Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

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To cite this Article Yagi, Shigeyuki , Yamada, Ryuhei , Tsuji, Norihiro , Murakami, Shinji and Takagishi, Toru(2000) 'Conformational Control of a Polyether-Linked Porphyrin Dimer Induced by Complexation with a Sodium Cation', Supramolecular Chemistry, 12: 3, 293 — 297

To link to this Article: DOI: 10.1080/10610270008029450

URL: http://dx.doi.org/10.1080/10610270008029450

SUPRAMOLECULAR CHEMISTRY, Vol. 12, pp. 293-297
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Conformational Control of a Polyether-Linked Porphyrin Dimer Induced by Complexation with a Sodium Cation

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(Received January 20, 2000)

A porphyrin dimer with a polyether linkage was newly synthesized and its conformational change triggered by complexation with an sodium cation was examined. It was confirmed by ^{1}H NMR titration experiments that the dimer bearing a pentaoxyehtylene linkage (**1b**) was effectively formed a 1:1 complex with a sodium perchlorate. A detailed investigation of the CIS values for the protons confirmed that the complex of **1b**•Na$^+$ adopts a slipped face-to-face conformation.

Keywords: Porphyrin dimer, sodium cation, conformational change, complexation-induced shift, face-to-face conformation

Regulation of orientations among porphyrin chromophores has been attracting much interest from the viewpoint of the importance for structural mimics of the special pair in the photosynthetic reaction center [1] and of the highly controlled orientation of bacteriochlorophylls at the photosynthetic light-harvesting system [2]. It is well known that electron and energy transfer processes are largely affected by the distance and orientation of the chromophores involved in the photochemical processes [3]. Thus, in order to arrange porphyrin chromophores in a defined geometry, many porphyrin dimers and oligomers have been prepared, where the chromophores are often fixed in a face-to-face manner through covalent bonds, metal coordination, hydrogen bonds, etc., to achieve biomimetic photochemical systems [4, 5, 6]. Another approach is to control a conformation of a porphyrin oligomer to a well-defined structure by an external stimulus, such as a metal cation or a guest molecule. In this paper, we report the synthesis and conformational control of the porphyrin dimer **1** with a polyether linkage, which is forced to be folded in a slightly slipped face-to-face conformation upon complexation with a sodium cation.

As shown in Scheme 1, porphyrin dimers **1a** and **1b** were prepared by a typical ether synthesis with tetra- or pentaethylene glycol ditosylate and two equivalents of the porphyrin derivative **7**, which were obtained in 41% and 54% yields, respectively [7]. The reference monomer **2**, in

