Available online at www.sciencedirect.com
SCIENCE DIRECT®
Tetrahedron Letters
Tetrahedron Letters 46 (2005) 5347–5350

Template-assisted control of porphyrin aggregation by ladder-type supramolecular assemblies

Takahiro Sugimoto,[a] Kazuki Sada,[a,*] Yuichi Tateishi,[a] Takayuki Suzuki,[a] Yoshihisa Sei,[b] Kentaro Yamaguchi[c] and Seiji Shinkai[a]

[a]*Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan*
[b]*Chemical Analysis Center, Chiba University, Inage Chiba 263-8522, Japan*
[c]*Faculty of Pharmaceutical Sciences at Kagawa Campus, Tokushima Bunri University, 1314-1 Shido, Sanuki City, Kagawa 769-2193, Japan*

Received 10 May 2005; revised 1 June 2005; accepted 2 June 2005
Available online 22 June 2005

Abstract—A new strategy to control the orientation and aggregation numbers of porphyrins by alignment along well-defined templates has been demonstrated. Porphyrin-bridged bisPYBOX ligands were arranged along the oligomeric secondary dialkylammonium cations as templates to form well-defined supramolecular complexes. The templates controlled the aggregations of the porphyrins.

Controlled aggregation of dyes offers interesting electronic and photonic functional materials that are different from their monomeric state. For example, a light-harvesting system in bacteria has a wheel-like arrangement of chlorophylls surrounded by polypeptide chains to produce different energy transfer.[1] However, the rational control of a dye aggregate is still difficult, because the dyes tend to spontaneously align into a one-dimensional infinite aggregate in the face-to-face manner by π–π stacking and/or van der Waals interactions.[2–4] The development of the method to control the aggregation numbers and orientations of the dyes in the one-dimensional aggregates is still in its infancy, and only a limited number of examples of the controlled dye aggregates have so far been reported in artificial systems.[5–9] In this report, we demonstrate a new strategy to control the aggregation of porphyrins by alignment along well-defined template molecules as 'a controlling unit'. The absorption spectra of the porphyrin aggregates changed as a function of the controlling units.

2,6-Bis(2-oxazolyl)pyridine (PYBOX) is a well-known ligand for transition metal catalyzed asymmetric reactions.[10] Recently, we demonstrated that the convergent molecular structure of PYBOX was suitable for the recognition of the secondary dialkylammonium cations.[11] Moreover, we reported the formation of supramolecular ladders by complexation of a bisPYBOX ligand with the oligomers of a secondary dialkylammonium.[12] This led us to control the aggregation of the porphyrins by their incorporation between the two PYBOX ligands (Fig. 1).

The porphyrin-bridged bisPYBOX ligand (**Por**) was prepared according to the scheme described in the supporting information. The complexation properties of **Por** with the oligomeric secondary ammoniums (**nN**) were investigated by UV–vis absorption spectroscopy, as shown in Figure 2. According to the absorption maxima of the Soret band at 465 nm, a part of the **Por** aggregated to form *J*-aggregates[2] in this condition. The addition of **1N** decreased the absorption of the *J*-aggregate and induced a slight blue shift from 465 nm to 459.5 nm and a blue shift from 685 nm to 676.5 nm in the Q-band as shown in Figure 2a. These spectral changes are attributed to complexation of the PYBOX group with the secondary dialkylammonium and dissociation of the *J*-aggregate of the porphyrins. The titration curve showed that they were saturated at a nearly

Keywords: Porphyrin; Aggregate; Ladder-type assembly; Template; Hydrogen bonding.
* Corresponding author. Tel.: +81 92 642 3584; fax: +81 92 642 3611; e-mail: sadatcm@mbox.nc.kyushu-u.ac.jp

