

Photoinduced Dithiolation of Fullerene[60] with Dendrimer Disulfide

Yutaka Takaguchi,* Yoshiaki Katayose,[†] Yasushi Yanagimoto, Jiro Motoyoshiya,[‡] Hiromu Aoyama,[‡]
Takatsugu Wakahara,^{††} Yutaka Maeda,^{††} and Takeshi Akasaka*^{††}

Faculty of Environmental Science and Technology, Okayama University, Okayama 700-8530

[†]Faculty of Textile Science and Technology, Shinshu University, Ueda 386-8567

^{††}Center for Tsukuba Advanced Research Alliance, University of Tsukuba, Tsukuba 305-8577

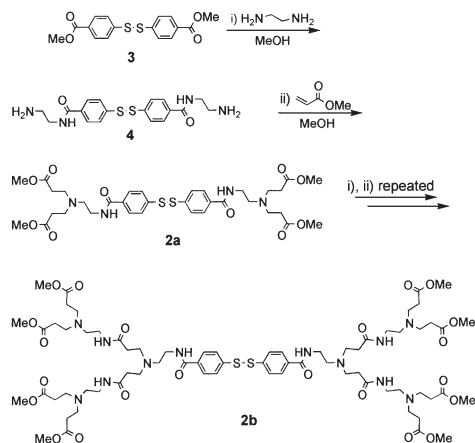
(Received August 13, 2003; CL-030754)

A new fullerodendrimer having fullerene–sulfur bonds as a linkage was prepared by the use of a binary system of organic dichalcogenide. Aggregation of the fullerodendrimer on mica surface was observed by atomic force microscopy (AFM) experiment.

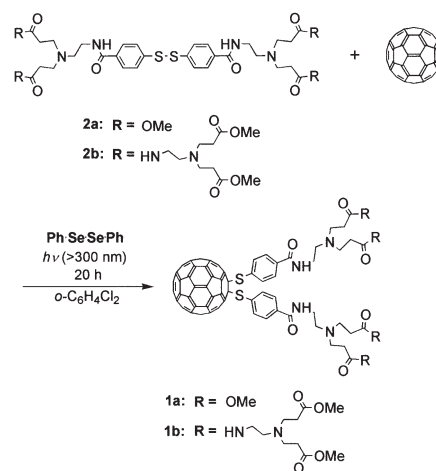
Fullerene-based derivatives have been attracting a great interest in the field of structural and synthetic organic chemistry.¹ In particular, there is an increasing focus on developing applications for fullerene-functionalized dendrimers, fullerodendrimers, because of a variety of interesting features in supramolecular chemistry and materials.² Fullerodendrimers having fullerene–carbon bonds as a linkage between C₆₀ and dendritic wedge have been extensively reported.² Recently, we have described the reversible formation of fullerodendrimers by the use of a Diels–Alder reaction of C₆₀ with anthryl dendron.³ However, much less is known about the fullerene–heteroatom bond within the fullerodendrimer.⁴ In particular, fullerodendrimer containing a fullerene–sulfur bond has never been reported. In the view point of tunability of the property of C₆₀,^{5–7} fullerodendrimer having a fullerene–sulfur bond, might be quite useful. In this context, we have found that the dendrimer disulfide underwent addition reaction with C₆₀ upon photoirradiation. This paper describes the first preparation and characterization of a fullerodendrimer (**1**) having fullerene–sulfur bonds as a linkage. Furthermore, aggregates of **1** on mica surface are also discussed.

Poly(amidoamine) dendrimer disulfide, (**2a**) and (**2b**), were prepared by using a method as previously reported (Scheme 1).⁸

The treatment of bis(4-carbomethoxyphenyl)disulfide (**3**) with ethylenediamine produced a core of dendrimer (**4**), quantitatively. Subsequently, **4** was allowed to react with methyl acryl-



Scheme 1. Syntheses of PAMAM dendrimer disulfides **2a** and **2b**.



Scheme 2. Preparation of fullerodendrimer **1**.

ate to give a dendrimer disulfide **2a** in 70% yield. This two-step process could be repeated to prepare dendrimer **2b** in 92% yield. The structures of **2a** and **2b** were confirmed by ¹H, ¹³C NMR spectroscopies, and MALDI-TOF MS.⁹

Ogawa and Sonoda reported that a binary system of organic dichalcogenides, i.e., a (PhS)₂–(PhSe)₂ system, successfully effects the desired vicinal dichalcogenation of carbon–carbon unsaturated compounds under radical conditions.¹⁰ In order to clarify the utility of their system, we examined photoinduced addition reaction of dendrimer disulfide with fullerene in the presence of diphenyl diselenide as shown in Scheme 2.

