



Coordination-induced branched self-assembly of porphyrins bearing two redox-active phenylenediamine chains

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ABSTRACT

The porphyrins bearing two three-dimensionally regulated oligoaniline chains with terminal pyridyl groups were synthesized. The self-assembled branched polymer complex by introducing Zn(II) to the porphyrin was achieved in solution, which underwent dropcasting on the surface of mica to result in dome-like nanostructures.

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Controlled assembly of π -conjugated molecules can provide an organized redox-active nano-space.¹ Especially, construction of such structures on a surface as well as in solution is promising to make a nanotechnology press forward.² Transition metal-directed assembly is regarded as a useful approach to architecturally controlled formation of various complexes.³ We have focused on the design, synthesis, and catalytic and materials application of dimensionally controlled π -conjugated systems.⁴ In previous Letters, aniline oligomers as redox-active π -conjugated ones were arranged on the porphyrins scaffold,⁵ in which intramolecular photoinduced electron transfer is performed from the phenylenediamine moiety to the porphyrin scaffold. We also demonstrated the sandwich-type assembly of the zinc complexes of such molecules by coordination of bidentate ligands.⁶ Furthermore, Zn(II)-directed intermolecular one-dimensional self-assembly was achieved by introduction of a pyridyl group at the end of an oligoaniline chain.⁷ The assembly on the Au nanoparticles surface was also carried out.⁷ In this context, we designed the porphyrin bearing two oligoaniline chains, which have the pyridyl groups at the chain terminal. Such molecule is considered to lead to a branched self-assembly to form a kind of a dendric supramolecular structure as shown in Figure 1. There are a lot of examples of the self-assembly using axial coordination to the Zn–porphyrins. On the other hand, such branched assembly using coordination to Zn–porphyrins with two coordination moieties as a AB₂ monomer has not been reported, to the best of our knowledge. Herein, we report the synthesis of the porphyrins **1** and **2** bearing two three-dimensionally

regulated oligoaniline chains with terminal pyridyl groups (Scheme 1) and their Zn(II)-induced assembly in solution, which underwent dropcasting on the surface of mica to result in dome-like nanostructures.

Scheme 1 shows the synthesis of **1**, **2**, and their Zn(II) complexes **Zn-1** and **Zn-2**. *cis*-Diester **3**, where the *cis*-configuration was determined by the X-ray crystallographic analysis after the complexation with Zn(II) (Fig. S1),⁸ was hydrolyzed to result in the carboxylic acid, followed by the amidation with *N*¹,*N*^{1'}-(1,4-phenylene)dibenzene-1,4-diamine⁹ using EDCI in the presence of HOBT

