

Metal Assembly in Novel Dendrimers with Porphyrin Cores

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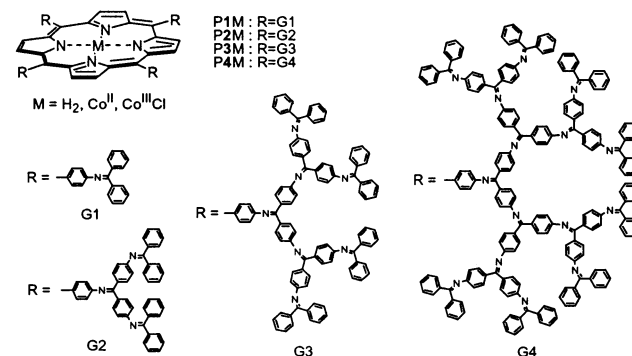
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The highly regulated architecture of dendrimers is valuable for the construction of microenvironment surrounded by a molecular cage.¹ The nanospace around a catalytic center also plays an important role in various biocatalyst systems. Metallo-dendrimers² having coordination sites on the core,^{3–5} structural units,^{6,7} or surface^{8,9} are one of the most remarked-upon subjects, because of their availability as unique ligands which incorporate metal ions in the cage. The large steric effect of dendrimers can induce an encapsulating effect on coordination chemistry,³ electrochemistry,⁴ or catalysis^{5,9} and provides a new ability of the functional core unit. Recently, dendrimers with a porphyrin core, which is an important unit for life reactions, especially deserve much attention and are applicable for mimicking the functions of life, such as energy funneling,⁶ enzyme reactions,^{5a} or dioxygen carrying.^{3a,b} In general, the characteristics of the porphyrin core unit could be emphasized by the regulated metal-ion arrangement; for example, a copper complex arranged on the axial position of the FeP center makes a contribution to the catalytic ability of cytochrome oxidase.¹⁰

Unlike the dendrimer ligand reported previously,⁷ dendritic phenylazomethine (DPA), which has a multicoordination site on the branches, can assemble metal ions with stepwise fashion to each layer.¹¹ Here, we employed the phenylazomethine dendrimer with a porphyrin core to assemble a multimetal ion through complexation on each imine, since the phenylazomethine backbone is suitable for modification with the electrochemical¹² or photophysical functions of metal ions to the dendrimer. A series of dendrimers with a porphyrin core (**PnH₂**) were synthesized by dehydration using TiCl₄ from *meso*-tetrakis(4-aminophenyl)porphyrin and the corresponding DPA dendron.¹³ These compounds were characterized by ¹H and ¹³C NMR spectroscopies, elemental analysis, and matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF MS). The porphyrin core was metalated with CoCl₂ in dehydrated THF. These metal ions do not coordinate to imines of the dendron in the presence of triethylamine, and no evidence of the complexation was found in their UV-vis spectra.

The absorption around 300–350 nm increases with the increment of the generation number due to the increase in the phenylazomethine units. According to the generation number increase, the red-shift of the Soret band from 426 nm (**P1H₂**) to 434 nm (**P4H₂**) in CHCl₃ was observed without increase in the absorption. A similar bathochromic effect has been observed with the Fréchet-type dendrimer, which is caused by an encapsulation effect or by interaction between the core and the branches.¹⁴ The core-shell effect of the dendrimer was also supported by the electrochemical analysis. The redoxes of **PnCo^{II}** were examined by cyclic voltammetry in DMF under an argon atmosphere. The half-wave potential (*E*_{1/2}) of the Co^I/Co^{II} couple is –1.33 V (**P2Co^{II}**) vs Fc/Fc⁺ and –1.35 V (**P3Co^{II}**) vs Fc/Fc⁺, lower than that of *meso*-tetrakis(phenyl)porphyrin cobalt (CoTPP –1.29 V vs Fc/Fc⁺). The redox wave of the Co^I/Co^{II} couple became broadened according to the generation number due to the shell effect of the dendrimer.^{4d,14a}

Chart 1. Structures of Dendrimers



The clear redox wave of **P4Co^{II}** was not observed because of the low electron-transfer rate constant ($k_0 \approx 10^{-5} \text{ cm s}^{-1}$).

