

Fine-Control of Metal Ion Assembly in Novel Topological Poly(phenylazomethine)s

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Abstract. Dendritic and cyclic polyphenylazomethines (DPAs and CPAs, respectively) were synthesized as novel π -conjugated polymer ligands with a single molecular weight and a clearly-defined structure, and we first realized the precise metal-assembling in DPAs based on the unique stepwise complexation behavior.

Key words: dendrimer, phenylazomethine, stepwise complexation, macrocycle

1. INTRODUCTION

Organic-metallic hybrid nano-materials have received much attention for use in electronic, photonic, or magnetic nano-devices, or catalysts, because chemical or electrochemical interactions amplified by fine-controlled-blending of organic materials and metal ions/clusters are expected to enhance their properties and cause novel functions. π -Conjugated polymers, which have excellent redox properties and unique chromic functions, are especially attractive organic components in the hybrid nano-materials. For example, polyaniline and polypyrrole, which are representative π -conjugated polymers having coordination sites, show redox-activity by complexation with metal ions such as copper, iron, or palladium, and the polymer complexes work as efficient oxidation catalysts under oxygen atmosphere based on the electrochemical interaction between their π -conjugated polymers and the metal ions. For the development of organic-metallic hybrid nano-materials, it is essential to control the number and position of the metal ions in the polymer complexes, but this is quite difficult when using linear polymers. Because the conventional linear polymers have a "spaghetti-like" flexible structure with various molecular weights, metal ions are randomly complexed with the coordination sites of the polymers. In order to solve this problem, we focused on polymeric ligands having novel topologies such as dendrimers and macrocycles with a single molecular weight and a single structure [1-6]. Their clearly-defined structures should enable both precise metal-assembling inside the polymers and regular polymer-assembling, which is important for constructing nano-devices.

2. RESULTS AND DISCUSSION

2.1 DENDRITIC POLYPHENYLAZOMETHINES [7-13]

DPAs were synthesized by the convergent method via dehydration of aromatic ketones with aromatic amines in the presence of TiCl_4 , and showed a high solubility and high thermal

stability (Td10% 521 °C in DPA G4). DPA derivatives having tris(thienylphenyl)amine, tetraphenylporphyrin, and aniline as the core were also prepared (TPA-DPAs, Por-DPAs, and aniline-capped DPAs, respectively, Figure 1). In addition, we exploited more efficient synthetic method of DPAs, and successfully obtained the fifth generation of DPA (DPA G5). Based on the conformational rigidity of the π -conjugated backbone, DPA G4 molecules was revealed to have a sphere-like structure (diameter: 2.3 nm) and are regularly assembled on a plate without deformation by means of X-ray crystal analysis, a molecular model, GPC, TEM, AFM, and p-A measurements. The stepwise complexation was observed in DPAs as stepwise shifts of the isosbestic point in the UV-vis spectra. DPA G4 has 2, 4, 8, and 16 imine groups in the 1st, 2nd, 3rd and 4th shells, respectively (total, 30 imine groups). DPA G4 can trap 30 equivalents of SnCl_2 molecules, because the imine group is complexed with SnCl_2 at a ratio of 1:1. During addition of 30 equivalents of SnCl_2 to DPA G4, four shifts in the isosbestic point were observed in the UV-vis spectra; the amount of SnCl_2 added in each step is in agreement with the number of the imine groups in each shell of DPA G4.

This result shows that the complexation of the imine groups in DPA G4 with SnCl_2 occurs stepwise in the order of the 1st, 2nd, 3rd, and 4th shells. The stepwise complexation was supported by TEM, NMR, and a novel shell-selective reduction (SSR) method for imines. The stepwise complexation is caused by the different basicity of the imine groups between the shells, which was supported by the chemical shifts of the peaks attributed to the imine carbons in the ^{13}C NMR spectra. In addition, the gradients in the basicity were controlled by the introduction of electron-withdrawing or -releasing groups to the core of the dendrimers; the core imines were complexed