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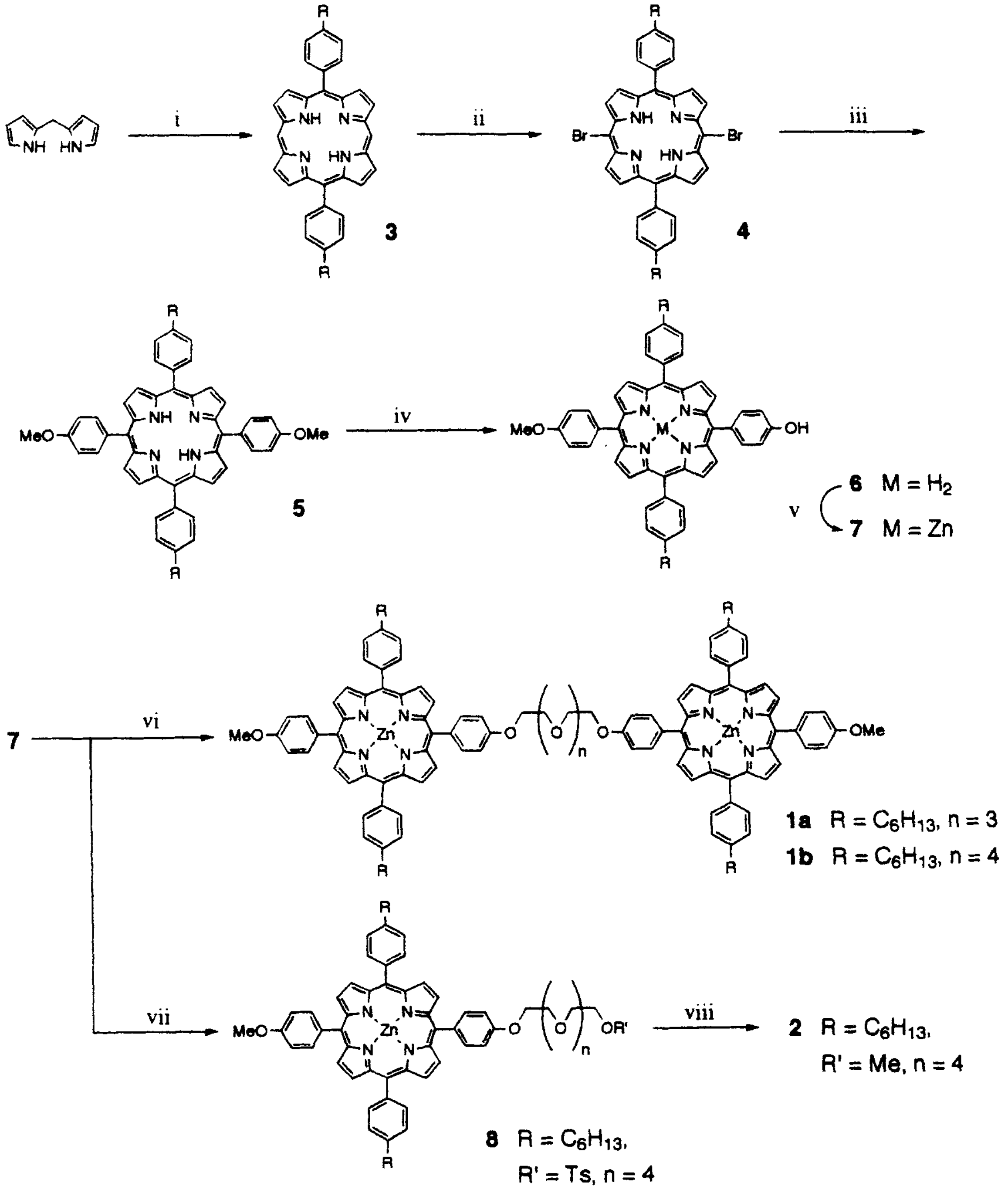

SCHEME 1 (i) 4-Hexylbenzaldehyde diethylacetal, $BF_3 \bullet Et_2O$, chloranil in CH_2Cl_2, 35%; (ii) NBS, pyridine in $CHCl_3$, 96%; (iii) 4-methoxyphenylboronic acid, $Pd(PPh_3)_4$, Na_2CO_3 aq. in benzene, reflux, 91%; (iv) BBr_3 in CH_2Cl_2, 38%; (v) $Zn(OAc)_2$ in $CHCl_3$-MeOH, reflux, 95%; (vi) tetra- or pentaethyleneglycol ditosylate, Cs_2CO_3, DMF, 41% for **1a** and 54% for **1b**; (vii) 3eq. of pentaethyleneglycol ditosylate, Cs_2CO_3, DMF, 41%; (viii) sodium methoxide in DMF, 48%.

