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Synthesis of Novel Phenylazomethine Derivatives as a Multi-Dentate Ligand for Advanced Metal-Organic Hybride Nano-Materials

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Summary: Oligophenylazomethines (OPAs) and the aniline-capped OPAs were synthesized via dehydration of 4-aminobenzophenone in the presence of $TiCl_4$ as a Lewis acid. $TiCl_4$ acts as an excellent dehydration agent for formation of the C=N bond. OPAs have some isomers, which are based on the *E*/*Z* conformation of the azomethine moieties. Novel cyclic molecules, the cyclic phenylazomethine trimer (CPA_3-ab) derivatives, were synthesized via the dehydration of the 4-aminobenzophenone. The yields of the macrocycles were enhanced to over 90% by induction of the bulky α-substituent to the substrate. The highly preferential formation of novel aabb-type phenylazo-methine macrocycles was also achieved. The resulting CPA_6-aabb has unique structure based on the *E*/*Z* conformation of the azomethine bonds, the extremely regular molecular-packing state. The novel dendritic phenylazomethines(DPAs), were synthesized by the convergent method. The DPAs have a high solubility unlike the conventional linear polyphenylazomethines. The tin chloride complexed to the imine groups of DPAs in a stepwise fashion. The complexation occurs in the order of 1st, 2nd, 3rd, and 4th layers of DPA G4.

Keywords: dendrimer; macrocycle metal-organic hybride; multi-dentate ligand; nano-materials; phenyazomethine

Introduction

In the past several years, much interest has been devoted to the study of rigid and/or π-conjugated chain polymers with metal ion, π-conjugated macromolecule-metal complexes, mainly because of their superior mechanical, electronic , photonic, and magnetic properties.[1-4] These malecules will provide novel advanced organic-metal hybrid nanomaterials for the next generation.[5,6] Azo-methine polymers which have a long history, should be carefully noted in order to find novel properties and applications becase the polymers act as useful multi-dentate ligands for metal assembling. [7-14] The phenylazomethine polymers exhibit an attractive thermal stability, good

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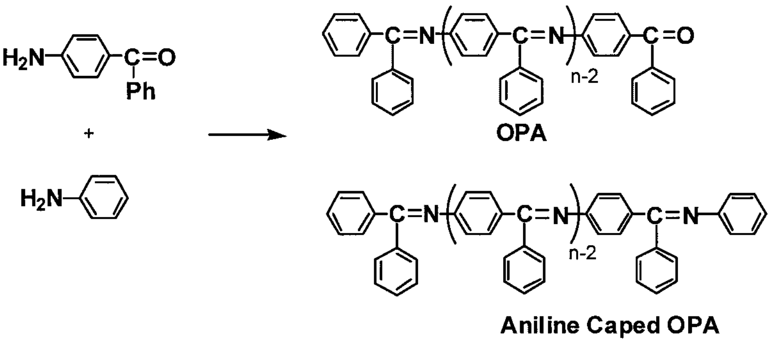
mechanical strength, meltability, fiber-forming properties, electronic conductivity, redox activity, photoluminescence, non-linear optical properties and so on. [15-17] We focused on the novel azomethine polymers[18-24] with a supramolecular structure such as cyclic and dendritic topology. Dendrimers[25-33] are highly branched organic macromolecules with successive layers or '*generations*' of branch units surrounding a central core with a beautiful sphere-like shape. The rigid dendrimers, especially dendrimers with a π-conjugated backbone, such as the phenylazomethine dendrimers are expected to expand the field of nano-marerials because dendrimers have the possibility to be regularly assembled with a packing structure on a plate. [34-37] Organic inorganic hybrid versions have also been produced by trapping metal ions or metal clusters within the voids of the dendrimers. [38-44] Here we show that the tin chroride, $SnCl_2$, complex to the imines groups of a spherical polyphenylazomethine dendrimer in a stepwise fashion[45-47] according to an electron gradient, with complexation in a more peripheral generation proceeding only after complexation in generations closer to the core has been completed. It is possible to control the number and location of metal ions incorporated into the dendrimer structures, which might are used as tailored catalysts or building blocks for advanced materials. In this review, the synthesis and properties of novel phenyl azomethine polymers including cyclic and dendritic structures were introduced in recent studies.

