Modification and Electrochemical Properties of Poly(phenylazomethine) Derivatives

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Summary: Oligo(phenylazomethine)s (OPAs) and aniline-capped OPAs (OPA’s) are used as model compounds of polyphenylazomethine (PPA), and their fundamental properties and their modification methods are investigated. Cyclic voltammograms of bis(diphenylmethyleneamino)benzene (OPA2′) showed irreversible redox response in the presence of trifluoroacetic acid. A selective synthesis of oligophenanthridine was achieved through the photocyclization of OPA2′ in concentrated sulfuric acid. Stepwise complexation behavior in dendritic poly(phenylazomethine)s (DPAs) was supported by the shell-selective reduction of the imines. Using the shell-selective reduction method and the terminal-modification method of the DPAs, the core and terminals of DPAs were functionalized by ferrocene units, respectively.

Keywords: cyclic voltammetry; dendrimers; oligo(phenylazomethine); photochemistry; stepwise complexation

Introduction

Organic-metallic hybrid nano-materials attract much attention in various areas of electronics and life science. Especially, introduction of metal ions into organic polymers is well considered since those hybrid materials are close to a natural phenomenon. Biological reactions such as photosynthesis in plants[1–4] or respiration[5,6] in animals are based on highly efficient electron or ion transfer in the metal-containing proteins with the controlled direction, amount, and rate. Such efficient transfers are caused by the definite configuration of metal ions in the proteins. Macromolecules containing metal species are examples of mimetic metal-containing proteins, and a number of nature-mimetic materials based on various combinations of polymers and metal species have been reported up to now.[7–9] However, most of these hybrid materials results in simple mixtures of organic polymers with metal species because there are no method for controlling the number and location of metal species in polymer materials. To develop such methods, polyphenylazomethines (PPAs) are used as polymeric ligands in organic-metallic hybrid nanomaterials since they have many imines with high coordination ability. We have succeeded to create novel topological PPAs with fine-controlled metal-assembling properties as “functional modules”.[10–13] For the future development of these compounds, it is necessary to investigate their fundamental properties and their modification methods. Here, we focus on aniline-capped oligo(phenylazomethine)s (OPA’s) and report electrochemical property and photocyclization of OPA’s under acidic conditions. Furthermore, we have an interest in dendrimers as polymer ligands, and so synthesized dendritic poly(phenylazomethine)s (DPAs) and exploited the modification methods of the core and terminals of DPAs using shell-selective

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reduction and terminal-modification method, respectively.

Experimental Section

Electrochemical analyses: Electrochemical analyses were performed using an electrochemical work station (BAS Co. Ltd. Model 660) under the following conditions. Cyclic voltammetry was carried out in a conventional two-compartment cell under a nitrogen atmosphere after nitrogen bubbling. A grassy carbon electrode was used as the working electrode and polished with 0.05 mm alumina before the experiments. The auxiliary electrode and the reference electrode were a coiled platinum wire and Ag/Ag^+, respectively. The potential was normalized to the couple ferrocene/ferrocinium in acetonitrile, and the scanning rate was 100 mV/s.

Photocyclization: A typical synthetic procedure is as follows. A solution of diphenylmethyleneaminobenzene (50 mg) in 97% sulfuric acid (30 mL) was irradiated for 10 h with a Xenon lamp in a water-cooled Pyrex photochemical reactor. The mixture, after dilution with ice and neutralization with sodium hydroxide, was extracted with chloroform. The photocyclized product (16 mg) was isolated by silica gel column chromatography and identified by NMR measurements.

Results and Discussion

1.1 Electrochemical Properties of OPA’s

To study fundamental properties of PPAs, OPA’s were synthesized as model compounds through dehydration of 4-aminobenzophenone with benzophenone in the presence of $TiCl_4$, followed by further dehydration with aniline. Electrochemical properties of one of OPA’s, bis(diphenylmethyleneamino)benzene (OPA2’), was investigated using cyclic voltammetry. OPA2′ itself does not show any redox respond at the potential between −1.0 and 0.0 V. However, two irreversible reduction waves based on the reduction of imine groups appear in the presence of trifluoroacetic acid (Figure 1). This result suggests that the reduction of OPA2′ occurs at relatively positive potential upon protona-