The addition of SnCl₂ to a dichloromethane/acetonitrile solution of dendritic cobalt porphyrin (**PnCo^{II}**) resulted in a stepwise spectral change, similar to that for the previously reported dendrimers.¹¹ However, **PnCo^{II}** was catalytically oxidized by air in the presence of Lewis acids; therefore, **PnCo^{III}Cl** was employed for accurate observation of the spectral changes. During the addition of SnCl₂, the solution color of the **P4Co^{III}Cl** changed from light yellow to a deeper color. We found that the complexation was complete in 10 min by the spectral change after the addition of SnCl₂; that is, the complexation equilibrium is reached within at least several minutes. Using UV-vis spectroscopy to monitor the complexation until an equimolar amount of SnCl₂ had been added, four changes in the position of the isosbestic point were observed, indicating that the complexation proceeds, not randomly, but stepwise. This result suggests that four different complexes are successively formed upon the SnCl₂ addition.

The absorption band around 400 nm attributed to the complex increases with a decrease in the absorption bands around 320 nm and 450 nm, which are attributed to the phenylazomethine unit and porphyrin, respectively. The spectra of **P4Co^{III}Cl** gradually changed, with an isosbestic point at 369 nm up to the addition of 4 equiv of SnCl₂ (Figure 1d). The isosbestic point then shifted upon the further addition of SnCl₂ and appeared at 367 nm between 5 and 12 equiv. While adding between 13 and 28 equiv of SnCl₂, an isosbestic point appeared at 365 nm, moving to 362 nm when adding between 32 and 88 equiv. Overall, the number of added equivalents of SnCl₂ required to induce a shift was in agreement with the number of imine sites present in the different layers of **P4Co^{III}Cl**. The titration results suggest that the complexation proceeds in a stepwise fashion from the core imines to the terminal imines of **P4Co^{III}Cl** (Scheme 1).

A similar stepwise complexation was also observed with **P3Co^{III}Cl** (Figure 1c). For **P2Co^{III}Cl**, two isosbestic points appeared at 349 and 353 nm, when 0–8 and 8 equiv of SnCl₂ were added, respectively, which is a different pattern from the other generation. We calculated the concentration profiles of the multiequilibria for

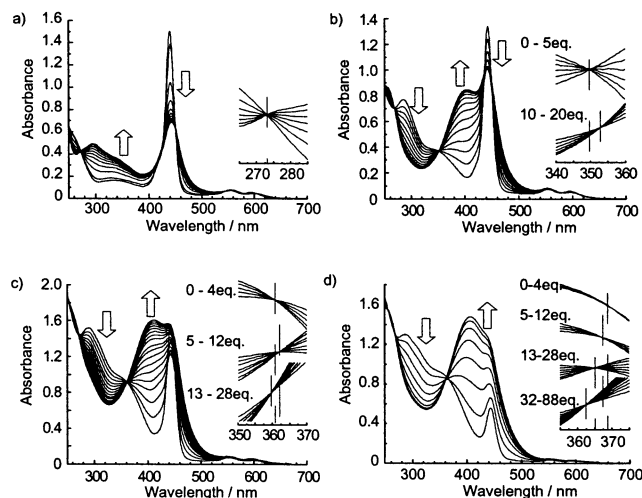
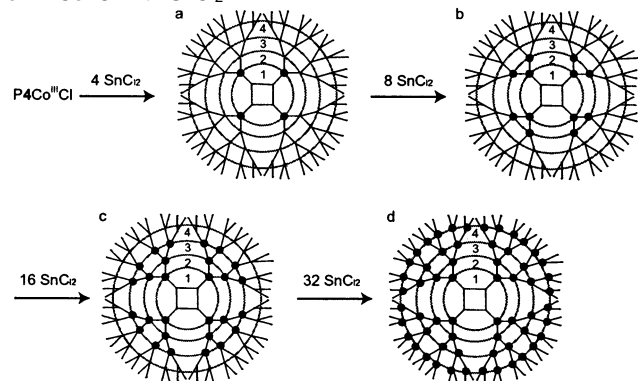


