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Supramolecular assembly of light harvesting porphyrin hexamer

Hideyuki Shinmori, Takashi Kajiwara and Atsuhiro Osuka*

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

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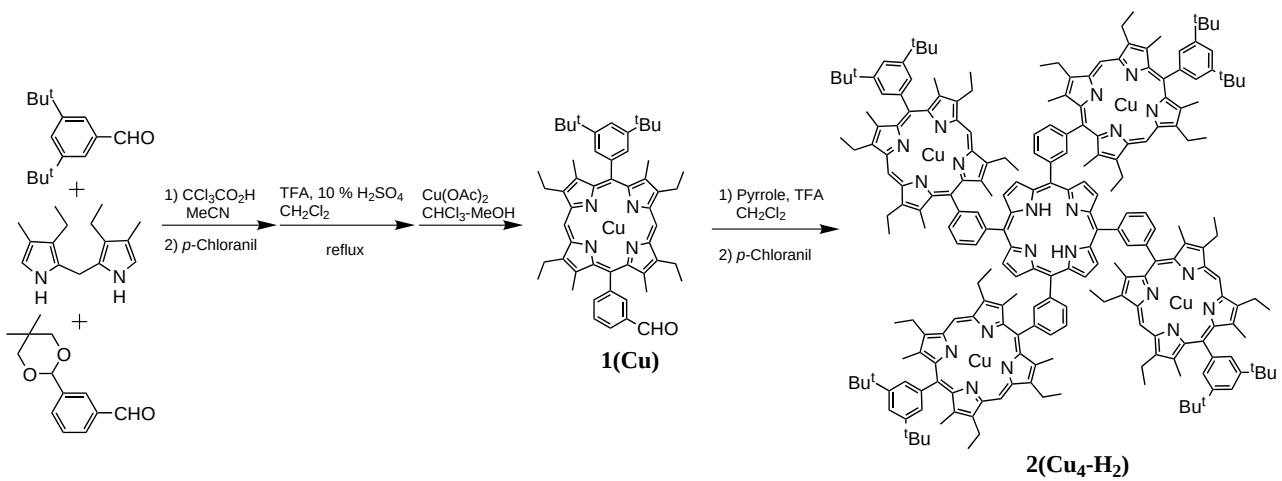
Abstract—Pentameric porphyrin hosts, in which a TPP type porphyrin was attached to four OEP type zinc porphyrins through a 1,3-phenylene spacer, were synthesized. Its spectroscopic investigations suggest that the host binds a one molecule of *meso*-tetrapyridyl porphyrin by coordination to the central metals of the peripheral four zinc porphyrins to constitute a light harvesting porphyrin hexameric assembly.

A number of porphyrin molecules participate in electron and energy transfer events in natural photosynthesis.[1] The chromophore orientation is a key factor for their functions, and thus a variety of covalently and noncovalently assembled multi-porphyrins[2,3] have been studied for understanding the biological photosynthetic systems, as well as for devising artificial molecular systems that can achieve effective charge separation. A popular trend is to use the host–guest molecular recognition strategy with the aim to mimic the way employed in the natural systems, but guest molecules have so far been limited to small molecules[4,5] except for a few examples.[6] Here, we report the synthesis of porphyrin pentamers that bind a porphyrin monomer through cooperative ligation of four pyridinyl-substituents to the zinc porphyrin side wall.

Formyl-substituted Cu^{II}-porphyrin **1(Cu)** was prepared by the acid-catalyzed condensation of 3,5-di-*tert*-butylbenzaldehyde, 3-(5,5-dimethyl-1,3-dioxan-2-yl)benzaldehyde and bis(3-ethyl-4-methyl-2-pyrrolyl)methane[7] and subsequent Cu^{II}-ion insertion. Porphyrin pentamer **2(Cu_4-H_2)** (*m*/*z* 3517; calcd for $C_{228}H_{246}Cu_4N_{20}$, 3521) was then prepared in 39% yield from **1(Cu)** and pyrrole by Lindsey's method (Scheme 1).[8] In this reaction, the use of **1(Cu)** as a substrate was crucial, since the reactions of **1(H_2)** and **1(Zn)** afforded the corresponding pentamers only in trace amounts under similar conditions, probably due to very strong electron-attracting properties of the respective porphyrins. These effects can be somehow mitigated by the employment of Cu(II)- and Ni(II)-porphyrins.[9] The pentamer **2(Cu_4-H_2)** was quan-



Scheme 1.