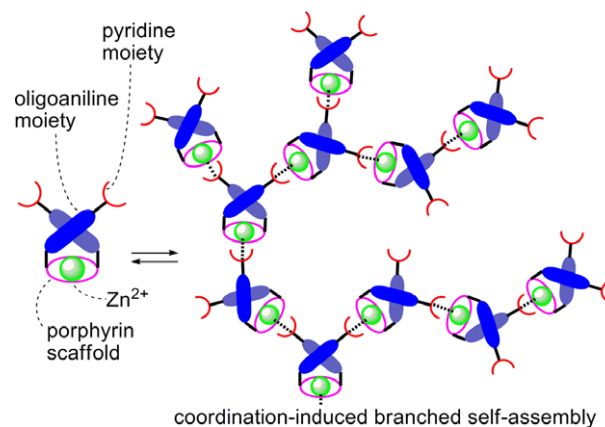
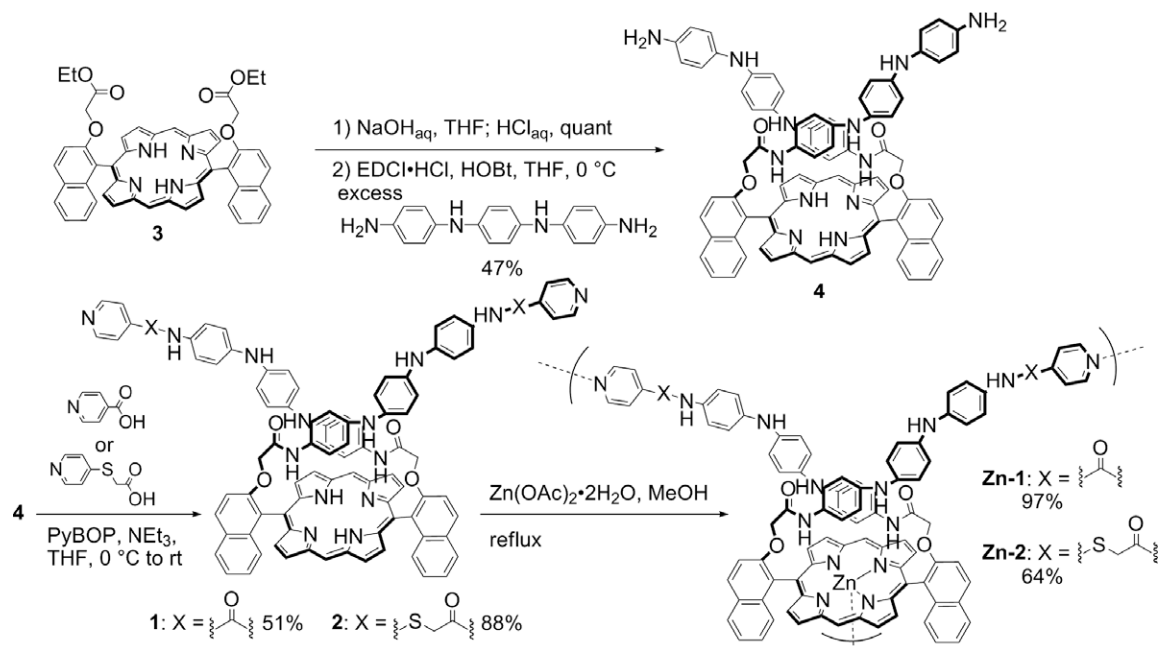


Figure 1. Schematic representation of a branched self-assembly to form a kind of a dendric supramolecular structure of the porphyrins bearing oligoaniline moieties with terminal pyridyl groups.

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Scheme 1. Synthesis of **1**, **2**, and their Zn(II) complexes **Zn-1** and **Zn-2**.

and NEt_3 to give the coupling product **4**. The thus-obtained porphyrin **4** was coupled with isonicotinic acid or 2-(pyridin-4-ylthio)acetic acid to afford the amide **1** or **2** in 51% or 88% yields, respectively. 4-Pyridylthio group has a higher basicity than the pyridyl group of the isonicotinic amide moiety. Therefore, the former is expected to show a greater affinity toward Zn(II)-porphyrins than the latter. Treatment of **1** and **2** with $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ gave the self-assembled product **Zn-1** and **Zn-2** in 97% and 64% yields, respectively. Conformation of **1**, **2**, **Zn-1**, and **Zn-2** in a $\text{DMSO}-d_6$ solution was investigated by ^1H NMR. $\text{DMSO}-d_6$ inhibits the coordination of a pyridyl group to **Zn-1** and **Zn-2**, which are probably present in a monomeric state. **Table 1** shows the selected chemical shifts for the aniline chains. The protons close to the porphyrin ring exhibited the remarkable higher field shift

in all compounds. The $\Delta\delta$, which is the difference of the chemical shift from the model aniline chain **5**, reached 2.1–2.4 and 1.2–1.3 ppm at the protons a and b, respectively (**Table 1**). These shifts are explained by the ring-current effect of the porphyrin π -system. This suggests that the aniline chains lean toward the porphyrin ring.¹⁰ Furthermore, the porphyrins with two *cis*-oligoaniline chains exhibit the higher field shift of the protons at the oligoaniline chains in ^1H NMR, as compared with **6** or **Zn-6**⁷ with a single chain (**Table 1**). It suggests that the conformation of the porphyrins with two *cis*-chains might be stabilized by the intramolecular hydrogen bonds and/or π - π stacking between two *cis*-oligoaniline chains.¹¹ In the present study, details of the synthesis and characterization are described in **Supplementary data**.