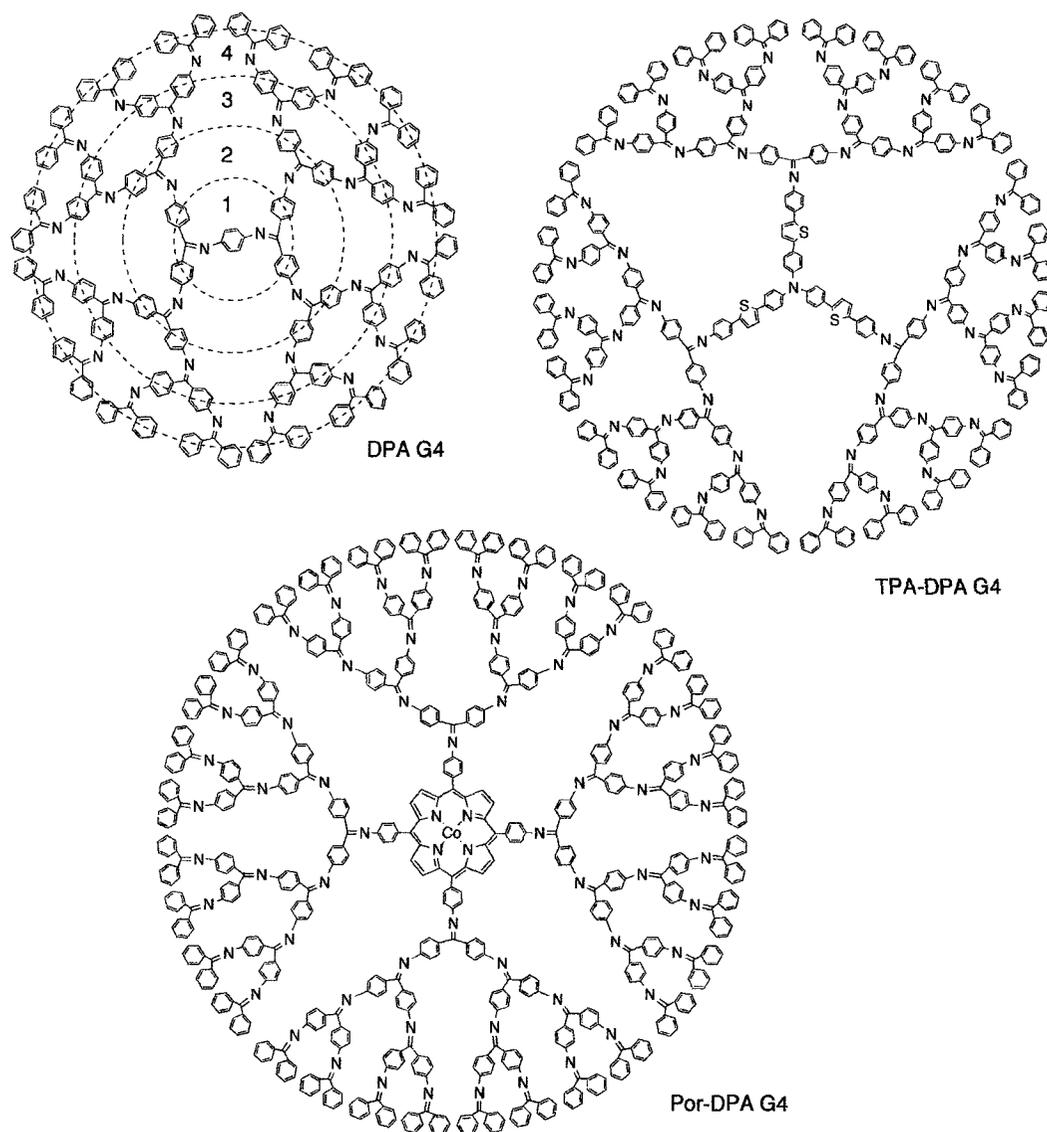


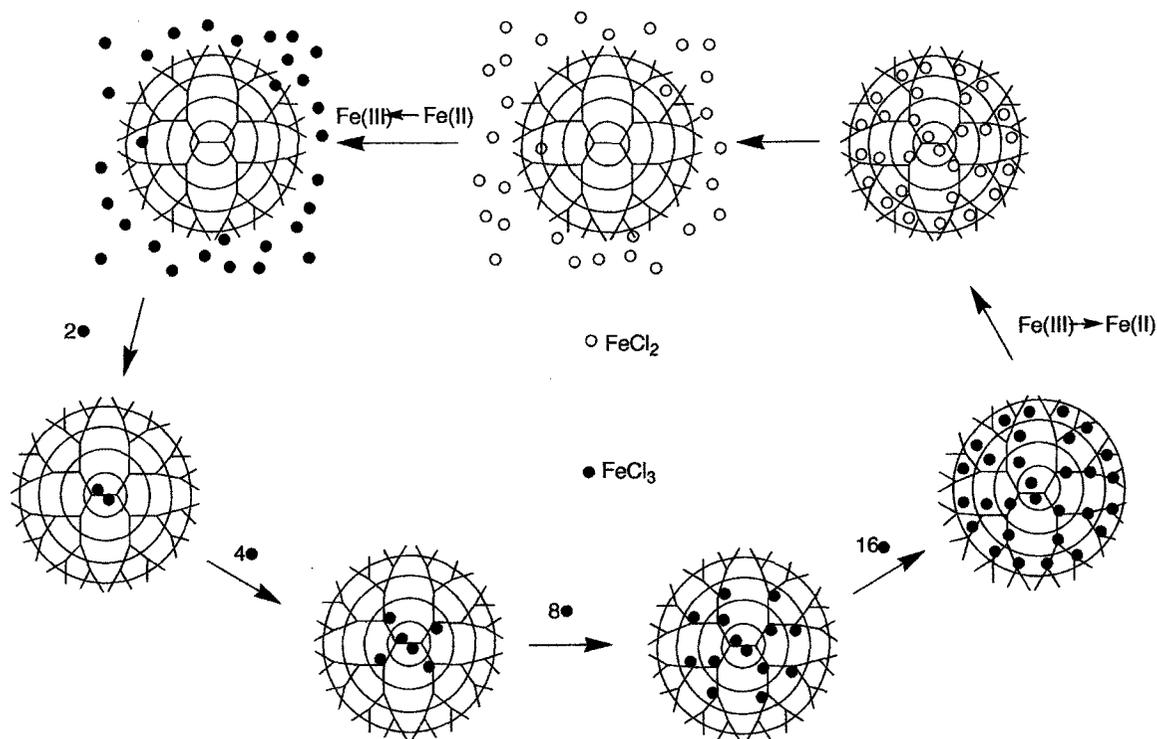
Fig. 1. Dendritic poly(phenylazomethine)s

last in DPAs having a 2,3,5,6-tetrafluoro- or 2,5-dichlorophenyl core due to the low basicity of the core imines. Stepwise radial complexation with Tin(II) chloride in DPAs, TPA-DPAs, Por-DPAs, and aniline-capped DPAs, was also found. Using the shell-selective reduction method and the terminal-modification method of DPAs, the core and terminals were functionalized by a ferrocene unit(s), respectively. Iron(III) chloride molecules were also complexed with the imines of the DPAs in a stepwise fashion. Encapsulation/releasing of iron ions in DPA was electrochemically controlled due to the different complexation ability of iron(II) and iron(III) ions with the imines (Scheme 1).

2.2 CYCLIC POLYPHENYLAZOMETHINES [14-17]

On the other hand, we established the selective synthesis of CPAs, and found redox activation of

CPAs based on the complexation. CPAs were synthesized in a one-step dehydration of 4-aminobenzophenones in the presence of TiCl_4 or *p*-toluenesulfonic acid (PTS), and isolated in over 90% yield under non-dilute conditions. When using TiCl_4 as the dehydration agent, the introduction of bulky substituents at the α -position of the substrate enhanced the yields of the CPAs. PTS served as an effective catalyst for the synthesis of the phenyl-substituted CPA. This different reactivity between TiCl_4 and PTS depends on the dehydration mechanism being dominated by a kinetic process or a thermodynamic one. The structures of the obtained CPAs were confirmed by the NMR, UV-vis spectra, and the result of a MM2 calculation to have only a Z conformation and a non-conjugated structure compared to the linear oligophenylazomethines (OPAs). Controlled cyclization was applied for dendrimer synthesis,



