Spontaneous Assembly of Dendrite Structure by Coordination of Al to 5,8-Dihydroxy-1,4-naphthoquinone

Yoshihiro Koide* and Yusuke Sato
Department of Material and Life Chemistry, Faculty of Engineering, Kanagawa University,
Yokohama 221-8686

(Received January 30, 2007; CL-070117; E-mail: ykoide01@kanagawa-u.ac.jp)

The reaction of boehmite ($[AlO(OH)]_n$) and 5,8-dihydroxy-1,4-naphthoquinone (DHNQ) in refluxing water led to spontaneous assembly of a mixture of coordination complexes, in which extended network of deprotonated DHNQ ($DONQ^{2-}$) is bridging between two Al^{3+} ions in the bis-O,O'-bidentate fashion. UV–vis spectroscopy, ^{13}C solid-state NMR, and size exclusion chromatography (SEC) analysis are consistent with the formation of dendrite structures.

Spontaneous assembly of supramolecular architectures with particular coordination geometries is an extremely efficient approach for the development of periodic metal–organic framework often found in such materials.[1] To date, numerous coordination open-framework materials[2] and dendrite complexes[3] have emerged using generality of the self-assembly approach, and became increasingly important as research expands into the fields of catalysis,[4] nonlinear optics,[5] magnetism,[6] molecular recognition,[7] and electron transfer[8] to name a few.

Most of coordination polymers and dendrimers are built around transition metals, but, to the best of our knowledge, no aluminum-based supramolecular structure is reported to date. Aluminum is, however, one of the most abundant element, and the utilization of aluminum can be a highly cost-efficient approach to the development of functional molecules. Indeed, novel properties of aluminum oxide-based materials have been discovered in recent years.[9] In this light, recently we explored spontaneous synthesis of aluminum complexes from boehmite ($[AlO(OH)]_n$), a naturally occurring aluminum oxide, and bidentate ligands under biphasic conditions. For instance, a stoichiometric reaction between $[AlO(OH)]_n$ and 2,4-pentanedione (Hacac) in refluxing water prepared tris(acetylacetonato)aluminum ($Al(acac)_3$) in a single step.[10] In an another example, a similar reaction between $[AlO(OH)]_n$ and 8-hydroxyquinoline (8-Hq) lead unexpectedly to the preparation of the facial isomer of tris(8-hydroxyquinolinato)aluminum (Alq_3), which is thermodynamically less stable than the meridional isomer, a well-known complex used in organic light-emitting devices.[11] These experiments demonstrate usefulness of $[AlO(OH)]_n$ as a quantitative source of Al^{3+} ion for the preparation of six-coordinate aluminum complexes. In purpose of harnessing $[AlO(OH)]_n$ for preparation of progressively complex structures, we attempted preparation of macromolecular Al coordination complexes using 5,8-dihydroxy-1,4-naphthoquinone (DHNQ) as a bridging ligand.

In a typical synthesis, 1.5 equiv. of DHNQ (240 mg, 1.25 mmol) was added to a water (40 mL) suspension of 50 mg (0.83 mmol) of $[AlO(OH)]_n$ powder[12] and refluxed for 72 h under vigorous stirring. After filtration, the resulting burgundy-colored solids were rinsed with ethanol (5 mL × 3) and dried under vacuum to obtain 248 mg (85.5%) of a solid product. The product is reasonably soluble in DMF and, to a lesser degree, in xylene.

The UV–vis spectra of DMF solutions of the product and DHNQ are shown in Figure 1. Characteristic absorption bands of DHNQ at 496, 526, and 566 nm are apparently red-shifted in the product (505, 535, and 575 nm), indicating the presence of naphthoquinone moieties. A new broad absorption band at 411 nm is considered to derive from charge transfer (CT) between donor ($DONQ^{2-}$) and acceptor (Al^{3+}) components.

An X-ray powder diffraction (XRPD) pattern shows a broad peak, indicating the absence of crystalline structures. The ^{13}C solid-state NMR spectrum of the product exhibits three sharp resonances, which are assigned to the aromatic carbons in the bridging naphthoquinone moieties, confirming the symmetric coordination to Al^{3+} ions via bis-O,O'-bidentate fashion (Figure 2). Size exclusion chromatography (SEC) of a DMF solution of the product shows multiple components as summarized in Table 1. Among the first two components, which occupy nearly 70% of the products, the heaviest component possesses number averaged molecular weight (M_n) and the calculated polydispersity (M_m/M_n) of 5011 and 1.133, respectively. It is speculated that relatively large molecular weight and unusually narrow polydispersity is difficult, if not impossible, to achieve in a single-step Lewis acid/base reaction product by assuming linear, block, or random oligomer structures. Such structures with narrow polydispersity are prepared when group transfer polymerization technique is used.[13] Possibility of a uniform decomposition of a larger molecule upon dissolution in DMF is also a very unlikely event and thus spontaneous assembly of a dendrite structure is implied. The converging polydispersity to a value of 1 in the smaller M_n components can be explained if they constitute younger generation dendrimers. Figure 3 shows possible structures of the dendrimer and its fragments. These

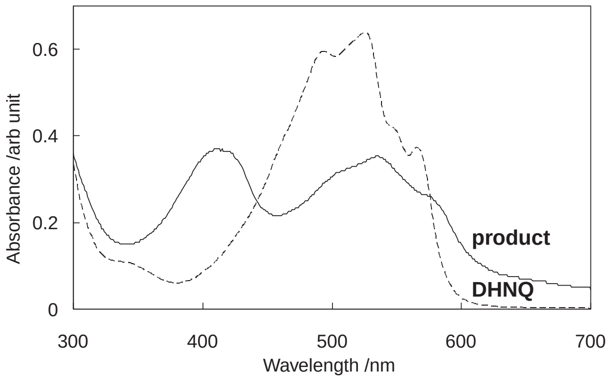

Figure 1. UV–vis spectra of the product and DHNQ in DMF.