Table 1
Chemical shifts of **1**, **2**, **6**, **Zn-1**, **Zn-2**, **Zn-6**, and **5** ($\text{DMSO}-d_6$, 600 MHz)

	$\text{R}^1\text{-O-CO-NH}^1$	H^1	a	b	H^2	c	d	H^3	H^3	H^3
	$\text{-OCH}_2\text{CO-}$	$\text{-NH}^1\text{-}$	a ($\Delta\delta$)	b ($\Delta\delta$)	$\text{-NH}^2\text{-}$	c	d	$\text{-NH}^3\text{-}$		
1	4.49	7.13	5.36 (2.1)	5.72 (1.21)	7.31	6.61	6.92	7.79		
2	4.48	7.12	5.35 (2.11)	5.71 (1.22)	7.31	6.60	6.89	7.73		
6	4.55	7.30	5.55 (1.89)	5.87 (1.06)	7.46	6.67	6.95	7.89		
Zn-1	4.49	6.73	5.07 (2.39)	5.63 (1.3)	7.29	6.61	6.94	7.81		
Zn-2	4.42	6.69	5.03 (2.43)	5.60 (1.33)	7.26	6.58	6.88	7.72		
Zn-6	4.56	6.89	5.36 (2.08)	5.85 (1.08)	7.43	6.65	6.93	7.87		
5	4.77	9.91	7.46	6.93	7.82	7.00	7.00	7.86		

5: $\text{R}^1 = \text{C}_6\text{H}_4$, $\text{R}^2 = \text{C}_6\text{H}_5$

6: M = 2H
Zn-6: M = Zn

To estimate the binding constant of the pyridyl group to the Zn(II)–porphyrin, the titration experiment was conducted using the model oligoaniline compounds **S1** and **S2** with a pyridyl and a thiopyridyl group, respectively (Fig. S4). The CH₂Cl₂ solution of **S1** or **S2** was added to the CH₂Cl₂ solution of **Zn-3**, and the complexation behavior was tracked by UV–vis absorption spectroscopy (Fig. S4). The peaks of the Soret and Q bands red-shifted as the coordination of the pyridyl group progressed. The binding constants *K* for **S1** and **S2** were calculated to be 5.6×10^3 and $7.6 \times 10^3 \text{ M}^{-1}$, respectively. As expected, the latter exhibited the larger value.

First oxidation and reduction potentials were obtained from the differential pulse voltammograms of **1**, **2**, **3**, **5**, and their Zn complexes **Zn-1**, **Zn-2**, and **Zn-3** (Fig. S5). Measurement was carried out in their $2.5 \times 10^{-4} \text{ M}$ THF solution with Bu₄NClO₄ as an electrolyte under argon atmosphere. Table 2 shows the potentials versus Fc/Fc⁺ and the driving force of photoinduced charge separation ΔG_{CS} estimated by the equation: $\Delta G_{\text{CS}} = E(D^+/D) - E(A/A^-) - E_{00}$, where *E*₀₀ is the energy of photoexcitation. First oxidation potentials are approximately –0.16 to –0.14 V for **1**, **2**, **Zn-1**, and **Zn-2** assigned to the one-electron oxidation of the two aniline chains. On the other hand, the first reduction potentials are –1.70 to –1.66 V for free base porphyrins **1**, **2**, and **3**, and –1.97 to –1.90 V for Zn(II) complexes **Zn-1**, **Zn-2**, and **Zn-3**. Negative ΔG_{CS} was observed with **1**, **2**, **Zn-1**, and **Zn-2**.

