ORGANIC
LETTERS

2006
Vol. 8, No. 4
569−571

Synthesis and Properties of a Novel Phenylazomethine Dendrimer with a Tetraphenylmethane Core

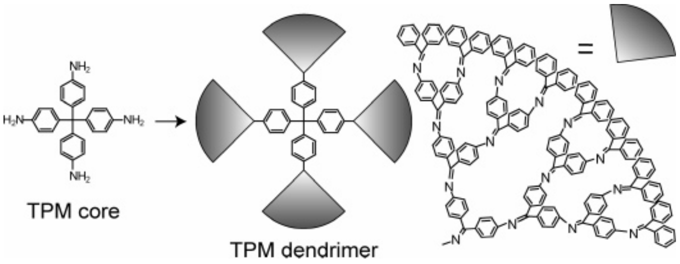
Osamu Enoki, Hideaki Katoh, and Kimihisa Yamamoto*

Department of Chemistry, Faculty of Science and Technology, Keio University,
Yokohama 223-8522, Japan

yamamoto@chem.keio.ac.jp

Received November 4, 2005

ABSTRACT



A new type of phenylazomethine dendrimer with a tetraphenylmethane core was synthesized by a convergent method. The properties of the dendrimer were confirmed by thermal, rheological, TEM, and AFM measurements. A stepwise radial complexation was clearly observed with $SnCl_2$.

A dendrimer is a unique macromolecule that has a regular structure and a definite molecular weight.[1] Applications of the “internal cavity” of the dendrimer have been widely carried out;[2] however, its spatial structure is still controversial. According to computational and neutron scattering investigations,[3] a dendrimer that consists of a flexible architecture gives rise to “back-folding”, therefore the entire structure is described as a “dense-core” model, which means that there are no cavities in the dendrimer. On the other hand, it was experimentally confirmed that the Müllen-type dendrimer, which consists of a fully aromatic structure, displays no back-folding.[4] This means that a dendrimer that has a solid architecture could form a “dense-shell” structure, and has an internal cavity.

We have synthesized several types of dendrimers with phenylazomethine architecture.[5] Because it has already been confirmed that phenylazomethine architectures are rigid, these dendrimers are appropriate for creating a series of dense-shell dendrimers. It is also essential for fabrication of the dense-shell structure to synthesize a dendrimer whose core is small, three-dimensionally symmetrical, and multisubstituted. In this Letter, we describe the synthesis and properties of a new kind of tetrasubstitutive phenylazomethine dendrimer having a tetraphenylmethane (TPM) core (Figure 1).

A core molecule, tetrakis(*p*-aminophenyl)methane, was obtained in good yield according to the literature method.[6]

---

(1) Tomalia, D. A. *Prog. Polym. Sci.* **2005**, *30*, 294.

(2) (a) Jansen, J. F. G. A.; de Brabander-van den Berg, E. M. M.; Meijer, E. W. *Science* **1994**, *266*, 1226. (b) Scott, R. W. J.; Wilson, O. M.; Crooks, R. M. *J. Phys. Chem. B* **2005**, *109*, 692.

(3) (a) Maiti, P. K.; Çagin, T.; Wang, G.; Goddard, W. A., III *Macromolecules* **2004**, *37*, 6236. (b) Rosenfeldt, S.; Dingenouts, N.; Ballauff, M.; Werner, N.; Vögtle, F.; Lindner, P. *Macromolecules* **2002**, *35*, 8098. (c) Scherrenberg, R.; Coussens, B.; van Vliet, P.; Edouard, G.; Brackman, J.; de Brabander, E. *Macromolecules* **1998**, *31*, 456.

(4) (a) Rosenfeldt, S.; Dingenouts, N.; Pötschke, D.; Ballauff, M.; Berresheim, A. J.; Müllen, K.; Linder, P.; Saalwächter, K. *J. Luminescence* **2005**, *111*, 225. (b) Rosenfeldt, S.; Dingenouts, N.; Pötschke, D.; Ballauff, M.; Berresheim, A. J.; Müllen K.; Linder, P. *Angew. Chem., Int. Ed.* **2004**, *43*, 109. (c) Wind, M.; Saalwächter, K.; Wiesler, U.-M.; Müllen, K.; Spiess, H. W. *Macromolecules* **2002**, *35*, 10071.

