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The First Electroresponsive Phenylazomethine Macrocycles: Highly Preferential Formation and Regular Molecular Packing

Masayoshi Higuchi, Hirohiko Kanazawa, and Kimihisa Yamamoto*

Kanagawa Academy of Science & Technology (KAST), and Department of Chemistry, Faculty of Science & Technology, Keio University, Yokohama 223-8522, Japan

yamamoto@chem.keio.ac.jp

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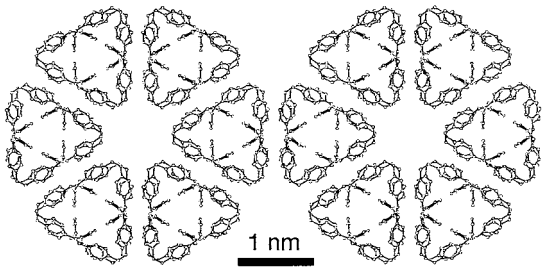
ABSTRACT



Highly preferential formation of novel polyphenylazomethine macrocycles was achieved by further addition of $TiCl_4$ and/or the monomer during the course of the polycondensation. These macrocycles have unique structures based on the (*E*)/(*Z*)-conformation of the azomethine bonds, the extremely regular molecular-packing state, and the reversible redox properties by protic acid doping.

Redox-active nanomaterials have received much attention for use in electronic nanodevices. π-Conjugated polymers are promising materials due to their excellent redox properties. Regular molecular packing is essential for this type of application. This is facilitated by the introduction of novel topological structures such as dendrimers or macrocycles to the polymer backbone. We have already found that dendritic polyphenylazomethines (DPAs) are assembled with a regular packing structure on a plate and possess a unique metal-collecting behavior at the imine sites.[1] We now report the highly selective synthesis of novel macrocyclic polyphenylazomethines, which have both a unique packing structure and reversible redox properties.

Polyphenylazomethines (PPAs)[2] are π-conjugated polymers with high thermal stability and good mechanical strength, but their very low solubility and poor redox properties prevent practical applications as polymer materials. They are relatively easily synthesized via the AABB-type polycondensation of dialdehydes with diamines or the AB-type of aminoaldehydes, but the obtained polymers have a linear structure due to the preferential (*E*)-conformation of the azomethine bonds. In previous papers, we reported the synthesis of cyclic phenylazomethine trimers during the AB- and AB_2-type polycondensations in the presence of a Lewis acid.[3] However, it is very difficult to isolate any macrocycles in the AABB-type polycondensation or the macrocycles

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except for the trimer in the AB- and AB_2-type polycondensations under the synthetic conditions. This is due to the formation of linear oligomers (in the case of AABB- and AB-type polycondensations) or macrocycles randomly substituted by the monomer (in the case of AB_2-type polycondensation) that lowers the yields of the desired macrocycles and/or makes the isolation difficult. In other words, the total cyclization of the linear oligomers allows high yields and easy isolation of the cyclic oliogmers in the AABB- and AB-type polycondensations.

The total macrocyclization was realized by further addition of $TiCl_4$ and 1,4-phenylenediamine during the course of the AABB-type polycondensation of 1,4-dibenzolybenzene with 1,4-phenylenediamine in the presence of $TiCl_4$.[4] 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 1).

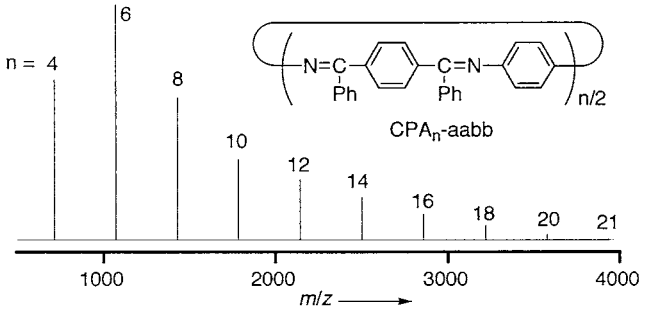

Figure 1. MALDI-TOF-MS spectrum of CPA_n-aabb.

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. Using a similar synthetic procedure also allowed the macrocyclic oligomers, CPA_n-ab (n = 3−9 and >10) to be isolated in 59, trace, 3, 9, 4, 2, 3, and 4% yields (total: 84%), respectively, in the AB-type polycondensation of 4-amino-4′-bromobenzophenone. The very poor solubility of the conventional PPAs prevents a structural study and their actual application as a polymer material, while all of the obtained macrocycles show a high solubility in chloroform and tetrahydrofuran; therefore, the structural study became feasible.