Electronic environment of **1**, **2**, **4**, and their Zn(II) complexes **Zn-1**, **Zn-2**, and **Zn-4** was investigated by UV–vis absorption spectroscopy. Measurement was carried out in a $5.0 \times 10^{-6} \text{ M}$ solution of CH₂Cl₂/THF = 995/5 under argon atmosphere.¹² Porphyrins bearing the aniline chains showed a broad absorption around 280–350 nm derived from the aniline chain as well as the characteristic Soret and Q bands (Fig. 2a and Fig. S6). In the Zn complexes, the red-shift of Soret and Q bands was observed with **Zn-1** and **Zn-2**, as compared with **Zn-4** which does not have a pyridyl moiety (Fig. 2a). The coordination of the pyridyl group to the Zn–porphyrin is likely to contribute to the red-shift. Thus, the branched self-assembly of the porphyrin **Zn-1** and **Zn-2** bearing two oligoaniline chains was demonstrated in solution.¹³

Fluorescence emission spectroscopy was studied with **1**, **2**, **3**, **4**, and their Zn(II) complexes, **Zn-1**, **Zn-2**, **Zn-3**, **Zn-4**, and **Zn-6** (Fig. 2b and Fig. S7). Measurement was also carried out in a $5.0 \times 10^{-6} \text{ M}$ solution of CH₂Cl₂/THF = 995/5 under argon atmosphere. Significant quenching was observed with **1**, **2**, **4**, **Zn-1**, **Zn-2**, and **Zn-4** bearing two aniline chains, as compared with that of **3** or **Zn-3**. It is likely due to the intramolecular photoinduced electron transfer as supported by the negative ΔG_{CS} (Table 2). This phenomenon was also consistent with our previous reports.⁵ On the other hand, **Zn-6** with a single aniline chain did not show such significant quenching despite the negative ΔG_{CS} (–0.26 V).⁷ Therefore, the thus-observed significant quenching in **Zn-1** and **Zn-2**

Table 2

The redox potential (V vs Fc/Fc⁺) and driving force of the photoinduced charge separation ΔG_{CS} (V) for **1**, **2**, **3**, **Zn-1**, **Zn-2**, **Zn-3**, and **5** ($2.5 \times 10^{-4} \text{ M}$ in THF containing 0.1 M Bu₄NClO₄)

	Redox potential (V vs Fc/Fc ⁺)		ΔG_{CS}^a (V)
	<i>E</i> (Por/Por [–])	<i>E</i> (D ⁺ /D)	
1	–1.68	–0.14	–0.51
2	–1.66	–0.16	–0.47
3	–1.70	+0.61	–
Zn-1	–1.90	–0.14	–0.38
Zn-2	–1.91	–0.16	–0.39
Zn-3	–1.97	+0.35	–
5	–	–0.11	–

^a $E(D^+/D) - E(A/A^-) - E_{00}$, where *E*₀₀ is the energy of photoexcitation.

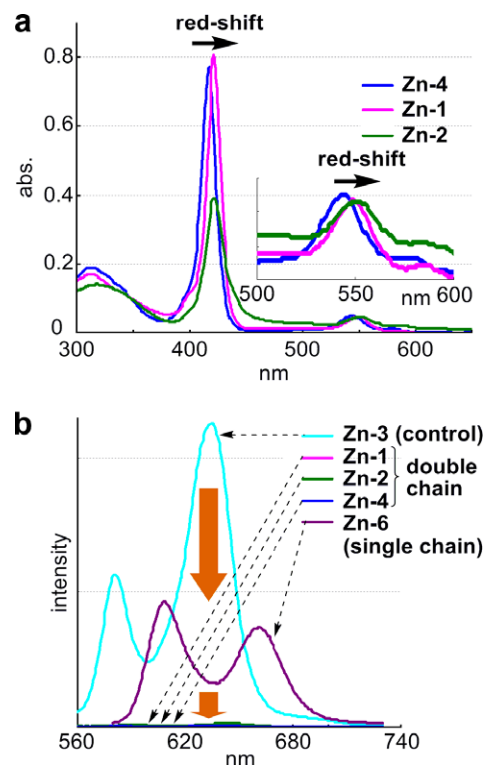


Figure 2. (a) UV–vis absorption spectra of **Zn-1**, **Zn-2**, and **Zn-4**. (b) Emission spectra of **Zn-1**, **Zn-2**, **Zn-3**, **Zn-4**, and **Zn-6** with excitation at 549, 549, 542, 544, and 561 nm, respectively. $5.0 \times 10^{-6} \text{ M}$ solution of CH₂Cl₂/THF = 995/5 under argon atmosphere.