Synthesis of Oligophenylazomethines

For the dehydration of aldehydes/ketones with amines, the addition of an acid is sometimes necessary to enhance the electrophilicity of the carbonyl carbon. $TiCl_4$ is an effective Lewis acid for this dehydration. On the other hand, *p*-toluenesulfonic acid (PTS) is often used for the dehydration of aldehydes with amines, but ineffective in the reaction of aromatic ketones with aromatic amines because of the low electrophilicity of the carbonyl carbon having expanded π-conjugation. Oligophenylazomethines (OPAs) are synthesized via the dehydration of 4-aminobenzophenone in the presence of $TiCl_4$ and diazabicyclo[2.2.2]octane (DABCO) (Scheme 1). This dehydration is known to proceed via metathesis of benzophenone with a Ti=N compound, which is formed by the reaction of aniline with $TiCl_4$. In this oligomerization using PTS, the oligomers over the tetramer were not obtained due to the low reactivity. Aniline-capped OPAs are obtained in a one-pot synthesis. These results support the fact that $TiCl_4$ is a useful dehydration agent to form additional azomethine bonds without hydration of the already-formed azomethine bonds, because the dehydration using $TiCl_4$ is an irreversible reaction unlike PTS. ^{13}C NMR measurement revealed that the OPA3(trimer) and OPA4(tetrame) have 2 and 4 isomers, respectively, based on the *E/Z* conformation of the azomethine moiety. On the basis of the area ratio of 2 peaks attributed to the carbonyl carbon in OPA3, the formation ratio of the *E/Z* isomers in an α-phenyl-substituted azomethine bond, in principle, is 1:1. The ratio in OPA4 was determined to be 9:6:3:1. Thses results show that the formation ratio of isomers in the OPAs changes based on the steric hindrance between the intramolecular phenyl rings. The α-Ph-phenylazomethine polymers are considered to have various non-linear structures due to the *Z* conformational azomethine bonds unlike the H/Me-substituted ones.

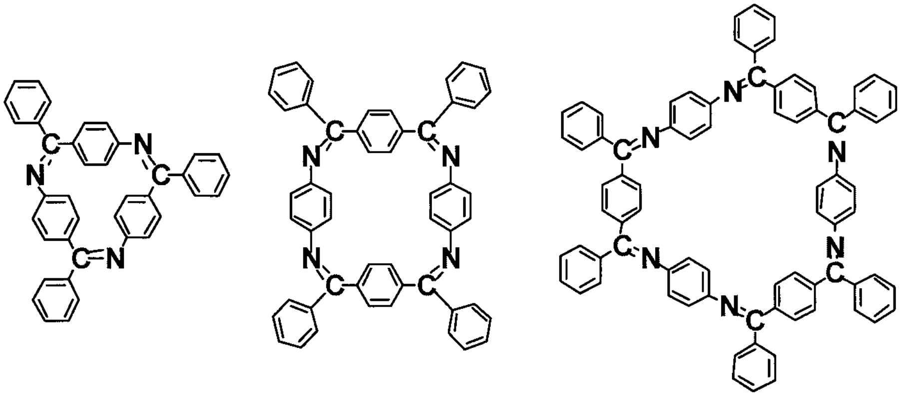


Scheme 1. Synthesis of OPAs by dehydration in the presence of $TiCl_4$.

Selective Synthesis of Macrocycles

We succeeded in the selective synthesis of cyclic tris[(α-phenyl)phenyl-azomethine] derivatives with a high yield using $TiCl_4$(Figure 1). Our results reveal that benzophenone with a bulky group at the α-position facilitates the predominant formation of the cyclic structure. The formation of the novel cyclic (α-phenyl) phenylazomethine trimer (CPA_3-ab) was carried out by dehydration of 4-aminobenzophenone using $TiCl_4$. [48,49] Using titanium(IV) tetrachloride as a Lewis acid, only the CPA_3-ab trimer was obtained with a 20% yield in spite of the non-dilute conditions. The high yield and the selectivity are caused by the steric effect of the bulky α-phenyl ring of the monomer. The selectivity and yield were emphasized by the bulkiness of the monomer. The dehydration of the 4-amino-4'-octylaminobenzophenone resulted in the formation of the corresponding cyclic trimer in 49% yield. The dehydration of 4-amino-4'-dioctylamino-benzophenone gave the corresponding trimer with a 92% isolated yield. These results indicate that bulky substituents at the α -position of the phenylazomethine facilitate the forming of the cyclic phenylazomethine trimers. The single conformation of CPA$_3$-ab is supported by NMR, and molecular modeling of the *E* isomer of CPA$_3$-ab is very difficult to build. These results support the idea that CPA$_3$-ab only has the *Z* conformation.