(4) Further addition of the diamine monomer is needed in the AABB-type polycondensation in order to compensate for the amount of diamine monomer consumed in the neutralization of HCl, which is generated in the dehydration. Of course, the polycondensation is carried out in a large excess of DABCO, which prevents the neutralization of HCl with the diamine monomer. However, the neutralization of HCl with the diamine monomer is not prevented completely, even in the presence of a large excess of DABCO. In fact, linear oligomers having carbonyl groups at both ends remain in the reaction mixture before further addition of the diamine monomer, which was confirmed by TOF-MS measurement. Total cyclization of the linear oligomers is extremely important for easy isolation of the cyclic oligomers, which is achieved by the further addition of the diamine monomer.

The obtained macrocycles are expected to have various (*E*)/(*Z*)-isomers on the azomethine bonds. However, the ^{13}C NMR spectra of CPA_4-aabb, CPA_6-ab, and CPA_6-aabb are relatively simple, which support the fact that they have only one or a few stable 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 (Figures 2a). Three peaks attributed to azomethine carbon in the spectrum of CPA_6-ab support the C_2-symmetry of an oblong isomer having the *E*/*Z* combination shown in Figure 2b, and the isomer was also

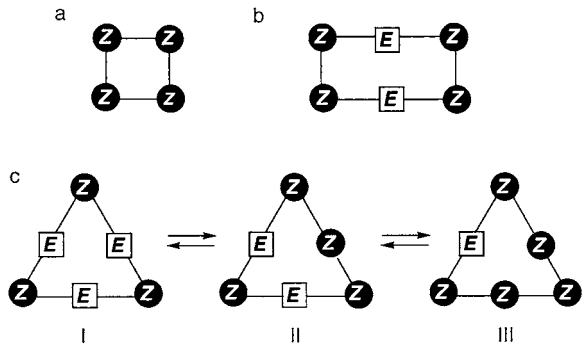

Figure 2. Shapes and (*E*)/(*Z*)-conformations of (a) CPA_4-aabb, (b) CPA_6-ab, and (c) CPA_6-aabb supported by NMR and MD calculations.

determined by molecular dynamics (MD) calculations to be the stable one of CPA_6-ab. Two strong peaks and twelve weak ones in the spectrum of CPA_6-aabb show that CPA_6-aabb has three isomers, i.e., I−III, as shown in Figure 2c. That is, among the structurally possible (*E*)/(*Z*)-isomers of CPA_6-aabb, only the triangle isomer I gives the two peaks attributed to the azomethine carbon in the spectrum due to its C_3-symmetric structure, and only the asymmetry of isomers II and III results in the six peaks in the spectra. The triangle structure as a stable isomer in CPA_6-aabb was also supported by the MD calculations. These results revealed that CPA_6-aabb and CPA_6-ab, which have the same number of azomethine bonds, have different shapes and (*E*)/(*Z*)-conformations based on the different linking-patterns (head-to-head or head-to-tail) of the azomethine bonds.

The stable structure and regular 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 shown in Figure 2c (Figure 3a).[5] The phenyl rings shown as "X" in Figure 3a

(5) The equilibrium among the geometrical isomers of CPA_6-aabb was supported by ^1H NMR spectrum of the crystals: one isomer of CPA_6-aabb was isolated by recrystallization, and the geometry was determined by X-ray crystal analysis. However, the ^1H NMR spectrum of the crystals in $CDCl_3$ was in agreement with that of the original CPA_6-aabb, which includes geometrical isomers. That is, the isomers isomerized each other in the solution due to the equilibrium based on the easy *E*/*Z* transformation of imines. This result shows that crystals of the single isomer of CPA_6-aabb were obtained because crystal packing forces the equilibrium to shift toward one isomer.