0040-4039/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2005.06.001

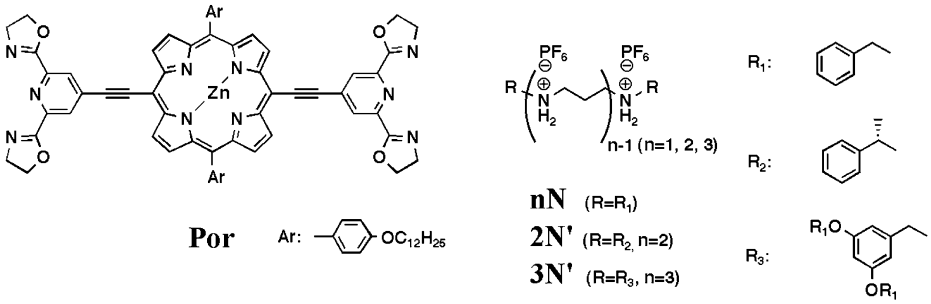


Figure 1. Structure of **Por**, **nN** (n = **1**–**3**), **2N**′ and **3N**′.

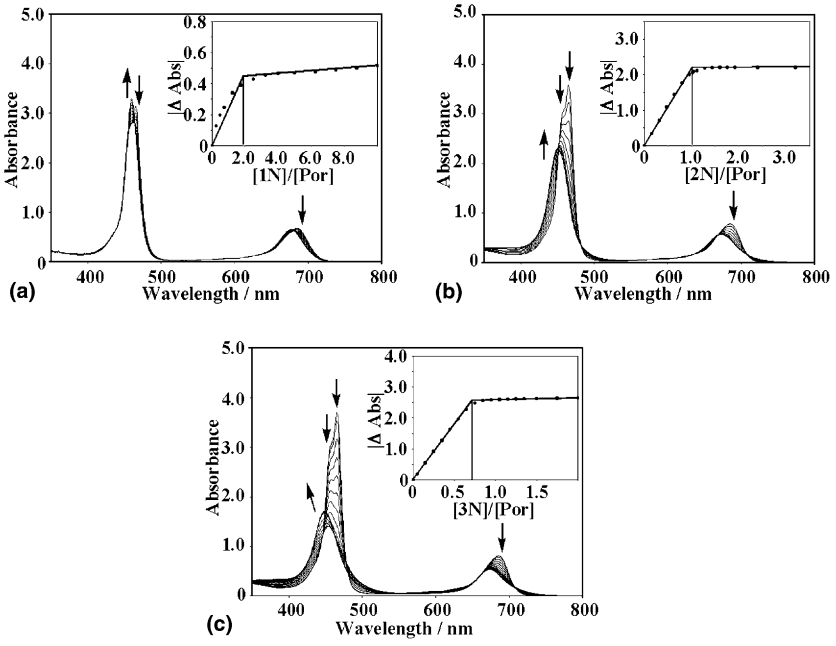


Figure 2. Absorption spectral changes of **Por** (1×10^{-4} mol dm^{-3}) in $CHCl_3$–CH_3CN (40:1, v/v) at 298 K upon addition of (a) **1N** (0–10×10^{-4} mol dm^{-3}), (b) **2N** (0–2×10^{-4} mol dm^{-3}) and (c) **3N** (0–2×10^{-4} mol dm^{-3}). Inserted graphs show the absorption changes at 465 nm.

1:2 ratio, suggesting the formation of a 1:2 complex. The cationic group led to the dissociation of the *J*-aggregate between the porphyrins due to the electrostatic repulsions.