Figure 1. UV-vis spectra changes of (a) $5 \mu\text{mol L}^{-1}$ $\text{P1Co}^{\text{III}}\text{Cl}$, (b) $5 \mu\text{mol L}^{-1}$ $\text{P2Co}^{\text{III}}\text{Cl}$, (c) $5 \mu\text{mol L}^{-1}$ $\text{P3Co}^{\text{III}}\text{Cl}$, (d) $2.5 \mu\text{mol L}^{-1}$ $\text{P4Co}^{\text{III}}\text{Cl}$ on stepwise addition of equimolar SnCl_2 in $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2 = 1/1$. (Insert) Enlargements focusing isosbestic points.

Scheme 1. Schematic Representation of Stepwise Complexation of $\text{P4Co}^{\text{III}}\text{Cl}$ with SnCl_2^a



^a This complexation thermodynamically proceeds in a stepwise fashion from the core imines to the terminal ones of based $\text{P4Co}^{\text{III}}\text{Cl}$ on the electron gradients.

the determination of the coordination constant of two kinds of imines. The simulations of the titration curve and isosbestic points supported the idea that metal ions are incorporated, filling first the peripheral layers (eight imines) and then progressively the inner layers (four imines, see Scheme S2 in Supporting Information). The coordination constants of SnCl_2 to the inner and outer imines were estimated to be $K_1 = (1 \pm 3) \times 10^5 [\text{mol}^{-1} \text{L}]$, $K_2 = (1 \pm 1) \times 10^6 [\text{mol}^{-1} \text{L}]$, respectively. The difference may be attributed to electron withdrawing by the cobalt(III) porphyrin core, and it results in a decrease in the electron density on imines at the inner sphere, which is similar to that of the previously reported DPA dendrimers with 4F-substituted benzene as a core.⁷ Comparing $K_1 (= 1.4 \times 10^4 [\text{mol}^{-1} \text{L}])$ of $\text{P1Co}^{\text{III}}\text{Cl}$ with that of $\text{P2Co}^{\text{III}}\text{Cl}$ suggests that the coordination constant of inner imines increases with the generation number increase due to the electron-donating effect of the dendron. Thus, coordination from the core in $\text{P3Co}^{\text{III}}\text{Cl}$ and $\text{P4Co}^{\text{III}}\text{Cl}$ can take place.

Absorptions of the Co^{III} -porphyrin Soret band (440 nm) are breaching except for $\text{P4Co}^{\text{III}}\text{Cl}$. The breaching was not observed when SnCl_2 was added to the solution of $\text{Co}^{\text{III}}(\text{TPP})(\text{Cl})$. Thus, it suggests that coordinating SnCl_2 affects the environment of the porphyrin core or axial position where the solvents and Cl^- coordinate.

In conclusion, the controlled assembly of metal ions with Lewis acidity¹⁵ could be demonstrated for phenylazomethine dendrimers having a metalloporphyrin core, although the stepwise radial complexation is sensitive to the electron density of the core. The effects of metal ions were also observed in the UV-vis spectra and Zn-porphyrin fluorescence quenching by metal ions. An application study about acceleration of the catalytic reaction at the core is now in progress.¹⁶

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Supporting Information Available: Synthetic procedures, calculation of absorbance and isosbestic points, additional data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (15) Various metal ions including SnCl_2 , AuCl_3 , $\text{La}(\text{OTf})_3$ (La: lanthanide), and HOTf can coordinate to the dendrimer.
- (16) We have already found that CO_2 can be reduced at extremely high electrode potential using the dendrimer with Co-porphyrin core (see Supporting Information).

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