(5) (a) Higuchi, M.; Shiki, S.; Yamamoto, K. *Org. Lett.* **2000**, *2*, 3079. (b) Imaoka, T.; Horiguchi, H.; Yamamoto, K., *J. Am. Chem. Soc.* **2003**, *125*, 340. (c) Satoh, N.; Cho, J.-S.; Higuchi, M.; Yamamoto, K. *J. Am. Chem. Soc.* **2003**, *125*, 8104. (d) Enoki, O.; Imaoka, T.; Yamamoto, K. *Org. Lett.* **2003**, *5*, 2547.

10.1021/ol052673y CCC: $33.50

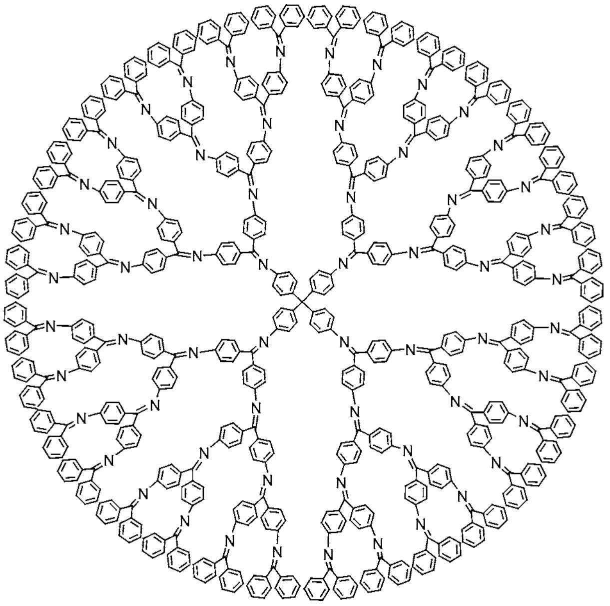


Figure 1. Structure of the TPM G4 dendrimer.

The G1 to G4 phenylazomethine dendrons were synthesized by repeating both the dehydration and oxidation reactions, using $TiCl_4$ and $KMnO_4$, respectively.[7] The phenylazomethine dendrimers were obtained by the same dehydration reaction between the core and the dendrons. All products were identified by ^{1}H NMR, ^{13}C NMR, IR, MALDI-TOF MS, and elemental analysis.

The obtained dendrimer had a high thermostability. The $Td_{10\%}$ temperatures were above 500 °C at high generations (Table 1), indicating that the core TPM was thermally stable.[8]

Table 1. Results of Thermal Analysis and Mean Diameters from Three Different Measurements[a]

			diameter/nm	
generation	$Td_{10\%}$/°C	gyration	TEM	AFM
G1	400	1.6		
G2	519	2.4		
G3	522	3.2	1.9	2.4
G4	534	4.0	2.1	2.9

[a] The G1-2 dendrimers were not measured by TEM and AFM because they were too small to identify.

The rheological properties were measured by gel permeation chromatography with a three-dimensional detector for refractive index, light scattering, and viscosity. The Mark−Houwink−Sakurada plots of three types of dendrimers are displayed in Figure 2. The TPM core dendrimer showed the lowest viscosity, which meant that it is the smallest and densest molecule in the phenylazomethine dendrimer family. It is also notable that the plot had no maximum that indicates back-folding.[4]

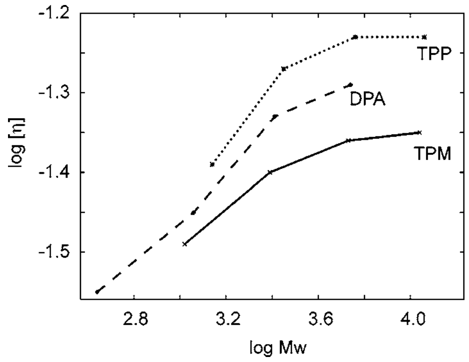


Figure 2. Mark−Houwink−Sakurada (MHS) plots for three kinds of dendrimers, having a core of *p*-phenylene (DPA), porphyrin (TPP), or tetraphenylmethane (TPM).

The TEM image was obtained with RuO_4 staining. The TPM G4 dendrimer had a spherical shape despite the G3 one appearing slightly distorted (see the Supporting Information). The mean diameters are listed in Table 1.

The diameters of the dendrimers were also measured by AFM. The dendrimers were scattered on a mica substrate by casting a dilute solution of them and then were observed. The AFM image showed many particles but their heights were almost the same, which indicated that each dendrimer stood alone without forming layers. The mean heights of the particles are also listed in Table 1. The TEM and AFM results were quite similar, which means that the dendrimer is rigid enough to keep the molecular structure from collapsing on the substrate.[9]

Finally, the coordination chemistry of the dendrimer was confirmed by UV−vis titration with $SnCl_2$. Upon the addition of $SnCl_2$ to the dendrimer in solution, the UV−vis spectra of the dendrimer gradually changed until the stoichiometry of the added $SnCl_2$ was equal to the number of the imine groups in the dendrimer. This means that the $ScCl_2$ and the imine group form a 1:1 complex quantitatively.