On the other hand, the addition of **2N** or **3N** exhibited different behaviors in the absorption spectra. The addition of **2N** induced a blue shift in the Soret band to 450.5 nm and a blue shift of the Q-band to 673 nm, and the intensity of the Soret band significantly decreased with the increasing concentration of **2N**, as shown in Figure 2b. These shifts in the absorption bands indicated parallel stacking of the porphyrins (*H*-aggregate). The titration curve was saturated at a 1:1 stoichiometry. However, the formation of the 1:1 complex is not presumable due to the rigid molecular structure of **Por**. The most probable structure is a 2:2 complex due to the dimeric template of **2N** according to the blue shift in the Soret band. The aggregate made the two porphyrins associate very closely to each other. In the case of **3N**, the titration experiment indicates two steps in the complex formation. In the first step, the addition of **3N** decreased the absorption of the Soret band till ca. a 0.7 molar ratio with the isosbestic points at 445 and 478.5 nm. The absorption maximum did not move, but the shoulder at 465 nm assigned to the *J*-aggregate of **Por** decreased. Therefore, this step should indicate the formation of the 3:2 complex. The decreased intensity supports aggregation of the porphyrins. The further addition of **3N** then produced a new absorption band that was blue-shifted at 448.5 nm with a higher intensity. This spectral change was nearly saturated at 1:1.3, and the final spectrum is quite similar to that of the **2N** complex. Thus, the excess amount of **3N** induced a structural rearrangement from the 3:2 ladder complex to the 2:2 complex similar to that of **Por** with **2N**. The recovery of the intensity should be attributed to the change in the aggregation numbers of the porphyrins along the templates. These results indicate that the oligomeric **2N** and **3N** templates change the aggregation mode of the porphyrins.

Moreover, the addition of the **2N** template to the solution of the 1:2 complex of **Por** and **1N** changed the spectra from the monomeric complex to the *H*-aggregate as shown in Figure 3. The 2:2 complex of **2N** was more

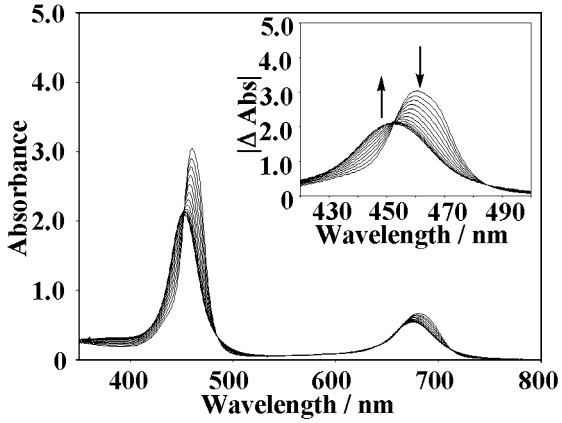
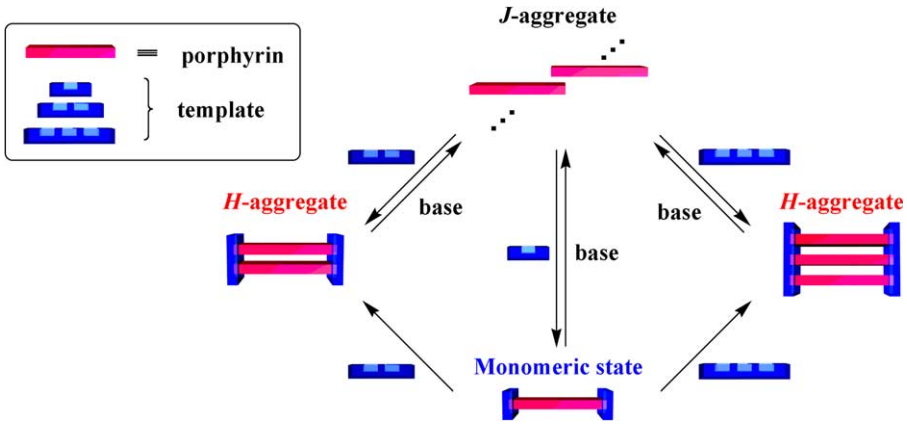


Figure 3. Absorption spectral changes of **Por** (1×10^{-4} mol dm^{-3}) in the presence of **1N** (3×10^{-4} mol dm^{-3}) in $CHCl_3$–CH_3CN (40:1, v/v) upon addition of **2N** (0–2×10^{-4} mol dm^{-3}).

stable than the 1:2 complex of **1N** because the π–π stacking between the porphyrins stabilized the complex. Methanol or triethylamine decomposed the ladder complexes to yield the monomeric porphyrins. Therefore, both the size of the aggregates and the orientations of the porphyrins in the aggregate are controlled by the number of secondary ammonium cations in the templates (Scheme 1).

