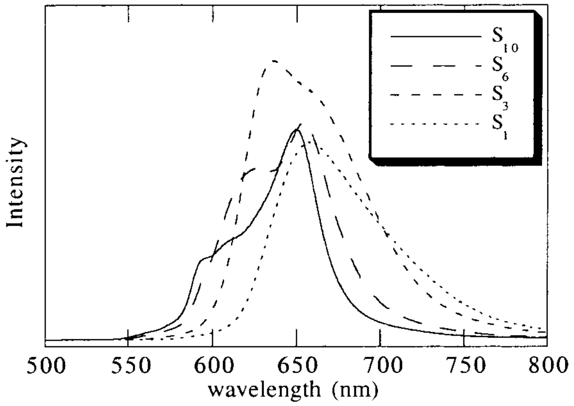


Figure 4. Fluorescence spectra of $\mathbf{S}_n$ in CH_2Cl_2.

One-electron oxidation potentials of $\mathbf{B}_n$ and $\mathbf{S}_n$ were measured by the differential pulse voltammetry method in

---

(8) Yoshida, N.; Aratani, N.; Osuka, A. *Chem. Commun*. **2000**, 197.

Table 3. First Oxidation Potential (vs Ferrocene/Ferrocenium) of $\mathbf{B}_n$ and $\mathbf{S}_n$[a]

	E_{Ox1} (V)		E_{Ox1} (V)
$\mathbf{S}_{10}$ (94°)	0.33	$\mathbf{B}_{10}$	0.28
$\mathbf{S}_{8}$ (90°)	0.32	$\mathbf{B}_{8}$	0.27
$\mathbf{S}_{6}$ (80°)	0.31	$\mathbf{B}_{6}$	0.26
$\mathbf{S}_{4}$ (71°)	0.30	$\mathbf{B}_{4}$	0.30
$\mathbf{S}_{3}$ (53°)	0.28	$\mathbf{B}_{3}$	0.29
$\mathbf{S}_{2}$ (42°)	0.27	$\mathbf{B}_{2}$	0.29
$\mathbf{S}_{1}$ (36°)	0.22	$\mathbf{B}_{1}$	0.33

[a] Calculated dihedral angles of $\mathbf{S}_n$ are given in parentheses.

DMF (Table 3). One-electron oxidation potentials of most of $\mathbf{B}_n$ were slightly lower than that of **2** except for the case of $\mathbf{B}_1$. It may be plausible that a diporphyrin having a flexible chain can form a stacked dimer upon one-electron oxidation, which may lead to lower oxidation potentials as were observed. Such a conformational freedom may not be allowed in $\mathbf{B}_1$. On the other hand, the one-electron oxidation potentials of $\mathbf{S}_n$ became increasingly lower with the decrease in the strap length. These results seem to be in accord with enhanced electronic communication in strapped diporphyrins with small dihedral angles, which was estimated by MM2 calculation (Table 3). In addition, the results in Table 3 may have some important relevance to the reaction yields of $\mathbf{S}_n$ from $\mathbf{B}_n$. The relatively good yields of $\mathbf{S}_n$ with a longer strap can be explained in terms of easy oxidation of $\mathbf{B}_n$ and the slightly harder oxidation of $\mathbf{S}_n$ that can lead to accumulation of the $\mathbf{S}_n$ product. On the contrary, the one-electron oxidation potentials of $\mathbf{S}_n$ with a short strap ($n = 3-1$) were lower than those of $\mathbf{B}_n$, thereby giving rise to further coupling reaction of $\mathbf{S}_n$. Such a tendency seems to be strongest for $\mathbf{S}_1$ that can be oxidized by as much as ca. 0.1 V easier than $\mathbf{B}_1$. Actually, the GPC analysis revealed that the reaction mixture of $\mathbf{B}_n$ contained large amounts of higher oligomeric products.

In summary, a series of the meso−meso linked strapped diporphyrins $\mathbf{S}_n$ with various strap lengths were effectively synthesized by the intramolecular Ag(I)-promoted coupling of the bridged diporphyrins $\mathbf{B}_n$. The low yield of $\mathbf{S}_1$ is most probably ascribed to further oligomerization of formed strapped diporphyrins due to lower one-electron oxidation potentials. With the decrease of the strap length, the electronic communications between the two porphyrins are enhanced as revealed by the absorption and fluorescence spectra and the one-electron oxidation potentials. Uses of these meso−meso coupled strapped diporphyrins for studies on energy transfer and electron transfer as well as magnetic interactions are now actively in progress in our laboratory.

Acknowledgment. This work was supported by Grant-in-Aid for Scientific Research (No.11223205 and No. 12440196) from the Ministry of Education, Science, Sports and Culture of Japan and by CREST (Core Research for Evolutional Science and Technology) of Japan Science and Technology Corporation (JST). N.Y. is grateful for a JSPS Research Fellowship for Young Scientists.

Supporting Information Available: ^{1}H NMR spectra of $\mathbf{S}_{10}-\mathbf{S}_1$. This material is available free of charge via the Internet at http://pubs.acs.org.

OL006216N