Scheme 1. Release and encapsulation behavior of iron ions in DPA.

and a novel dendrimer with a cyclic structure was quantitatively obtained via controlled cyclization on the basis of a steric effect using a monomer with a bulky dendron. Cyclization in hyperbranched polymer synthesis was first controlled on the basis of a steric effect using a Lewis acid with a bulky ligand. Only phenylazomethine oligomers having a cyclic structure were formed during the polymerization of 4,4'-diaminobenzophenone in the presence of $\text{TiCl}_4(\text{THF})_2$ as a Lewis acid with bulky ligands. The structure of a cavity in an isolated cyclic oligomer was determined by X-ray crystal analysis. Highly preferential formation of CPAN was achieved by further addition of TiCl_4 and/or the monomer during the course of the polycondensation. All of the obtained macrocycles show a high solubility unlike the conventional linear polyphenylazomethines. NMR, MD calculations, X-ray crystal analysis, and CV measurements revealed their unique structures based on the E/Z conformation of the azomethine bonds, the extremely regular molecular-packing state, and the reversible redox-activity by protic acid doping.

3. CONCLUSION

Dendritic and cyclic polyphenylazomethines (DPAs and CPAs, respectively) were synthesized as novel π -conjugated polymer ligands with a single molecular weight and a clearly-defined structure, and we first realized the precise metal-assembling in DPAs based on the unique stepwise

complexation behavior.

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