In order to confirm the aggregation behavior of **Por**, we further investigated the CSI-MS[13] and ^{1}H NMR titration. The monomeric template **1N** showed a 1:2 complex at $m/z = 884.7$ ([**Por** + 2**1N**]$^{2+}$), and the dimeric templates of **2N** illustrate a 2:2 complex at $m/z = 813.9$ ([2**Por** + 2**1N**]$^{4+}$ – 4PF_6). The corresponding 3:2 complex was observed from a mixture of **Por** and **3N** at $m/z = 3012.6$ ([3**Por** + 2**3N**]$^{2+}$). On the other hand, in the ^{1}H NMR titrations, the **2N** and **3N** templates did not have enough solubility. We then used **2N**′ and **3N**′ for the ^{1}H NMR experiments at room temperature in $CDCl_3$–THF-d_8–CD_3CN (10:2:1, v/v/v, ca. 1 mM). The addition of a **1N** solution into a solution of **Por** caused the oxazoline and pyridine proton resonances of **Por** to move downfield from 4.53 to 4.67 ppm, and upfield from 8.43 ppm to 7.89 ppm, respectively. No induced chemical shift changes were observed for the proton resonances of the bridging porphyrin. These changes indicate complexation of the PYBOX moieties and the secondary dialkylammonium cations, but no stacking or aggregation of the porphyrins. The titration curve was not saturated even at the **Por/1N** ratio of more than 4.0, but was nearly bent at a 1:2 ratio, which suggests that the two PYBOX moieties independently form 1:1 complexes with two **1N**s. On the other hand, the addition of a **2N**′ or **3N**′ solution to the **Por** solution yielded several new resonances in the ^{1}H NMR. For the **2N**′, the pyridine protons and oxazoline protons at 8.42 ppm and 4.53 ppm disappeared and new peaks assigned to these two resonances were observed at 7.11 ppm and 4.89 ppm, respectively. This corresponds to the complexation of the PYBOX moieties and the *sec*-dialkylammonium cations. The resonances for the pyrrole protons at 9.71 and 8.95 ppm also disappeared and new signals at 8.71 and 8.48 ppm became visible. The addition of the **3N**′ solution also provided shift changes similar to those of **2N**′. The upfield shifts are understood to be due to the deshielding of the large aromatic porphyrin rings. The dimeric and trimeric templates provide stacking of the porphyrin moieties. Moreover, the separation of the resonances between the complex species and uncomplexed **Por** indicates that the complex had the slower exchange rate. The spectral changes were saturated at 1:1 and 1:0.7 ratios for the **2N**′ and **3N**′, respectively. These results correspond to the 2:2 and 3:2 complexes. Therefore, one-dimensional porphyrin arrays assembled along the oligomeric template were confirmed by the ^{1}H NMR titrations and CSI-MS spectra.

In conclusion, we demonstrated a new method to control the size and the orientation of the aggregates of the porphyrins by the well-defined template molecules. The difference in the absorption spectra corresponds to the number of controlling units in the template molecules and represents the output of molecular information of the template molecules by changing the aggregation of the porphyrins. This template strategy allows control of the aggregation of the many dyes by



Scheme 1.

incorporation into the bridging groups, and a wide range of secondary ammonium cations should provide many controlled arrangements of the dyes.

Acknowledgments

We thank the Ministry of Education, Science, and Culture of Japan (No. 14550836) for their generous financial support.