When the G4 dendrimer was used, four isosbestic points were observed during the titration. Each isosbestic point shifted stepwise (not continuously), as 368 (0 to 4 equiv), 365 (5 to 12 equiv), 363.5 (13 to 28 equiv), and 362 nm (28 to 60 equiv). The equivalent numbers to shift the isosbestic points, i.e., 4, 8, 16, and 32, were equal to the number of the imine groups on each layer of the dendrimer (Figure 3).

This indicated that the $SnCl_2$ was radially coordinated to the imine group from the center to the periphery, i.e., a

---

(6) Laliberte, D.; Maris, T.; Wuest, J. D. *Can. J. Chem.* **2004**, *82*, 386.

(7) Takanashi, K.; Chiba, H.; Higuchi, M.; Yamamoto, K. *Org. Lett.* **2004**, *6*, 1709.

(8) Tanaka, R.; Imaoka, T.; Yamamoto, K. *J. Photopolym. Sci. Technol.* **2004**, *17*, 323.

(9) Lemcoff, N. G.; Spurlin, T. A.; Gewirth, A. A.; Zimmerman, S. C.; Beil, J. B.; Elmer, S. L.; Vandeveer, H. G. *J. Am. Chem.* Soc. **2004**, *126*, 11420.

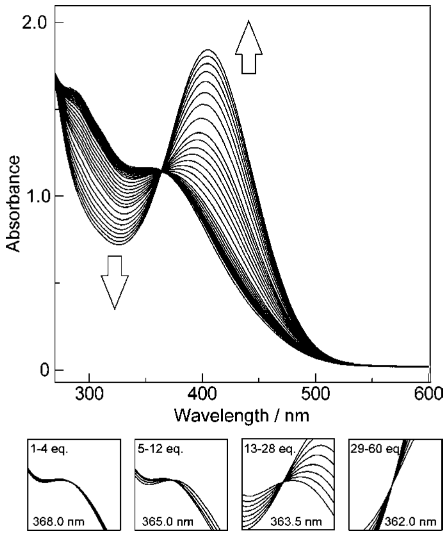
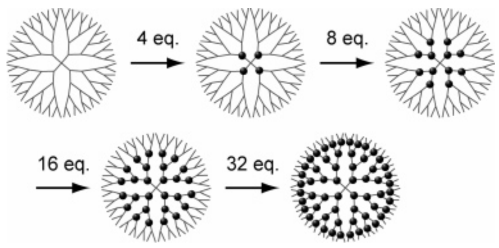


Figure 3. UV−vis spectral change of the G4 TPM dendrimer upon the addition of $SnCl_2$ (5μM in chloroform−acetonitrile (1:1)).

stepwise radial complexation occurred[10] (Scheme 1). These phenomena were also similarly observed for the G1−G3 dendrimers.

Scheme 1. Stepwise Radial Complexation of TPM G4 with $SnCl_2$



In summary, we synthesized a novel phenylazomethine dendrimer with a tetraphenylmethane core up to generation 4. The dendrimer had the densest structure among the previously reported phenylazomethine dendrimers, and enough rigidity not to collapse on a substrate. The dendrimer clearly showed a stepwise radial complexation with $SnCl_2$. As a consequence, this dendrimer can produce not only dense-shell, but metal−organic hybrid architecture, with numerically and spatially controlled metal moiety. It would be available as a new kind of nanomaterial.

Acknowledgment. This work was supported in part by the Core Research for Evolutional Science and Technology (CREST) program of the Japan Science and Technology (JST) Agency, by a Scientific Research Program for the 21st Century Center of Excellence (COE) (Keio-LCC) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan, and by a research grant (Project No. 23) from the Kanagawa Academy of Science and Technology (KAST).

Supporting Information Available: The synthetic procedure and characterization of the dendrimers, thermal and rheological measurements, TEM and AFM images, and UV−vis spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

OL052673Y

---

[10] (a) Yamamoto, K.; Higuchi, M.; Shiki, S.; Tsuruta, M.; Chiba, H. *Nature* **2002**, *415*, 509. (b) Higuchi, M.; Tsuruta, M.; Chiba, H.; Yamamoto, K. *J. Am. Chem. Soc.* **2003**, *125*, 9988.