In a typical run, a mixture of C₆₀ (24 mg, 0.033 mM), dendrimer disulfide **2b** (250 mg, 0.027 mM), and diphenyl diselenide (51 mg, 163 mM) in *o*-dichlorobenzene (5 mL) was irradiated with a high-pressure mercury lamp ($\lambda > 300$ nm) at room temperature under a nitrogen atmosphere for 20 h to give dithiolation product, fullerodendrimer **1b** (12 mg, 0.005 mM), as brown oil in 16% yield. In contrast, fullerodendrimer **1** was not obtained in the absence of diphenyl diselenide at all. The fullerodendrimer **1** remained quite stable for several months when stored in a dark at room temperature.

The structures of fullerodendrimers **1a** and **1b** were confirmed by means of ¹H and ¹³C NMR, UV–vis, and LD-TOF mass spectroscopic analyses.¹¹ The ¹³C NMR spectrum of fullerodendrimer **1b** shows 19 resonances in the aromatic region (120–140 ppm), of which 15 signals correspond to the sp² carbons for the C₆₀ skeleton. These results clearly indicate that the product has a C_{2v} symmetry. The chemical shift of **1b** at $\delta = 58.4$ is reasonably assigned to the connecting sp³ carbon of C₆₀ framework. The UV–vis spectrum of **1b** in toluene exhibited absorptions at 433 nm, which is known to be a typical absorption in

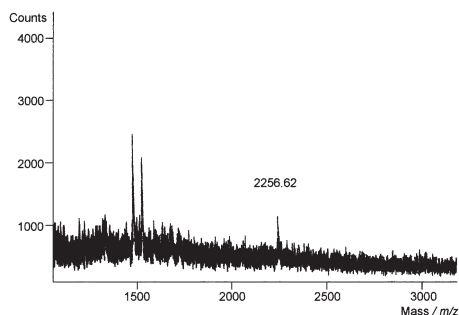


Figure 1. Negative-ion LD-TOF mass spectrum of fullerodendrimer **1b**.

the 1:1 adduct on the 6,6-ring junction.¹² The LD-TOF mass spectrum of **1b** by the use of negative-ion mode showed a molecular ion peak at m/z : 2256.62 (**1b**, $C_{130}H_{110}N_{12}O_{22}S_2$ requires m/z : 2256.47), together with peaks at m/z : 1536.41 ($[M - C_{60}]^-$) and 1488.77 ($[M - 2b/2]^-$) (Figure 1). The fullerodendrimer **1b** has a more negative oxidation potential ($E_{ox}^1 = 0.77$ V vs SCE) than C_{60} ($E_{ox}^1 = 1.12$ V vs SCE) by 0.35 V, although its reduction potential ($E_{red}^1 = -1.10$ V vs SCE) was similar to that of pristine C_{60} .¹³

It is notable that the fullerodendrimer **1b** is readily soluble in acidic water (more than 30 mg/mL at pH 1.50).

To obtain information on the state of aggregation of the dendrimer, we examined the chloroform solution of **1b** on mica surface by atomic force microscopy (AFM) (Nanoscope III, Digital Instruments, Santa Barbara, CA). A chloroform solution of **1b** (1.5 mM) was deposited on freshly cleaved mica under air, and dried with nitrogen stream. The sample was then observed by AFM in the tapping mode of operation with single crystal conventional Si tip. The AFM image showed flat round-shaped objects corresponding to the aggregated **1b**. The size of the aggregates ranges from 100 to 220 nm in diameter and from 3 to 5 nm in height. A typical object in Figure 2 measures 200 nm in diameter and 3.7 nm in height. The aggregation of fullerodendrimer **1b** in chloroform was also observed by dynamic light scattering (DLS; 25 °C, He-Ne laser). The particle size of the aggregate was 45.9 ± 0.2 nm in chloroform solution (1.5 mM). An analogous result has been observed by Nakamura et al.¹⁴

The results described herein show a new class of dendrimer of C_{60} , which attached to poly(amidoamine) dendron wedge via