* Corresponding author. Fax: +81 75 753 3970; e-mail: osuka@kuchem.kyoto-u.ac.jp

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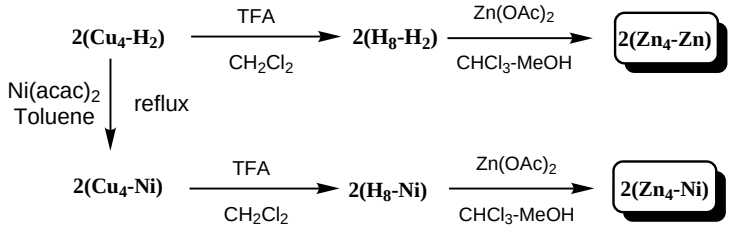
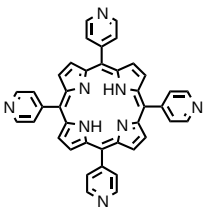


Scheme 2.

titatively converted to **2(Zn$_4$-Zn)** (*m*/*z* 3589; calcd for $C_{228}H_{244}N_{20}Zn_5$, 3591) and **2(Zn$_4$-Ni)** (*m*/*z* 3585; calcd for $C_{228}H_{244}N_{20}NiZn_4$, 3585),[10] as shown in Scheme 2.



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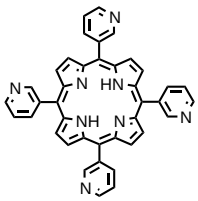

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The pentamer **2(Zn$_4$-Zn)** exhibits a split Soret band at 412 and 435 nm owing to exciton coupling between the chromophores bridged by 1,3-phenylene spacer (Fig. 1). Upon addition of 1 equiv. of 5,10,15,20-tetrakis(*p*-pyridyl)porphyrin (**3**) to a solution of **2(Zn$_4$-Zn)** (1.0×10^{-6} M), clear spectral changes of red shift of λ_{max} from 412 to 420 nm and concurrent increase of the absorbance were observed for the Soret band. These spectral changes are indicative of coordination of the pyridyl groups to the peripheral four Zn(II)-porphyrin sites in **2(Zn$_4$-Zn)**,[11] and thus supramolecular assembly of **2(Zn$_4$-Zn)** and **3**. Similar absorption spectral change was observed for a 1:1 mixture of **3** and **2(Zn$_4$-Ni)** but not for a 1:1 mixture of **3** and **2(H$_8$-Ni)**, whose absorption spectrum was a simple sum of the two solutes. These results also support the cooperative coordination of the four pyridyl groups of **3** with the peripheral four zinc porphyrins in the pentamers **2(Zn$_4$-Zn)** and **2(Zn$_4$-Ni)**. Essentially, similar spectral change was observed for a mixture of 5,10,15,20-tetrakis(*m*-pyridyl)porphyrin (**4**) and **2(Zn$_4$-Zn)** and a mixture of **4** and **2(Zn$_4$-Ni)**. The detailed examination of the absorption spectral changes of **2(Zn$_4$-Zn)** and **2(Zn$_4$-Ni)** against the concentrations of **3** or **4** using a non-linear least-squares method gave the following association constants (*K*); $(5.4\pm1.9)\times10^7$ M^{-1} for **2(Zn$_4$-Zn)** and **3**; $(2.7\pm0.9)\times10^7$ M^{-1} for **2(Zn$_4$-Ni)** and **3**; $(6.7\pm3.5)\times10^7$ M^{-1} for **2(Zn$_4$-Zn)** and **4**; $(1.9\pm0.1)\times10^7$ M^{-1} for **2(Zn$_4$-Ni)** and **4**. These values are greater than those determined for ZnTPP and pyridine derivatives (10^4–10^5 M^{-1}).[12]

The supramolecular assembling of **2(Zn$_4$-Zn)** with **3** or **4** was also confirmed by fluorescence spectroscopy. The fluorescence spectral changes of **2(Zn$_4$-Zn)** exhibited typical zinc porphyrin emission at 598 and 646 nm (Fig. 2). Addition of **3** up to 1.0×10^{-6} M induced a progressive decrease in the fluorescence intensity, and further addition led to an increase of the fluorescence intensity of **3** at 647 and 713 nm. These observations indicate that the fluorescence of **2(Zn$_4$-Zn)** was effectively quenched by **3**, most probably through the intracomplex energy transfer. Therefore, the light harvesting, namely the energy transfer from the peripheral Zn(II)-porphyrin to the free base porphyrin guest is taking place in the complex of **2(Zn$_4$-Zn)** and **3**. The fluorescence intensity of **2(Zn$_4$-Zn)** was steadily decreased up to the addition of 1 equiv. amount of **3** but displayed saturation behavior for the addition of more amounts of **3** (Fig. 3), suggesting 1:1 stoichiometry for the complex.[13] The fluorescence of **3**

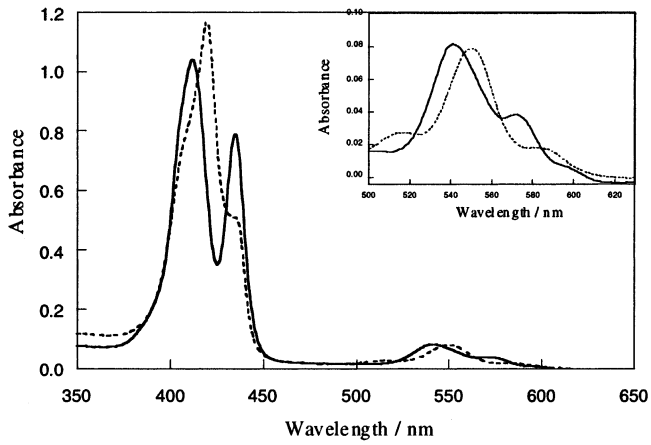

Figure 1. Absorption spectra of **2(Zn$_4$-Zn)** without (solid line) and with 1 equiv. of **3** (dashed line) in $CHCl_3$ at room temperature; $[\mathbf{2(Zn_4\text{-}Zn)}]=[\mathbf{3}]=1.0\times10^{-6}$ M.

