# Photoinduced Dithiolation of Fullerene[60] with Dendrimer Disulfide

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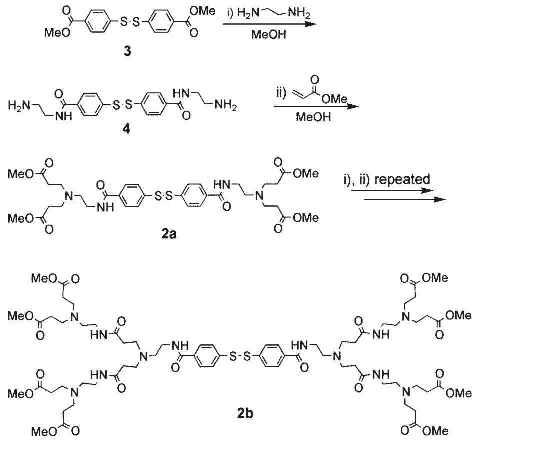
A new fullerodendrimer having fullerene–sulfur bonds as a linkage was prepared by the use of a binary system of organic dichalcogenide. Aggregation of the fullerodendrimer on mica surface was observed by atomic force microscopy (AFM) experiment.

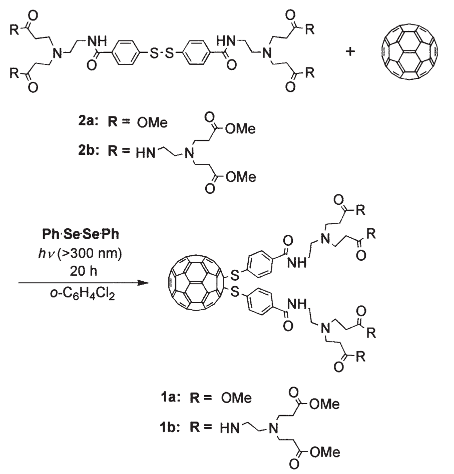
Fullerene-based derivatives have been attracting a great interest in the field of structural and synthetic organic chemistry.[1] In particular, there is an increasing focus on developing applications for fullerene-functionalized dendrimers, fullerodendrimers, because of a variety of interesting features in supramolecular chemistry and materials.[2] Fullerodendrimers having fullerene–carbon bonds as a linkage between $C_{60}$ 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 $C_{60}$ 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 $C_{60}$,[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 $C_{60}$ 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 acrylate 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 $^1$H, $^{13}$C NMR spectroscopies, and MALDI-TOF MS.[9]



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



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

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 $C_{60}$ (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 $^1$H and $^{13}$C NMR, UV–vis, and LD-TOF mass spectroscopic analyses.[11] The $^{13}$C NMR spectrum of fullerodendrimer **1b** shows 19 resonances in the aromatic region (120–140 ppm), of which 15 signals correspond to the sp$^2$ carbons for the $C_{60}$ 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 sp$^3$ carbon of $C_{60}$ framework. The UV–vis spectrum of **1b** in toluene exhibited absorptions at 433 nm, which is known to be a typical absorption in

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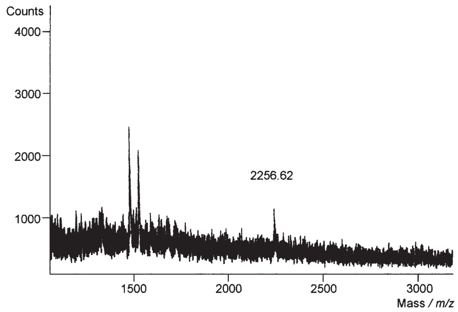

**Figure 1.** Negative-ion LD-TOF mass spectrum of fullerodendrimer **1b**.

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 ($[M - \mathbf{2b}/2]^-$) (Figure 1). The fullerodendrimer **1b** has a more negative oxidation potential ($E^1_{ox} = 0.77$ V vs SCE) than $C_{60}$ ($E^1_{ox} = 1.12$ 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 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.

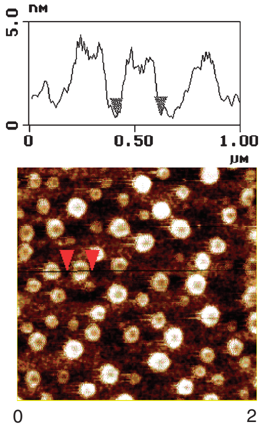

**Figure 2.** Atomic force microscope image of **1b** on mica and height profile corresponding to the line in the image.

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9 Selected data for **2a**: $^1$H NMR ($CDCl_3$) $\delta$ 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 ($CDCl_3$) $\delta$ 32.5, 37.2, 48.7, 51.4, 52.7, 126.4, 128.0, 133.5, 139.9, 166.2, 173.0. For **2b**: $^1$H NMR ($CDCl_3$) $\delta$ 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 ($CDCl_3$) $\delta$ 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 $C_{70}H_{110}N_{12}O_{22}S_2$: $m/z$ Calcd. 1536.83 [MH$^+$]; Found, 1536.07.

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11 Selected data for **1a**: $^1$H NMR ($CDCl_3$) $\delta$ 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 ($CDCl_3$) $\delta$ 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**: $^1$H NMR ($CDCl_3$) $\delta$ 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 ($CDCl_3$) $\delta$ 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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