During the course of the AABB-type polycondensation of 1,4-dibenzolybenzene with 1,4-phenylenediamine, the total macrocyclization was realized by further addition of $TiCl_4$ and the diamine monomer. Only peaks attributed to the novel cyclic polyphenylazomethines (CPA$_n$-aabb, where n is the degree of polymerization) were confirmed in the TOF-MS spectrum of the crude products (Figure 2).



CPA$_3$-ab **CPA$_4$-a^{2}b^2** **CPA$_6$-a^{2}b^2**

Figure 1. Structures of phenylazomethine macrocycles.

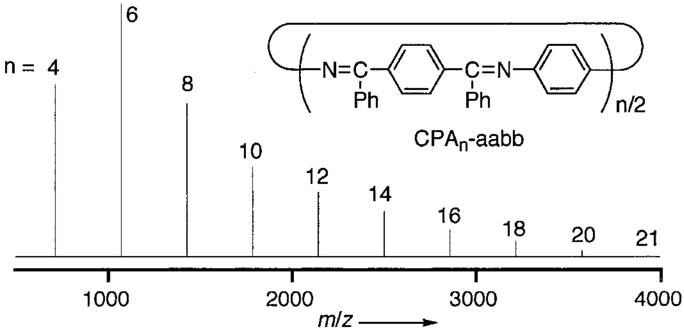
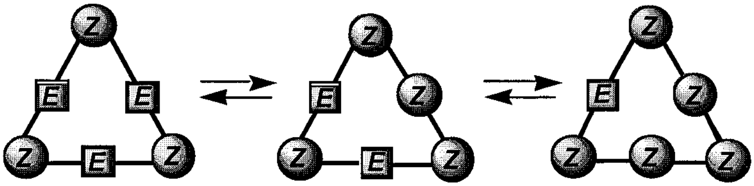


Figure 2. MALDI-TOF-MS spectrum of CPA$_n$-aabb.

The CPA$_n$-aabb products (n = 4, 6, 8, 10, 12, 14, 16, 18, and >20) were easily isolated in 13, 23, 16, 11, 8, 6, 5, 3, and 6% yields (total: 91%), respectively, by gel permeation chromatography. The ^{13}C NMR spectra of CPA$_4$-aabb and CPA$_6$-aabb are relatively simple, which support the fact that they have only one or a few isomers. One peak attributed to the azomethine carbon in the spectrum of CPA$_4$-aabb shows that CPA$_4$-aabb has a single isomer with one (*Z*) conformation of the azomethine bonds. The ^{13}C NMR spectrum of CPA$_6$-aabb shows that CPA$_6$-aabb has three isomers (Scheme 2).



Scheme 2. *E/Z* conformations of CPA$_6$-aabb.

The molecular structure and packing of CPA$_6$-aabb were directly confirmed by X-ray crystal analysis. The triangle shape and *E/Z* conformations of the crystal molecule agreed with those of isomer I. Interestingly, the triangle molecules are two-dimensionally fine-packed (Figure 3), and aligned in a column. Such a unique and regular packing structure of the π-conjugated macrocycles has not yet been reported to the best of our knowledge. [50-54]

