

A Novel Self-Assembled Porphyrin Polymer Constructed by a Pd(II)–Pyridine Interaction

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A novel self-assembled polymer, which has a fibrous structure with enough long and many large inside cavities, was constructed by a pyridine–Pd(II) interaction from one mole of pyridine-containing porphyrin derivative and four moles of Pd(II) complex.

A great deal of effort has been devoted toward multiporphyrin arrays useful for molecular wires,¹ molecular switches,² photosynthetic systems,³ photosensitizers for DNA cleavage,⁴ and photocurrent generation.⁵ Among them, porphyrin polymers have particular attention because of their large future potentials.^{6,7} The molecular design of such covalently-linked porphyrin polymers, however, frequently meets very serious synthetic difficulty. Here, it occurred to us that the utilization of coordination bonds to this class of molecular design would be an escaped idea, because Fujita et al.⁸ and Stang et al.⁹ have shown that the coordination bonds are very useful for the construction of novel self-assembled supramolecular architectures.¹⁰ Taking advantage of this kind of concept, a few self-assembled multiporphyrin arrays were recently constructed in organic solvents.¹¹ However, most precedents are related to two-dimensional macrocycles, whereas the construction of one-dimensional porphyrin polymers has been very limited so far.^{12,13} We previously found that porphyrin **1** bearing four pyridyl groups dimerizes with four *cis*-Pd(II) complexes **2** into a molecular capsule **4** according to a self-assembled manner.¹⁴ Moreover, the spectroscopic studies have shown that the molecular capsule thus formed can specifically include a large bipyridine guest **3**. This finding offers a new idea that if eight pyridyl groups are introduced into the upper and lower sides of each porphyrin, a porphyrin polymer **7** supported by a Pd(II)–pyridine interaction will grow up as a linear fibre structure.

Compound **5** was obtained in 22% yield by the reaction of 4-*n*-octyloxy-3,5-bis(pyridin-4-ylethynyl)benzaldehyde with pyrrole in propionic acid. Compound **5** was converted to **6** in 99% yield by the treatment with Zn(OAc)₂. These compounds were identified by IR, ¹H NMR, and MALDI-TOF mass {[M+H]⁺ = 1936.5 (calcd for C₁₃₂H₁₁₉N₁₂O₄, 1935.9) and 1998.3 (calcd for C₁₃₂H₁₁₇N₁₂O₄Zn, 1997.9) for **5** and **6**, respectively} spectral evidence and elemental analyses.

Firstly, we determined the stoichiometry of the complex formed from **6** and **2**. The UV–vis absorption spectra of **6** were measured in CHCl₃ at 25 °C as a function of **2** concentration (Figure 1). The Soret band (438 nm for **6**) shifted to longer wavelength without any isosbestic point. This result suggests that in the absence of **2**, the pyridyl moiety intermolecularly coordinates to Zn(II) as an axial ligand. As shown in an insert of Figure 1, a plot of Δ*A*₄₃₈ vs [2]/[6] has an inflection point at [2]/[6] = 4.0.¹⁵ This value supports the view that the complex is formed with a 1:4 **6**/2 stoichiometry. Since Δ*A*₄₃₈ was nearly constant over [2]/[6] = 4.0, one can regard that the pyridyl moieties of **6** scarcely interact with Zn(II) in a [2]/[6] = 4.0 complex. On the other hands,

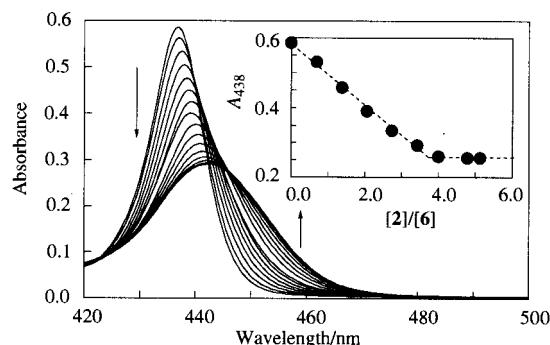
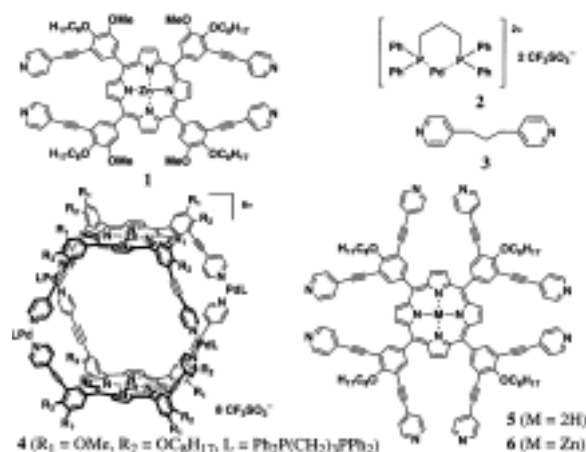


Figure 1. Absorption spectral change of **6** (1.26×10^{-6} mol dm⁻³) in CHCl₃ at 20 °C: [2] = 0–6.50 × 10⁻⁶ mol dm⁻³. Insert: Plots of Δ*A*₄₃₈ vs [2]/[6].

¹H NMR spectroscopy did not give any useful information because the solution containing polymer **7** in CDCl₃ showed a very complicated and very broadened spectrum.