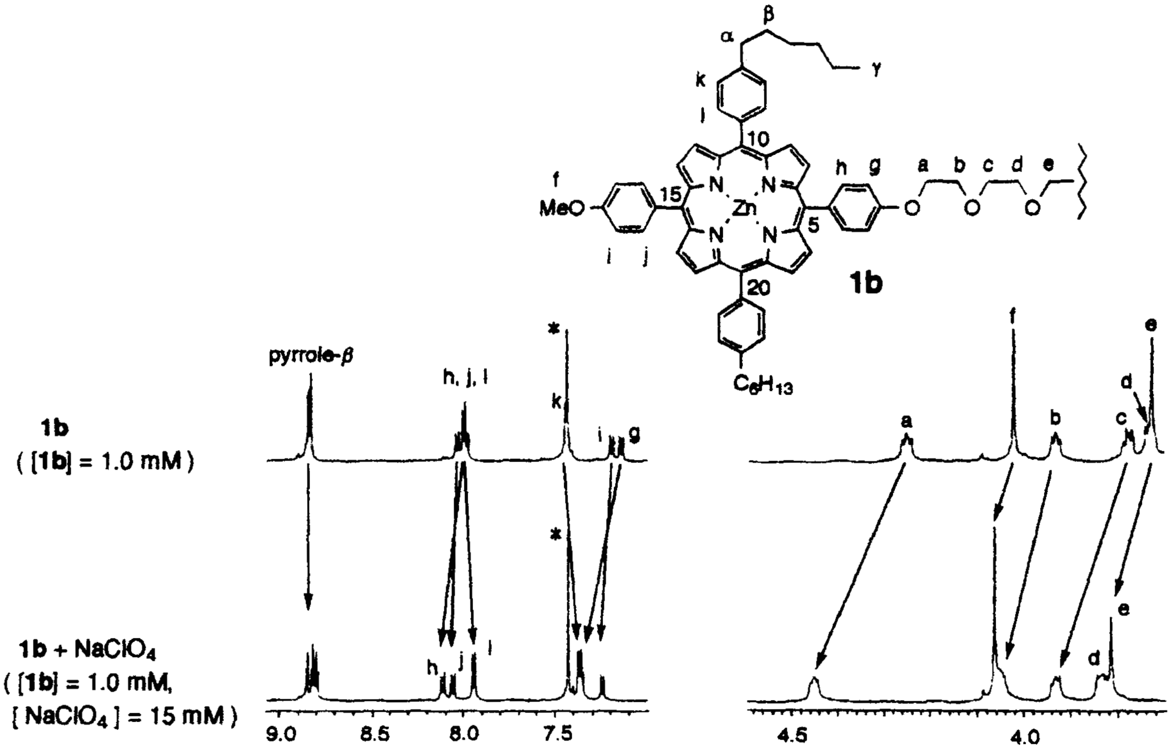

FIGURE 1 ^{1}H-NMR spectral change of **1b** upon complexation of $NaClO_4$ in $CDCl_3/CD_3CN$ = 7/3 (v/v) at 293 K. The symbol * represents the residual proton of $CHCl_3$. Under the present condition, the 90% of complexation between **1b** and $NaClO_4$ was achieved.

which one porphyrin moiety is replaced by a methyl group, was prepared by the reaction of **7** with an excess amount of pentaethylene glycol ditosylate followed by the substitution reaction of **8** with sodium methoxide. All the compounds were characterized by ^{1}H NMR and FAB mass spectra and by elemental analyses, and full assignment of all the protons except those at the peripheral positions of the porphyrin rings was achieved by ^{1}H-^{1}H COSY and ROE (rotation frame NOE) spectra.

As is well known, an alkali metal cation is effectively bound by polyethers such as glymes [8], and thus, it is expected that complexation with the metal cation leads to a drastic conformational change of the dimer **1**. The conformational change triggered by complexation with a sodium cation was examined by using a ^{1}H NMR spectroscopy [9]. As shown in Figure 1, adding $NaClO_4$ to a $CHCl_3$-CH_3CN (7/3, v/v) solution of **1b** led to changes of the chemical shifts by 0.057–0.232 ppm except for some protons, indicating that the two porphyrin units are within a close distance to be affected each other by ring current anisotropy. The Job's plot for **1b**, monitoring the complexation-induced shifts (CISs), clarified that the stoichiometry of **1b**-Na^+ system is 1:1. The CIS values in the presence of increasing amounts of $NaClO_4$ exhibited saturation behavior and led to determination of a binding constant *K* by using a least-squares calculation, where the value of *K* for **1b** was determined as 664 M^{-1} [10]. Although the similar tendency of the CISs was observed for **1a**, the CIS values were modest (< 0.15 ppm) under the same condition as **1b** ([1] = 1.0 mM,