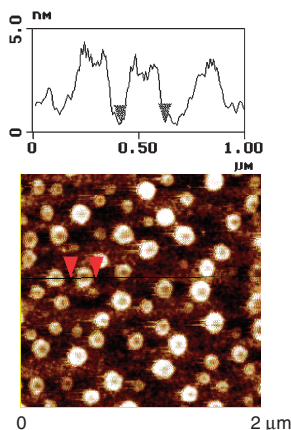


Figure 2. Atomic force microscope image of **1b** on mica and height profile corresponding to the line in the image.

a sulfur-carbon bond. This system is quite useful and versatile for the synthesis of fullerodendrimer, although formation of fullerodendrimer via photoreaction is quite rare. Aggregation of fullerodendrimer **1b** on mica surface might be important for nano-science. Further work is in progress to explore the applications and advantages of fullerodendrimer formed by the photoinduced dithiolation reaction.

This work was partly supported by Research Foundation for Materials Science, Saneyoshi Scholarship Foundation, and the Ministry of Education, Culture, Sports, Science and Technology, Japan (15750036).

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- Selected data for **2a**: 1H NMR ($CDCl_3$) δ 2.43 (t, $J = 6.4$ Hz, 8H), 2.62 (t, $J = 5.6$ Hz, 4H), 2.75 (t, $J = 6.4$ Hz, 8H), 3.53 (s, 12H), 3.55 (q, $J = 5.6$ Hz, 4H), 7.20 (t, $J = 5.6$ Hz, 2H), 7.51 (d, $J = 8.8$ Hz, 4H), 7.84 (d, $J = 8.8$ Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 32.5, 37.2, 48.7, 51.4, 52.7, 126.4, 128.0, 133.5, 139.9, 166.2, 173.0. For **2b**: 1H NMR ($CDCl_3$) δ 2.33–2.42 (m, 32H), 2.63–2.68 (m, 20H), 2.79 (t, $J = 6.4$ Hz, 8H), 3.18 (q, $J = 5.5$ Hz, 8H), 3.55 (q, $J = 5.3$ Hz, 4H), 3.63 (s, 24H), 6.83 (t, $J = 5.5$ Hz, 4H), 7.49 (d, $J = 8.8$ Hz, 4H), 7.83 (t, $J = 5.3$ Hz, 2H), 7.91 (d, $J = 8.8$ Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 32.6, 33.7, 37.0, 37.6, 49.1, 49.2, 51.5, 52.5, 52.8, 126.1, 128.2, 133.6, 139.8, 166.1, 172.2, 172.9; MALDI-TOFMS for $C_{70}H_{10}N_{12}O_{22}S_2$: m/z Calcd. 1536.83 [MH^+]; Found, 1536.07.
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- Selected data for **1a**: 1H NMR ($CDCl_3$) δ 2.42–2.46 (m, 8H), 2.62–2.65 (m, 4H), 2.71–2.78 (m, 8H), 3.53 (s, 12H), 3.55 (q, $J = 5.6$ Hz, 4H), 7.12–7.14 (m, 2H), 7.30 (d, $J = 8.8$ Hz, 4H), 7.49 (d, $J = 8.8$ Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 32.5, 37.2, 48.7, 51.4, 52.7, 61.7, 125.9, 126.5, 127.2, 127.5, 128.0, 128.7, 129.5, 129.7, 130.0, 131.5, 132.3, 132.6, 133.5, 133.9, 134.4, 135.6, 139.2, 139.8, 140.0, 166.2, 173.0; LD-TOFMS for $C_{94}H_{46}N_4O_{10}S_2$: m/z Calcd. 1455.49 [M^-]; Found, 1455.94. For **1b**: 1H NMR ($CDCl_3$) δ 2.38–2.44 (m, 32H), 2.66–2.69 (m, 20H), 2.80–2.82 (m, 8H), 3.19–3.20 (m, 8H), 3.49–3.52 (m, 4H), 3.64 (s, 24H), 6.77–6.83 (m, 4H), 7.43 (d, $J = 7.2$ Hz, 4H), 7.75–7.77 (m, 2H), 7.85 (d, $J = 7.2$ Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 32.6, 33.7, 37.0, 37.6, 49.1, 49.2, 51.5, 52.5, 52.8, 58.4, 126.1, 126.2, 127.2, 127.7, 128.0, 128.3, 129.1, 129.5, 129.9, 130.5, 131.5, 132.3, 132.6, 133.7, 133.9, 134.4, 135.6, 139.2, 139.9, 166.2, 172.3, 173.0; LD-TOFMS for $C_{130}H_{110}N_{12}O_{22}S_2$: m/z Calcd. 2256.47 [M^-]; Found, 2256.62.
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