Secondly, we determined whether polymer **7** holds a large cavity enough to bind guest molecules or not. Figure 2 shows the influence of added **3** on the absorption spectral change in polymer **7** (25 °C, CHCl₃). It is seen from Figure 2 that the λ_{max} for the Soret band (441 nm) slightly shifts to shorter wavelength (440 nm) with a tight isosbestic point (445 nm in the Soret band region). The result supports the view that two pyridine units in **3** bridge two porphyrin planes coordinating to Zn(II). From a plot of Δ*A*₄₄₀ vs [3] (inserted in Figure 2), one can obtain *K*_{ass} = 5.6 × 10⁶ dm³ mol⁻¹ for the binding of **3** to the cavities in polymer **7** (the cavity concentration was defined as [6]/2 because Zn(II) can accept only one axial ligand). Since the *K*_{ass} value is comparable to that for the formation of the 1:1 complex from **3** and molecular capsule **4** (*K*_{ass} = 2.6 × 10⁶ dm³ mol⁻¹),¹⁴ one can regard that polymer **7** holds large guest-binding cavities as shown in Scheme 1.

Thirdly, to obtain evidence for the formation of a self-assembled polymeric structure,¹⁶ we measured the molecular-weight of polymer **7** in solution by a dynamic light-scattering method (DLS:

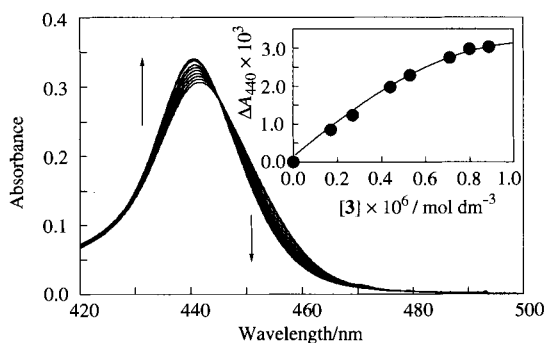
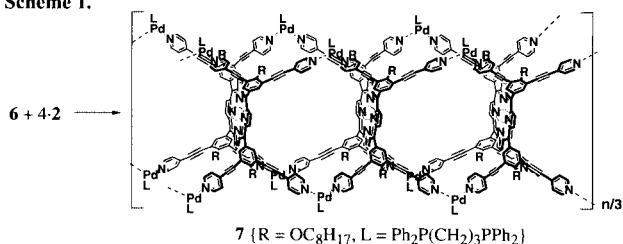


Figure 2. Absorption spectral change of **6** ($1.26 \times 10^{-6} \text{ mol dm}^{-3}$) and **2** ($5.04 \times 10^{-6} \text{ mol dm}^{-3}$) in CHCl_3 at 20°C : $[\mathbf{3}] = 0\text{--}8.9 \times 10^{-7} \text{ mol dm}^{-3}$. Insert: Plots of ΔA_{440} vs $[\mathbf{3}]$.

Scheme 1.



Otsuka Electronics DLS-7000). In CHCl_3 , an average particle size was estimated to be ca. 30 nm. The result indicates that the self-assembled polymer is formed in solution. On the other hand, the formation of such polymeric aggregate was not observed for the **6** + **2** system in polar solvents [e.g., $\text{CHCl}_3:\text{CH}_3\text{OH} = 7:3$ (v/v)], indicating that the stability of this polymeric structure related to the Pd(II)–pyridine interaction is profoundly affected by the solvent.

Finally, to obtain visual insights into the aggregation mode, we prepared dry samples for transmission electron microscopy (TEM) observation. Following a standard treatment procedure, we placed one drop of a **6** ($1.0 \times 10^{-4} \text{ mol dm}^{-3}$) + **2** ($4.0 \times 10^{-4} \text{ mol dm}^{-3}$) mixture in CHCl_3 on a carbon-coated TEM grid on a filter paper. The drop immediately penetrated into the filter paper, and the grids were allowed to dry in air. In the TEM picture thus obtained (Figure 3), the well-grown fibrous structures with diameters of ca. 10 nm were abundantly observed. The fibres were very long, suggesting that the polymer with porphyrin compartments is stably formed.

In conclusion, the present paper demonstrated that porphyrin derivative **6** can form the one-dimensional polymeric structure with *cis*-Pd(II) complex **2**. Owing to rigid acetylene spacers between *meso*-phenyl moieties and pyridyl moieties in **6**, resultant

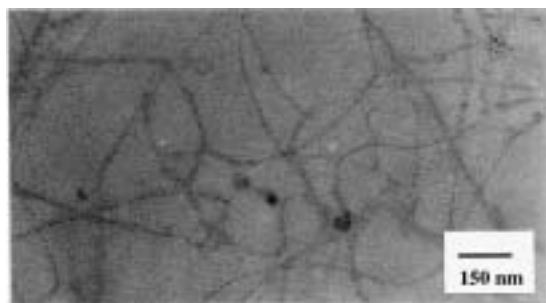


Figure 3. TEM image of polymer **7**.

polymer **7** can hold unusually large cavities enough to bind large bipyridine guest **3**. Since this novel polymer is expected to include various guest molecules, further applications of this system to nanowires, redox reactions, photochemical reactions, etc. are currently under investigation in these laboratories. The most intriguing idea related to this porphyrin polymer would be if the electroconductivity is changed by the guest binding. If it really occurs, it follows that this porphyrin polymer can show a novel switch function controlled by host–guest chemistry.

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- This result suggests that a **2/6** 4:1 complex is formed even in their low concentrations ($[\mathbf{2}] = 5.04 \times 10^{-6} \text{ mol dm}^{-3}$, $[\mathbf{6}] = 1.26 \times 10^{-6} \text{ mol dm}^{-3}$) and then grows up as a polymer.
- To estimate the MW of **7** in solution, vapor pressure osmometry (VPO: Knauer and Co.) of **7** was measured in CHCl_3 ; the MW value was 20000–100000, suggesting that the polymer with polphyrin compartments is stably formed in CHCl_3 . The broad range of the MW is due to the low solubility and the equilibrium in **7** ($[\mathbf{7}] = 0.031\text{--}0.124 \text{ g/kg}$).