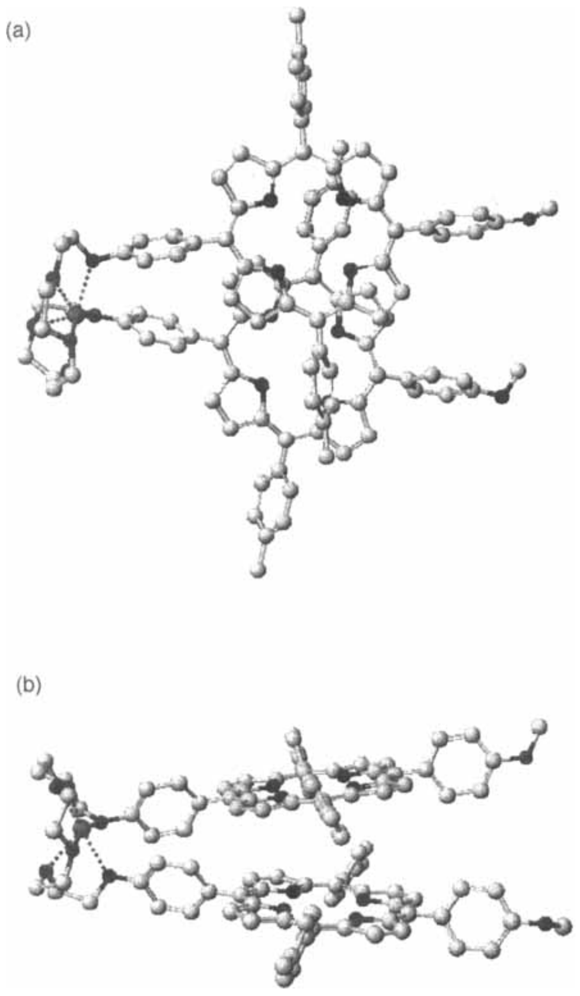

FIGURE 2 A proposed structure of the **1b**•Na^+ complex generated by a MM2 calculation (the CAChe System); (a) a top view and (b) a side view. In the calculation, the hexyl groups was replaced by methyls. The protons and zinc cations are omitted for clarity.

[$NaClO_4$] = 15 mM): the value of K (79 M^{-1}) for the **1a**•Na^+ complex was smaller than that for **1b**•Na^+, indicating that the length of the tetraoxyethylene moiety is less suitable to induce the conformational change of the porphyrin dimer with a sodium cation.

The CIS value for each proton afforded further information about the orientation between the two porphyrin moieties. In Table I are described the CIS values for the selected protons in **1b**. The protons in the polyether chain (H_a-H_e) and in the 5-aryl group (H_g and H_h) shifted downfield by 0.11–0.23 ppm upon complexation with $NaClO_4$, whereas the CIS values for the corresponding protons in **2** [11] were not more than 0.1 ppm, indicating that the CIS in **1b**•Na^+ complex is mainly due to the ring current anisotropy of the porphyrin rings. The downfield shifts of the protons H_f, H_i and H_j were also observed, although modest compared to those of the protons H_a, H_g and H_h. Thus, the site around the 5-position comes closer to the other porphyrin ring than the end of the dimer. It is noteworthy that the protons at the 10- and 20-positions (H_k, H_l and H_α-H_γ) exhibited upfield shifts by 0.01–0.08 ppm, indicating that the hexylphenyl groups are located over the other porphyrin ring. From the experimental results described above, we propose the structure of the **1b**•Na^+ complex as shown in Figure 2, which was generated by the MM2 calculation. The complex should mainly adopt a slightly slipped face-to-face conformation, although the structure of the complex is expected to be flexible in a short time scale.

