

Metal Ion Assembly in Phenylazomethine Dendrimers and Their Effect to the Porphyrin Core.

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Electronic potential-gradated multi-layers with plural coordination sites in the dendritic phenylazomethine (DPA) were revealed in our previous work.[1,2] In that case, metal ion coordinates from the layer closer to the core unit because basicity of the inner ligand is stronger than that of outside. The special property could be applied to precise tuning of electronic status on the core through environment and through bond interaction with assembling metals. Here, we report iron coordination effect to zinc porphyrin core by monitoring the redox potential using cyclic voltammetry.

DPA with a zinc porphyrin core were prepared by repetition of the dehydration reaction between carbonyl and amine group as previously. The G4 dendrimer was confirmed to be sphere like molecule with 5 nm diameter. The core unit is located at center of the molecule (Fig.1).

First, we confirmed the coordination behavior of FeCl_3 to the dendrimer. Fig.2 shows spectra change on the continuous addition of an equimolar FeCl_3 to the solution of G4 dendrimer. Taking notice of the isosbestic point, four different complexation events were successively appeared. The result indicates stepwise complexation by different layers as can be seen in Fig.3. Similar behavior was observed for the G2 and G3 dendrimer.

The zinc porphyrin core shows two quasi-reversible redox waves on a cyclic voltammogram. Each of them is characterized to the oxidation to monocation radical (ZnP^+) and dication (ZnP^{2+}), respectively. For the G1 dendrimer, the redox potential of ZnP/ZnP^+ redox couple shifted by +0.21 V after full complexation of FeCl_3 (Fig.4). The positive shift is attributed to coordination of FeCl_3 to four imine units involving electron withdrawing through covalent bond. The effect was compared with substituent effect on the *para*-position of *meso*-phenyl groups using the Hammett constant. The analysis was applicable to the redox behavior of G1 dendrimer, and represented that electronic effect to the core would change from weak electron donating ($\delta = -0.20$) to strong electron withdrawing ($\delta = 0.62$).

For the G2 dendrimer, the similar behavior was observed. The potential shift was saturated over 4 equivalents of FeCl_3 added, indicating stepwise complexation from inner 4 imines. This also shows small interaction between the core and peripheral imines. However, the potential shift behavior of larger dendrimer was unexpectedly different from that of G1 and G2. It is considered that large structural change of dendrimer should occurred by complexation of peripheral layers.

References

1. Yamamoto, K.; Higuchi, M.; Shiki, S.; Tsuruta, M.; Chiba, H. *Nature* **2002**, *415*, 509.
2. Imaoka, T.; Horiguchi, H.; Yamamoto, K. *J. Am. Chem. Soc.* **2003**, *125*, 340.

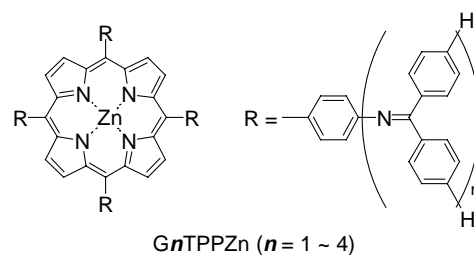


Fig.1. Chemical structure of DPA having porphyrin core.

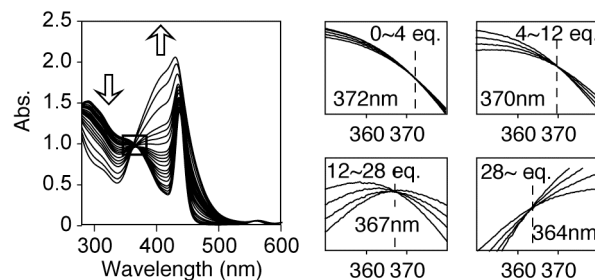


Fig. 2. UV-vis spectral changes (left) and enlargements of isosbestic points (right) on the addition of equimolar FeCl_3 to the solution of G4 dendrimer (2.5 mM) in $\text{C}_6\text{H}_6/\text{CH}_3\text{CN}$ (1/1).

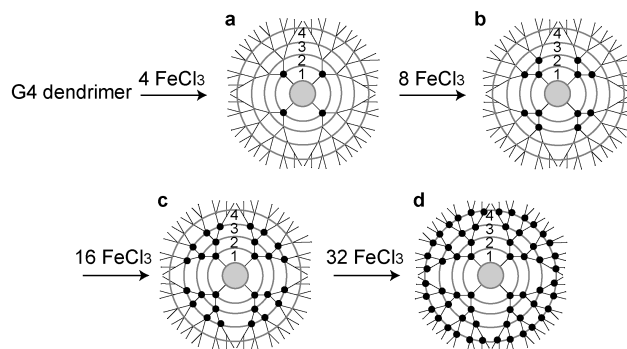


Fig. 3. Schematic representation of stepwise complexation in G4 dendrimer.

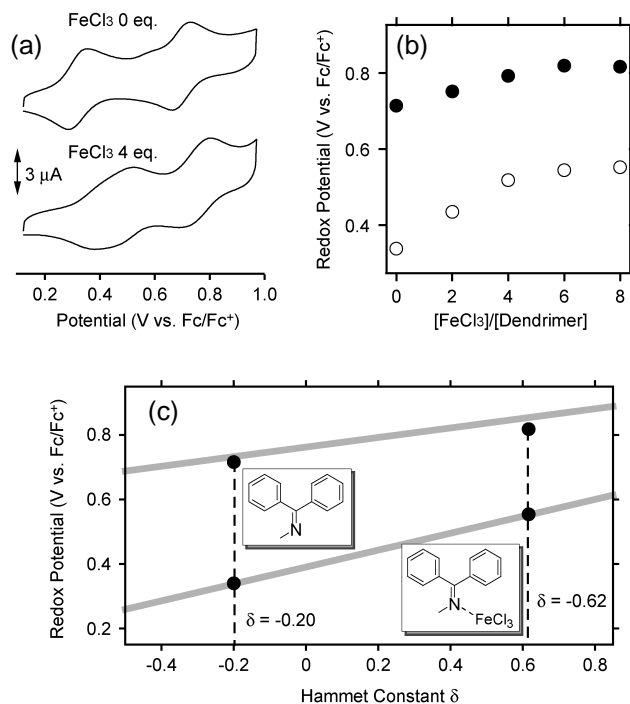


Fig. 4. (a) Cyclic voltammograms of G1 dendrimer in $\text{CHCl}_3/\text{CH}_3\text{CN}$ (4/1), (b) Variation of the redox potential on the addition, (c) Application to Hammett rule.