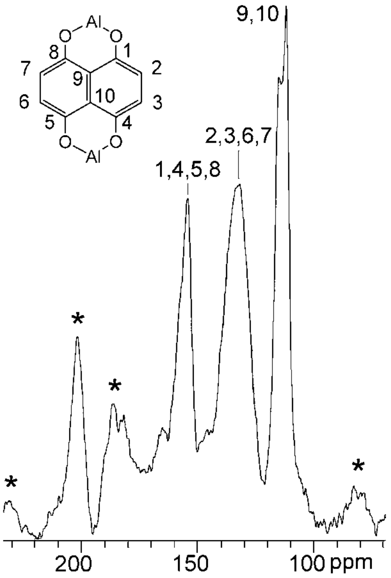

Figure 2. ^{13}C CP/MAS NMR of as-synthesized product. Inset shows the assignments of carbons. Spinning sidebands are labeled with stars.

Table 1. Summary of SEC analysis

Peak No.	M_n[a]	M_m/M_n	Area/%
1	5011	1.133	30.5
2	1954	1.044	38.2
3	1104	1.009	6.9

[a]Molecular weights are based on the calibration of standard polystyrene. Components with M_n < 1000 are omitted.

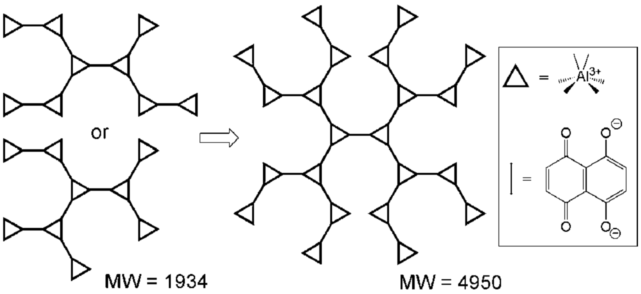

Figure 3. Proposed structures of the dendrimer and its fragments. Molecular weights are calculated using $Al^{3+} = 27$ and $DONQ^{2-} = 188$.

proposed structures are constructed under the following rules; (i) estimate the number of Al^{3+} and $DONQ^{2-}$ that is close to the M_n values in Table 1, (ii) connect them by postulating non-linear structures with high symmetry, (iii) each branch is terminated with the $-Al(OH)_2$ group. Since the structure of the second heaviest component agrees with that of the lower generation of the dendrimer, it is suggested that the dendrite structure expands outward in divergent fashion.[14]

In conclusion, spontaneous assembly of the Al-based dendrite structure is achieved in a biphasic reaction. Further study is needed to prepare and isolate a pure component that may allow structural determination. Since the resulting dendrimer is expected to possess terminal hydroxy groups, other functional groups can be readily tethered, rendering the molecule more practical. We are particularly interested in developing a dual functional fluorescent/hole-transport material for the development of high efficiency organic light-emitting devices.

This work was partly supported by Scientific Frontier Research Project of MEXT, Nippon Sheet Glass Foundation, and Tokyo Ohka Foundation.

References and Notes

1 Recent review articles: a) U. Mueller, M. Schubert, F. Teich, H. Puetter, K. Schierle-Arndt, J. Pastré, *J. Mater. Chem.* **2006**, *16*, 626. b) R. Robson, *J. Chem. Soc., Dalton Trans.* **2000**, 3735.
2 M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2001**, *34*, 319.
3 D. A. Tomalia, A. M. Naylor, W. A. Goddard, III, *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 138.
4 a) T. Uemura, K. Kitagawa, S. Horike, T. Kawamura, S. Kitagawa, M. Mizuno, K. Endo, *Chem. Commun.* **2005**, 5968. b) J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon, K. Kim, *Nature* **2000**, *404*, 982.
5 H. Kishida, H. Matsuzaki, H. Okamoto, T. Manabe, M. Yamashita, Y. Taguchi, Y. Tokura, *Nature* **2000**, *405*, 929.
6 M. J. Plater, M. R. S. J. Foreman, E. Coronado, C. J. Gómez-Garcia, A. M. Z. Slawin, *J. Chem. Soc., Dalton Trans.* **1999**, 4209.
7 M. Yoshizawa, N. Sato, M. Fujita, *Chem. Lett.* **2005**, *34*, 1392.
8 a) N. Satoh, J.-S. Cho, M. Higuchi, K. Yamamoto, *J. Am. Chem. Soc.* **2003**, *125*, 8104. b) M.-S. Choi, T. Aida, T. Yamazaki, I. Yamazaki, *Chem.—Eur. J.* **2002**, *8*, 2668.
9 K. Hayashi, S. Matsuishi, T. Kamiya, M. Hirano, H. Hosono, *Nature* **2002**, *419*, 462.
10 R. Katakura, Y. Koide, *Chem. Lett.* **2005**, *34*, 1448.
11 R. Katakura, Y. Koide, *Inorg. Chem.* **2006**, *45*, 5730.
12 Because commericially available $[AlO(OH)]_n$ is hydrated by unknown number of water molecules, the material was dried by heating at 180 °C under vacuum for 24 h.
13 J. Vraštil, L. Matějka, V. Špaček, M. Večeřa, L. Prokůpek, *Polymer* **2005**, *46*, 11232.
14 D. A. Tomalia, J. M. Fréchet, *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 2719.