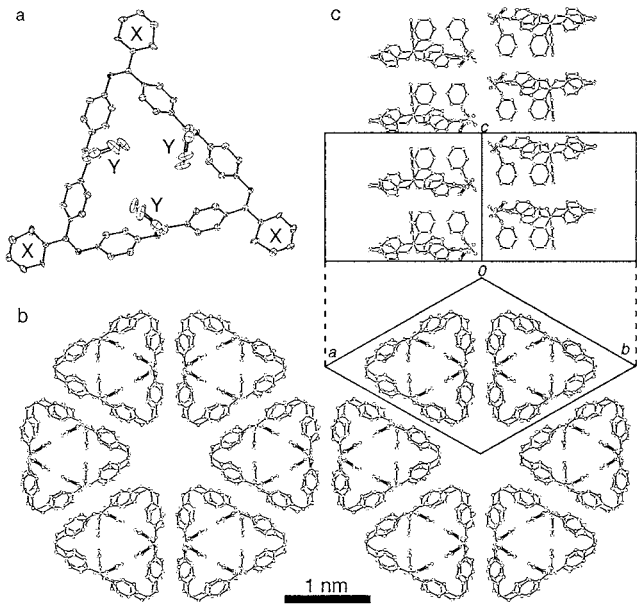

Figure 3. ORTEP drawing of (a) CPA_6-aabb with 20% ellipsoid and the packing structure; (b) top and (c) side views (the phenyl rings shown as "X" in Figure 3a are omitted for easy understanding of the packing structure). Crystal data: trigonal, space group *P*-3*c*1, $a = 21.090(3)$ Å, $b = 21.090(3)$ Å, $c = 15.77(1)$ Å, $U = 6075$ (4) Å^3, $Z = 4$, $R = 0.087$, w$R = 0.201$.

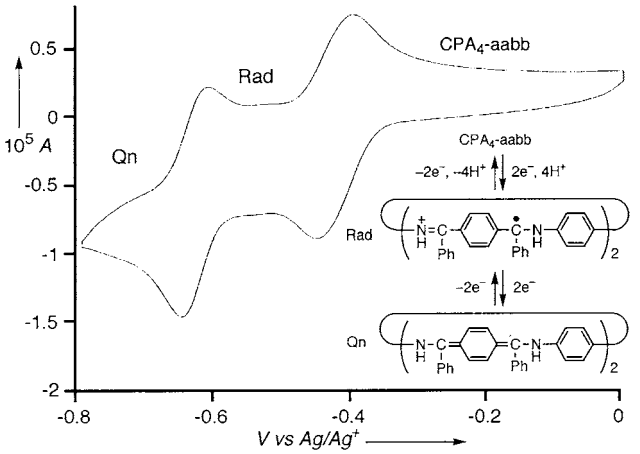

Figure 4. Cyclic voltammogram of CPA_4-aabb (1 mM) in 0.2 M $TBABF_4$/acetonitrile in the presence of trifluoroacetic acid (4 mM) (scan rate = 100 mV/sec; electrode = Pt) and a redox mechanism.

are parallel to the macrocycle plane, and the phenyl rings shown as "Y" are perpendicular to the macrocycle plane and gather on one side. Interestingly, the triangle molecules have an extremely regular molecular-packing state; they are two-dimensionally packed like the boxing up of "short cakes" (Figure 3b), and the packed "short cakes" are aligned in a column (Figure 3c).[6]

The conventional PPAs are known to have a poor and unstable redox property due to the easy hydrolysis of the azomethine bonds and/or further reduction to the amine during the electrochemical measurements in acidic solutions. On the other hand, CPA_n-aabb was revealed to have reversible redox activity in the presence of an acid. The cyclic voltammogram of CPA_4-aabb showed two stable redox waves at a negative potential (Figure 4). The result of the electrospectrochemical analysis showed the formation of a radical during the first reduction (the decrease of the absorption of azomethine at 400 nm) and the formation of a quinoid during the second reduction (the increase of the absorption at 450 nm). On the basis of the electrospectrochemical analysis and the Nernst plot (slope: −120 and 0 mV/pH, respectively), each redox process was determined to involve a two-electron transfer accompanied by a four-proton transfer and a two-electron transfer per molecule, respectively. The excellent redox properties arise with introduction of a phenyl group at the α-position of the azomethine, which stabilizes both the radical species (Rad) and the quinoidal one (Qn).[7]

In conclusion, highly preferential formation of novel polyphenylazomethine macrocycles 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.

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Supporting Information Available: Synthesis and characterization data, ^{13}C NMR and MD calculations, a CIF file, and electrospectrochemical analysis and the Nernst plot. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) The −CH═N− bonds in conventional PPAs are unstable during the electrochemical measurements in the acidic solution, but the −CPh═N− bonds in CPAn are rather stable, because a phenyl group at the α-position of the imine bond stabilizes both the radical species (Rad) and the quinoidal one (Qn) formed during the measurements.