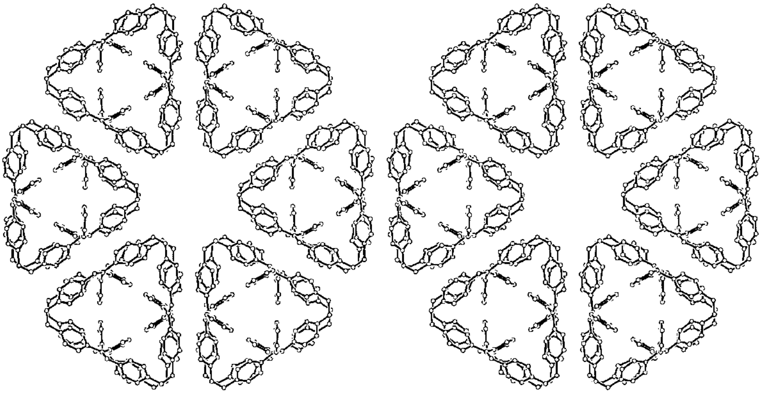
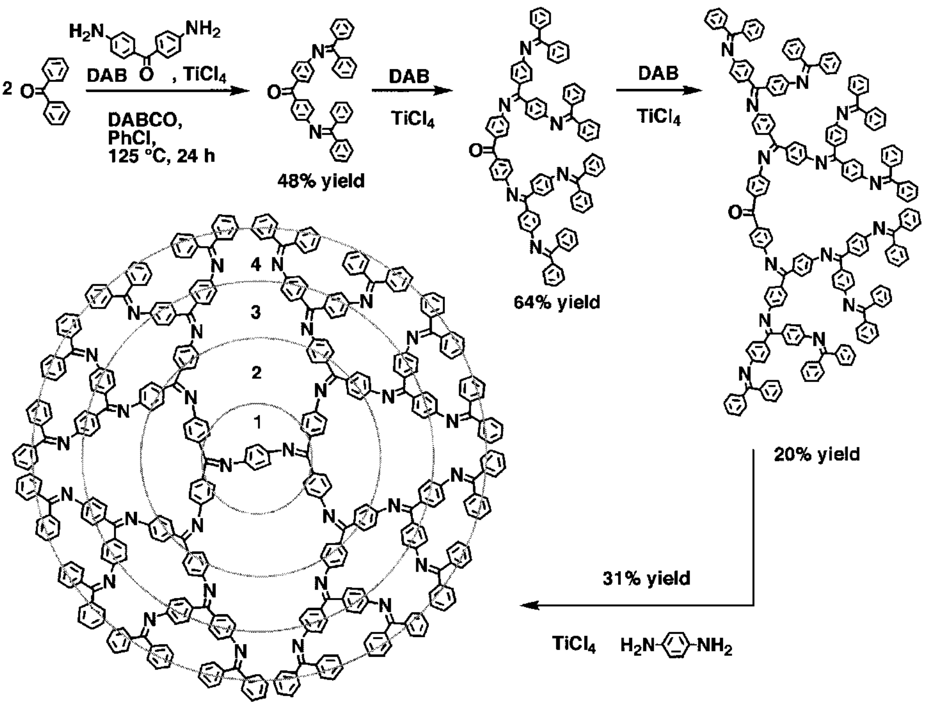


Figure 3. The packing structure(top view) of CPA_6-aabb. Crystal data, trigonal, space group $P\text{-}3c1$, a = 21.090(3) Å, b = 21.090(3) Å, c = 15.77(1) Å, U = 6075 (4) $Å^3$, Z = 4, R = 0.087, wR = 0.201.

Convergent Synthesis of Phenylazomethine Dendrimers (DPAs)

DPAs (DPA G1, G2, G3, and G4, designated as GX where X is the generation number) were synthesized by the convergent method as shown in Schemes 3. Benzophenone was allowed to react with 4,4'-diaminobenzophenone in the presence of $TiCl_4$ and DABCO. The DPA dendron G2 was synthesized via dehydration, and isolated by silica gel column chromatography with a 48% yield. DPA dendrons G3 and G4 were obtained in 64 and 20% yields by dehydration of the dendrons G2 and G3 with 4,4'-diaminobenzophenone, respectively. DPAs G1, G2, G3, and G4 were obtained by the dehydration with p-phenylenediamine, and isolated in 91, 62, 45, and 31% yields, respectively(Scheme 3). The high purity of the DPAs was confirmed by the GPC analysis, MALDI-TOF-MS, and ICP-MS.

The DPA dendrimers have a high solubility in the common solvents such as chloroform and DMSO, because their dendritic structures prevent intermolecular stacking. In each ^1H NMR spectrum of DPAs G1, G2, and G3, one singlet peak was observed at 6.6-6.3 ppm, which was attributed by COSY to the four protons of the phenyl ring in the core of the dendrimer. This singlet peak supports the symmetrical structure of the DPA. On the other hand, the singlet peak was not observed in the spectrum of DPA G4 because of the fixed conformation of the core by the bulky dendrons.



Scheme 3. The convergent synthesis of the DPA dendrons and dendrimers.

Spin-lattice (T1) relaxation measurements of the DPAs were perfomed. The NMR studies for the relaxation gave useful information about the structural density. With increasing generation, T1 of the external proton increased more than that of the internal one. This increase in T1 means a restriction in the molecular motion of the external phenyl rings; the exterior of DPA G4 is proposed to be close to the solid-state.