TABLE I The CIS values for the selected protons of **1b** upon complexation with $NaClO_4$ in $CHCl_3/CD_3CN$ (7/3, v/v) at 293 K

proton[a]	*CIS/ppm*[b]	*proton*[a]	*CIS/ppm*[b]
H_α	−0.068	H_c	+0.178
H_β	−0.058	H_d	+0.117
H_γ	−0.012	H_e	+0.105
H_k	−0.076	H_f	+0.051
H_l	−0.057	H_g	+0.247
		H_h	+0.148
H_a	+0.232	H_i	+0.061
H_b	+0.142	H_j	+0.030

a. The position of each proton is shown in Figure 1.
b. The positive and negative values of the CISs mean downfield and upfield shifts, respectively.

In summary, we have demonstrated the possibility to regulate the orientation of porphyrin chromophores by the complexation-triggered conformation control. Further study for longer oligomers and their photochemical properties is now under investigation and will be reported elsewhere in future.

Acknowledgements

This work was financially supported by the Sasakawa Scientific Research Grant from The Japan Science Society. We thanks to Prof. Hiroyuki Nakazumi for his cooperation in the molecular mechanics calculation.

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[7] **1a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.96 (t, *J* = 7.6 Hz, 12H), 1.26–1.51 (m, 24H), 1.87 (quint, *J* = 7.6 Hz, 8H), 2.89 (t, *J* = 7.6 Hz, 8H), 3.68–3.75 (m, 8H), 3.94 (m, 4H), 4.07 (s, 6H), 4.28 (m, 4H), 7.22–7.28 (m, 8H), 7.46 (d, *J* = 7.9 Hz, 8H), 8.02–8.09 (m, 16H), 8.89–8.91 (m, 16H); FAB MS *m/z* 1938 (M^+), 1939 (MH^+), 1940 ($MH^+ + 1$), 1941 ($MH^+ +2$), 1942 ($MH^+ + 3$), 1943 ($MH^+ +4$), 1994 (($MH^+ +5$); Anal. Calcd for $C_{122}H_{122}N_8O_7Zn_2$: C, 75.41; H, 6.33; N, 5.77. Found: C, 75.15; H, 6.42; N, 5.41. **1b**: ^{1}H NMR (500 MHz, $CDCl_3/CD_3CN$ = 7/3, v/v) δ 0.96 (t, *J* = 7.6 Hz, 12H), 1.26 –1.53 (m, 24H), 1.86 (quint, *J* = 7.6 Hz, 8H), 2.87 (t, *J* = 7.6 Hz, 8H), 3.72–3.79 (m, 12H), 3.93 (t, *J* = 4.3 Hz, 4H), 4.02 (s, 6H), 4.25 (t, *J*= 4.3 Hz), 7.14 (d, *J* = 8.6 Hz, 4H), 7.19 (d, *J* = 8.2 Hz, 4H), 7.43–7.44 (m, 8H), 7.97–8.04 (m, 16H), 8.81–8.85 (m, 16H); FAB MS *m/z* 1982 (M^+), 1983 (MH^+), 1984 ($MH^+ + 1$), 1985 ($MH^+ +2$), 1986 ($MH^+ + 3$), 1987 ($MH^+ +4$), 1988 (($MH^+ +5$); Anal. Calcd for $C_{124}H_{126}N_8O_8Zn_2$: C, 74.95; H, 6.39; N, 5.64. Found: C, 74.81; H, 6.64; N, 5.30.

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[9] Here a sodium cation was chosen as a guest because sodium perchlorate shows better solubility to the solvent employed here than the other alkali and alkaline earth metal salts.

[10] The standard deviations for complexation of **1a** and **1b** with $NaClO_4$ are less than 3%.

[11] The value of *K* for complexation of **2** with is 4620 ± 1020 M^{-1}. This relatively large value is probably due to the absence of the steric repulsion of the porphyrin ring.