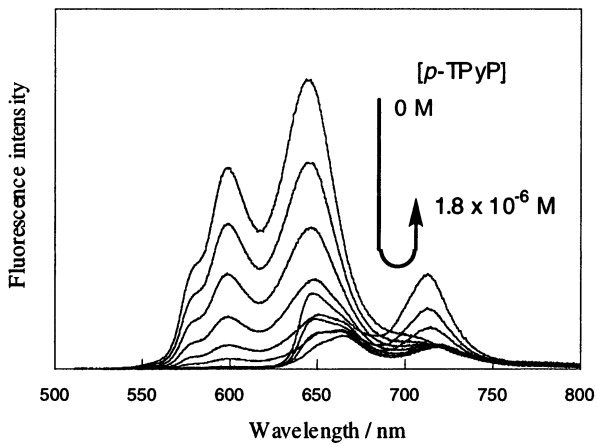

Figure 2. Fluorescence spectra of **2(Zn$_4$-Zn)** upon addition of **3** in toluene at room temperature; $[\mathbf{2(Zn_4\text{-}Zn)}]=1.0\times10^{-6}$ M, λ_{ex} 418 nm.

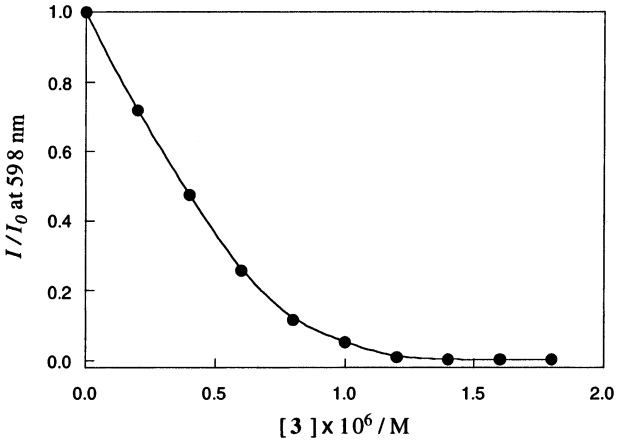

Figure 3. Plots of [**3**] versus I/I_0 for **2(Zn$_4$-Zn)** at 598 nm in toluene at room temperature; [**2(Zn$_4$-Zn)**] = 1.0×10^{-6} M, λ_{ex} 418 nm.

and **4** bound in the complex was also quenched by **2(Zn$_4$-Zn)**. The related Stern–Volmer plots indicated the fluorescence quenching arises not from diffusional dynamic quenching but static quenching within the complex. Since the singlet excitation energy levels of **3** and **4** are lower in comparison to those of **2(Zn$_4$-Zn)**, the fluorescence quenching of **3** and **4** by the host may be ascribed to charge transfer or electron transfer but the definitive conclusion on the photoexcited dynamics of these supramolecular complex must wait the detailed examinations by using time-resolved spectroscopy.

In summary, the porphyrin pentamer host **2(Zn$_4$-Zn)** binds the free base porphyrin monomers **3** and **4** effectively, in which the effective energy transfer from the Zn(II)-porphyrins to the **3** or **4** is taking place and is plausibly accompanied by the electron transfer between the excited guest and the surrounding host, as such in nature.

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10. **2(Zn$_4$-Zn)**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.33–10.09 (m, 8H), 9.66–9.63 (m, 8H), 9.50–7.75 (m, 28H), 4.28–3.98 (m, 32H), 3.28–3.18 and 2.50–2.35 (m, 48H), 2.02–1.68 (m, 48H), 1.57–1.44 (m, 72H); **2(Zn$_4$-Ni)**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.81 (bs, 8H), 9.39 (s, 8H), 8.47–7.80 (m, 28H), 4.07–3.99 (m, 32H), 3.04 and 2.41 (bs, 48H), 1.90–1.70 (m, 48H), 1.52–1.47 (m, 72H).

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13. In the presence of **2(Zn$_4$-Ni)**, the ^{1}H NMR spectrum of **3** (1.0×10^{-3} M each) indicated upfield shift for the inner NH protons of **3** from −2.9 to −5.3 ppm. The upfield shift was apparently due to the ring current effect of the porphyrin ring in **2(Zn$_4$-Ni)**, suggesting that **3** is located just over the central porphyrin of **2(Zn$_4$-Ni)**.