Stepwise Radial Complexation in DPA Dendrimers

The DPA dendrimers having many azomethine groups as the coordination site for metal ions increase their application as a novel nano-ordered film of the DPA-metal complex. The imine sites present in the DPAs strongly coordinate to various metal ions; $SnCl_2$ is a Lewis acid forming 1:1 complexes with imine compounds, and complexation of the 30 imine sites in DPA G4 should therefore yield a nano-sized spherical complex. The addition of $SnCl_2$ to a dichloromethane/acetonitrile solution of DPA G4 resulted in a color change from yellow to orange, attributed to complexation. Using UV-vis spectroscopy to monitor the titration until an equimolar amount of $SnCl_2$ had been added, we observed four changes in the position of the isosbestic point (Figure 4), indicating that the complexation proceeds not randomly, but stepwise. An isosbestic point appears when a compound is quantitatively transformed into another by complexation,[55] so the four different isosbestic points we observed suggest that four different complexes are successively formed upon the $SnCl_2$ addition. For DPA G4, four isosbestic points centered at 375, 364, 360 and 355 nm appeared when adding between 0-2, 3-6, 7-14 and 15-30 equivalents of $SnCl_2$, respectively. Overall, the isosbestic point shifted about 20 nm from 375 to 355 nm, and the number of added equivalents of $SnCl_2$ required to induce a shift was in agreement with the number of imine sites present in the different layers of DPA G4. The titration results suggest that based on our observations under equilibrium conditions, the process is proceeding in a stepwise fashion from the core imines to the terminal imines of DPA G4 as shown in Fig. 5. The metal ions are incorporated in a stepwise fashion, first filling the layers close to the dendrimer core and then progressively the more peripheral layers(Figure 5).

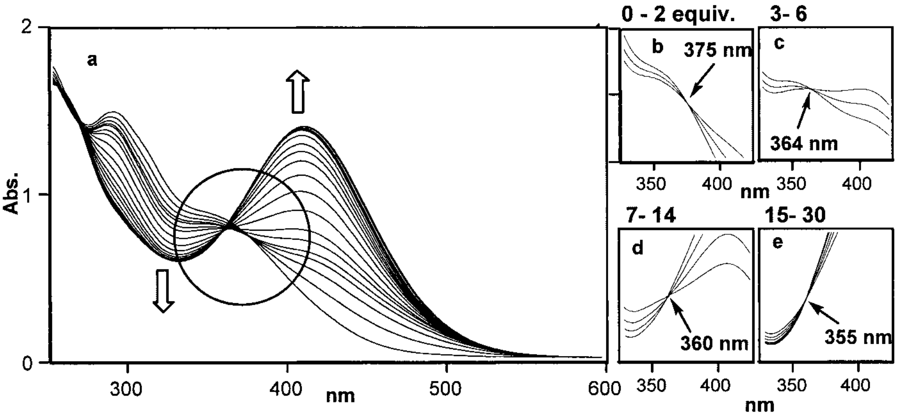


Figure 4. UV-vis spectra of DPA G4 (5 x 10^{-6} M) complexed with (a) 0-30, (b) 0-2, (c) 3-6, (d) 7-14, and (e) 15-30 equiv. of $SnCl_2$ (solv. 1:1 dichloromethane:acetonitrile).

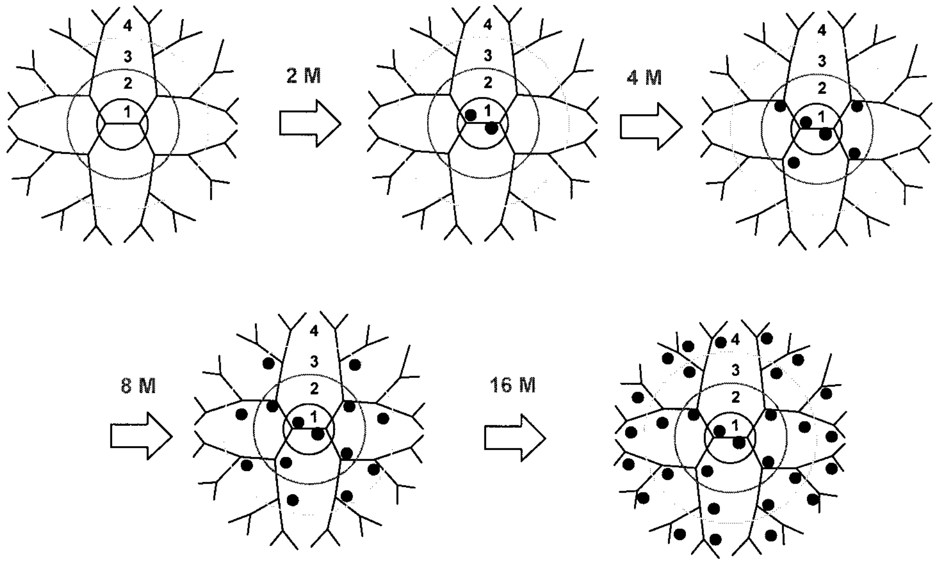


Figure 5. Stepwise radial complexation of $sncl_2$ in dpa g4 dendrimer.

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