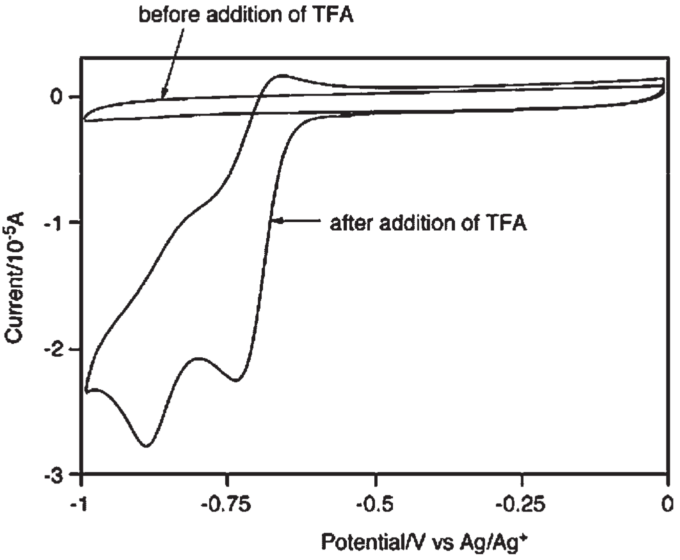
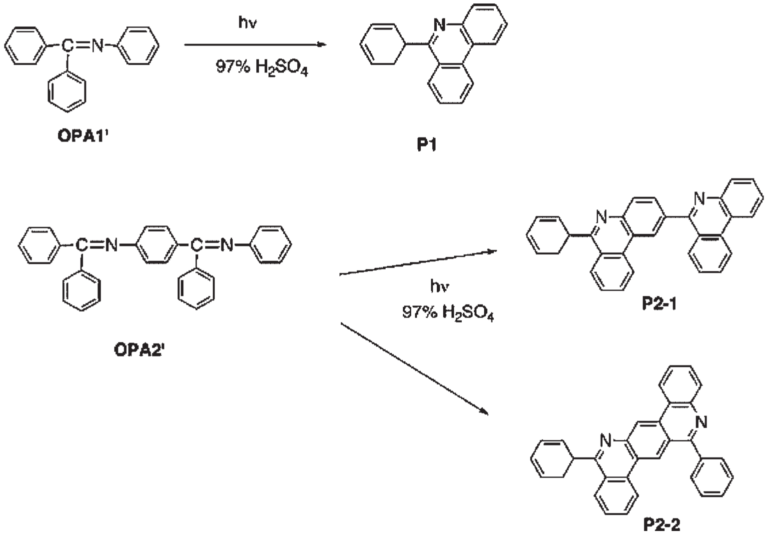


Figure 1.

Cyclic voltammograms of OPA2′ (2 mM) in acetonitrile (a) without an acid and (b) in the presence of trifluoroacetic acid (0.1 M). Supporting electrolyte: $TBABF_4$ (0.2 M), scan rate: 100 mV/s, electrode: grassy carbon.



Scheme 1.

tion. The electrochemically reduced species are probably further reacted chemically in solution, and they are not reversibly back oxidized.

1.2 Photocyclization of OPA's

To investigate the reactivity of PPAs, photochemical reactions of OPA's were studied. Photocyclization of OPA's leads to the formation of several kinds of products due to the difference in reaction sites. Diphenylmethyleneaminobenzene (OPA1′) was irradiated in a concentrated sulfuric acid (Scheme 1).[14,15] The absorption spectra before and after the irradiation were measured, and the spectra totally changed before and after the experiment as shown in Figure 2. Therefore, OPA1′ was successfully converted to the corresponding phenanthridine (P1), expected as only one product, through photocyclization

In the case of photocyclization of OPA2′, the formation of the two different kinds of cyclic products, oligophenanthridine compound (P2-1) and ladder-like compound (P2-2), are expected as shown in Scheme 1. However, P2-2 was not obtained at all and only P2-1 was formed as a product via this photocyclization. This result suggests that polyphenanthridines are selectively synthesized through the photocyclization of PPAs.

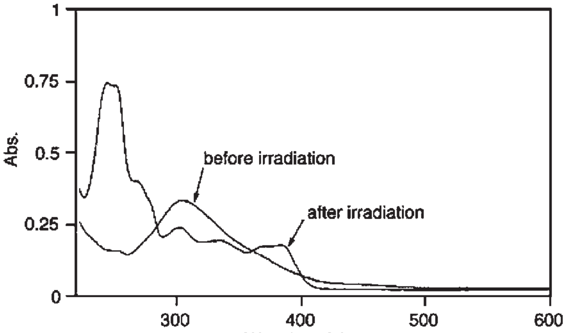


Figure 2.
The UV-vis spectra of (a) OPA1′ and (b) the photocyclized product, P1.

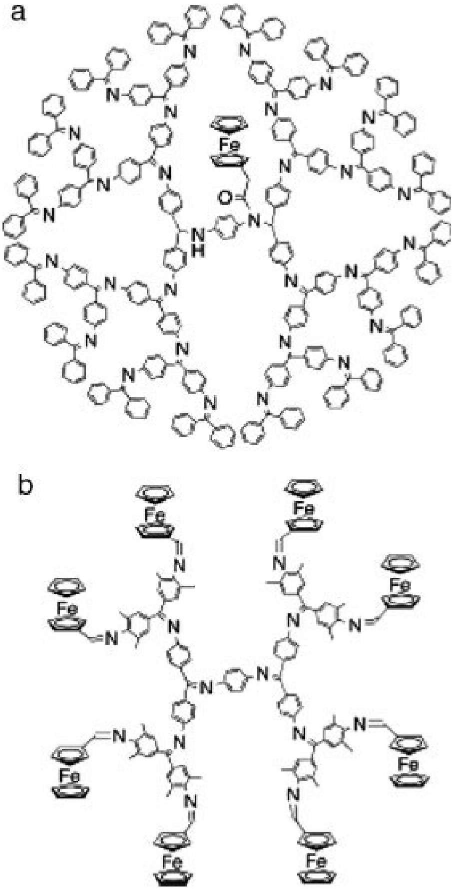


Figure 3.
DPA derivatives having ferrocene unit(s) at the (a) core and (b) terminals.