References and notes

1. For example, Choi, M.-S.; Yamazaki, T.; Yamazaki, I.; Aida, T. *Angew. Chem., Int. Ed.* **2004**, *43*, 150.
2. Kano, K.; Fukuda, K.; Wakami, H.; Nishiyabu, R.; Pasternack, R. F. *J. Am. Chem. Soc.* **2000**, *122*, 7494; Okada, S.; Segawa, H. *J. Am. Chem. Soc.* **2003**, *125*, 2792; Shirakawa, M.; Kawano, S.-i.; Fujita, N.; Sada, K.; Shinkai, S. *J. Org. Chem.* **2003**, *68*, 5037.
3. Mishra, A.; Behera, R. K.; Behera, P. K.; Mishra, B. K.; Behera, G. B. *Chem. Rev.* **2000**, *100*, 1973.
4. de la Escosura, A.; Martinez-Diaz, M. V.; Thordarson, P.; Rowan, A. E.; Nolte, R. J. M.; Torres, T. *J. Am. Chem. Soc.* **2003**, *125*, 12300–12308.
5. De Napoli, M.; Nardis, S.; Paolesse, R.; Vicente, M. G. H.; Lauceri, R.; Purrello, R. *J. Am. Chem. Soc.* **2004**, *126*, 5934; Moschetto, G.; Lauceri, R.; Gulino, F. G.; Sciotto, D.; Purrello, R. *J. Am. Chem. Soc.* **2002**, *124*, 14536; Micali, N.; Romeo, A.; Lauceri, R.; Purrello, R.; Mallamace, F.; Monsu Scolaro, L. *J. Phys. Chem. B* **2000**, *104*, 9416; Bellacchio, E.; Lauceri, R.; Gurrieri, S.; Monsu Scolaro, L.; Romeo, A.; Purrello, R. *J. Am. Chem. Soc.* **1998**, *120*, 12353; Purrello, R.; Monsu Scolaro, L.; Bellacchio, E.; Gurrieri, S.; Romeo, A. *Inorg. Chem.* **1998**, 3647.
6. Feiters, M. C.; Fyfe, M. C. T.; Martínez-Díaz, M.-V.; Menzer, S.; Nolte, R. J. M.; Stoddart, J. F.; van Ken, P. J. M.; Williams, D. J. *J. Am. Chem. Soc.* **1997**, *119*, 8119.
7. Asanuma, H.; Shirasuka, K.; Takarada, T.; Kashida, H.; Komiyama, M. *J. Am. Chem. Soc.* **2003**, *125*, 2217.
8. Tanaka, K.; Tengenji, A.; Kato, T.; Toyama, N.; Shionoya, M. *Science* **2003**, *299*, 1212.
9. Wang, M.; Dilek, I.; Armitage, B. A. *Langmuir* **2003**, *19*, 6449; Garoff, R. A.; Litzinger, E. A.; Connor, R. E.; Fishman, I.; Armitage *Langmuir* **2002**, *18*, 6330; Wang, M.; Silvia, G. L.; Armitage, B. A. *J. Am. Chem. Soc.* **2000**, *122*, 9977; Seifert, J. L.; Connor, R. F.; Kushon, S. A.; Wang, M.; Armitage, B. A. *J. Am. Chem. Soc.* **1999**, *121*, 2987.
10. Nishiyama, H.; Sakahuchi, H.; Nakamura, T.; Horihata, M.; Kondo, M.; Itoh, K. *Organometallics* **1989**, *8*, 846; Ghosh, A. K.; Mathivanan, P.; Cappiello, J. *Tetrahedron: Asymmetry* **1998**, *9*, 1.
11. Sada, K.; Sugimoto, T.; Tani, T.; Tateishi, Y.; Yi, T.; Shinkai, S.; Maeda, H.; Tohani, N.; Miyata, M. *Chem. Lett.* **2003**, *32*, 758.
12. Sugimoto, T.; Sada, K.; Yamaguchi, K.; Shinkai, S. *Chem. Commun.* **2004**, 1226.
13. Yamaguchi, K. *J. Mass Spectromet.* **2003**, *38*, 473.