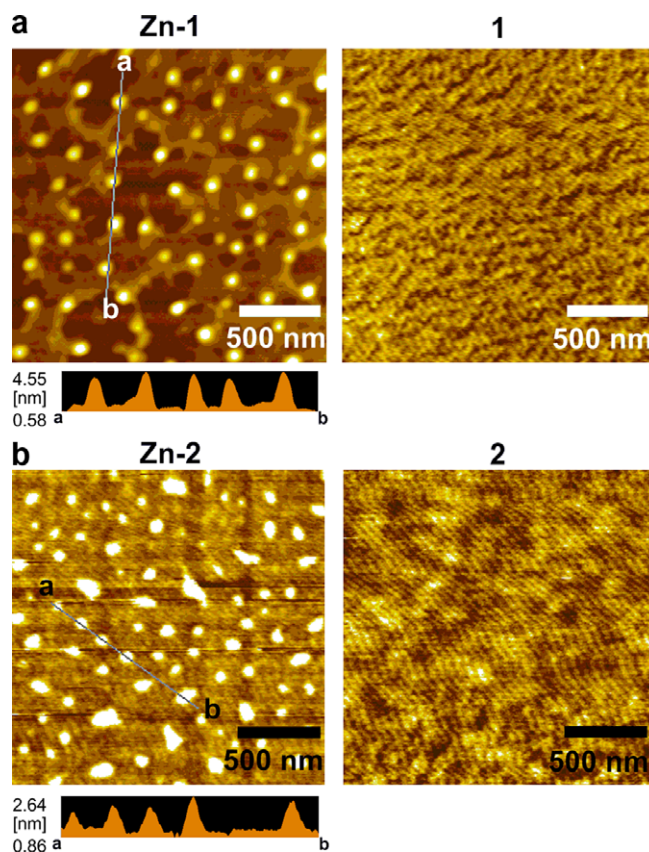


Figure 3. AFM images of (a) **Zn-1** and **1**, (b) **Zn-2** and **2**.

clearly depends on the effect of two oligoaniline chains, which might be accounted for by the close conformation of the aniline chains to the porphyrin scaffold induced by the hydrogen bonds and/or π - π stacking as described above.

The assembly on the surface of mica was investigated with **1**, **2**, **Zn-1**, and **Zn-2** by atomic force microscopy (AFM) (Fig. 3a for **Zn-1** and **1**, Fig. 3b for **Zn-2** and **2**). The dilute solution of THF (1 μ M) was dropcasted on mica. After drying, AFM observation was carried out (observed point is illustrated in Fig. S8). As shown in Figure 3a, the uniformly sized dome-like structures (diameter: 50–70 nm, height: ca. 3 nm, see the sectional view from a to b), which are characteristic with a dendric structure,¹⁴ were observed with **Zn-1**, but not with **1**. Such images with the similar tendency were also observed with **Zn-2** and **2**. Thus, the branched self-assembly of the porphyrin bearing two aniline chains was also clearly demonstrated on the surface of mica.

In summary, the porphyrins **1** and **2** bearing two three-dimensionally regulated oligoaniline chains with terminal pyridyl groups were synthesized. The branched complexation by introducing Zn(II) to the porphyrins was achieved in solution, which underwent dropcasting on the surface of mica to result in dome-like nanostructures. The present method provides a new approach of branched assembly using axial coordination to Zn-porphyrins. This system is of potential use in a variety of applications such as redox-active receptors and photo-active catalysts or materials. Further investigation is now in progress.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.04.088.

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