2.1 Modification of the Core in DPAs

Dendrimers with many coordination sites are attractive as polymeric ligands in organic-metal hybrid nano-materials. A number of branchings from the core in dendrimers are called ‘‘generations’’ or ‘‘shells’’. High generations of dendrimers have crowded terminals and a spacious core, and the entire shape of the dendrimers is close to a sphere.[16–20] The nano-space inside the dendrimers provides various unique functions such as light-harvesting, selective molecular conversion, and drug delivery.[21–26] Modification of the many terminals of the dendrimers can easily change their properties, such as solubility. These properties of dendrimers will become useful in many fields, for example, medicine, electronics, energy, micromachines.

DPAs were synthesized by the convergent method via dehydration of aromatic amines with aromatic ketones in the presence of $TiCl_4$. DPAs ends up with novel dendrimers having a π-conjugated backbone and many coordination sites. DPAs with different generations (DPA G1-4) were produced. For example, the fourth generation DPA (DPA G4) has 2, 4, 8, and 16 imines in the order of the 1st, 2nd, 3rd, and 4th shells, respectively (total 30 imines).

Reduction of azomethines to a secondary amine is accelerated in the presence of protic acids or Lewis acids. When DPA G2 complexed with two equivalents of $SnCl_2$ was reduced in the presence of $NaBH_4$, DPA G2 having two amines at the 1st shell was selectively obtained. Similarly, the reduction of DPA G4 complexed with two equivalents of $SnCl_2$ in the presence of $NaBH_4$ gave DPA G4 having two amines at the core. The ‘‘shell-selective reduction’’ supports the stepwise radial complexation, where two equivalents of $SnCl_2$ are coordinated to the two imines at the 1st shell of DPAs.

Furthermore, the amine units of the DPAs formed through the shell-selective reduction method can be functionalized by various carboxylic acids. Such DPA derivatives were successfully synthesized via the dehydration of DPA having two amines at the core with ferroceneacetic acid (Figure 3a).

2.2 Modification of the Terminals in DPAs

Dendrimers synthesized through the convergent method have inactive terminals, and so it is difficult to modify the terminals of the obtained dendrimers. However, we have found that the amino groups of the tetramethyl-substituted diaminobenzophenone do not react with the carbonyl group of benzophenone at all under the synthetic conditions of the imine formation reaction. Therefore, in the synthetic process of dendrimers, amino groups stay in dendrimers, and those amino groups are useful for further modification. Based on this substrate specificity in this reaction, the dehydration of tetramethyl-substituted diaminobenzophenone with diaminobenzophenone selectively gave the DPA dendrons G2 and G3 having four and eight amino groups at the terminals, respectively. As a result, DPA G3 with eight amino groups at the terminals obtained by this synthetic method was easily modified by ferrocene at the terminals (Figure 3b).

Conclusion

Novel topological poly(phenylazomethine)s such as oligo(phenylazomethine)s (OPAs), the aniline-capped OPAs (OPA's), and dendritic poly(phenylazomethine)s (DPAs) are expected as ''functional modules'' in organic-metallic hybrid nanomaterials. Cyclic voltammograms of OPA2′ showed irreversible redox waves in the presence of trifluoroacetic acid even though OPA2′ itself was redox-incative. Therefore, protonation of OPAs induces the electron transfer. Photocyclization of OPA's proceeded in concentrated sulfuric acid. In the case of OPA2′, only oligophenanthridine compound (P2-1), one of the two possible products, was obtained. Thus, selective synthesis of polyphenanthridines has been achieved through the photocyclization of PPAs.

A novel shell-selective reduction method for imines have confirmed the stepwise complexation of DPAs with metal. The shell-selective reduction of imines is useful not only to support the unique complexation behavior, but also to modify the core of DPAs with a ferrocene unit. On the one hand, terminals of dendrimers are usually inactive and not easily modified, and then, the synthetic method of DPAs was improved through the dehydration of tetramethyl-substituted diaminobenzophenone with diaminobenzophenone. DPA dendrons G2 and G3 with four and eight amino groups at the terminals, respectively were selectively obtained. Those terminals with amino groups of DPAs have been successfully functionalized by ferrocene units.

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