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Reversible Binding of C_{60} to an Anthracene Bearing a Dendritic Poly(amidoamine) Substituent to give a Water-Soluble Fullerodendrimer[**]

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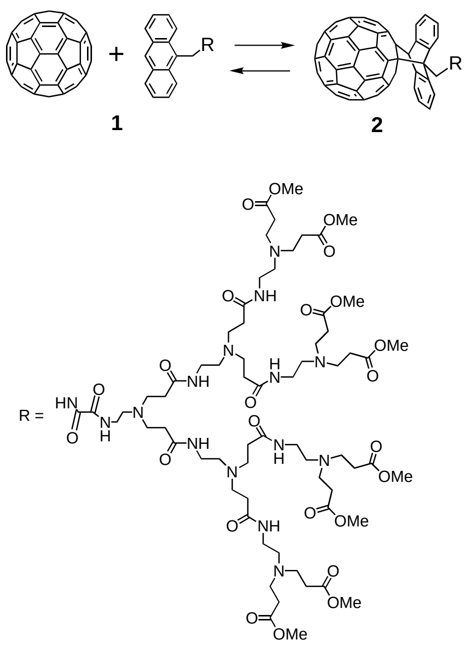
Fullerene-based compounds are attracting much interest in the fields of structural and synthetic organic chemistry.[1–3] In particular, there is an increasing focus on developing applications for fullerene-functionalized dendrimers (fullerodendrimers), because of a variety of interesting features in supramolecular chemistry and materials.[1, 2] Although a number of synthetic techniques have been devised, [4+2] cycloaddition proved to be one of the most expeditious methods for selective functionalization of [60]fullerene at the 6,6-ring junctions.[4] Several such reactions of C_{60} with anthracenes have been described.[5–7] However, the formation of fullerodendrimers by a Diels–Alder reaction of C_{60} with anthracene derivatives has never been reported. Recently, we described the synthesis, characterization, and photodimerization of a poly(amidoamine) dendron with an anthracene moiety at the focal point.[8] During our studies on the reactivity of this anthracene bearing a dendritic substituent, we found that it underwent reversible Diels–Alder reaction with C_{60}. Although a few examples of fullerodendrimers with amide dendrons have been reported, much less is known about the chemistry of poly(amidoamine) dendrimer grafted to C_{60}.[9] Here we describe the synthesis and characterization of a poly(amidoamine) dendron with C_{60} at the focal point. This fullerodendrimer also represents a new class of water-soluble fullerenes and acts as photosensitizer to generate singlet oxygen in water. To our knowledge, the only fullerodendrimer with reversible formation of bonds between C_{60} and the dendrimer is an iridium complex reported by Catalano et al.[10]

A mixture of C_{60} and dendron **1**[8] (1 equiv) in *o*-dichlorobenzene was irradiated with a high-pressure mercury lamp ($\lambda > 300$ nm) at room temperature under a nitrogen atmosphere for 1 h. The initial purple color of the solution became red as the reaction proceeded. After evaporation under reduced pressure below 60 °C, the products were separated by HPLC (LC 918, Japan Analytical Industry, Co. Ltd.) on gel-permeation columns (Jaigel 2H + 1H) with chloroform as eluent to give the fullerodendrimer **2** as a brown oil in 21% yield (Scheme 1). Notably, **2** is readily soluble in methanol, and hence unconsumed C_{60} was easily removed by filtration after the reaction. Fullerodendrimer **2** remained stable for several weeks when stored at −10 °C. The addition reaction was also conducted by heating at 45 °C for 4 d in *o*-dichlorobenzene in the dark to give **2** in 12% yield. When fewer equivalents of anthracenyl dendron **1** were used, the



Scheme 1. Reversible Diels–Alder reaction of C_{60} and **1**.

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equilibrium shifted towards the starting materials, and product yields were lower.

The structure of **2** was confirmed by ^{1}H and ^{13}C NMR and UV/Vis spectroscopy, and laser desorption ionization time-of-flight (LD-TOF) mass spectrometry.[11] The ^{13}C NMR spectrum of **2** shows 36 signals in the sp^2 region, which indicate that the product has a C_s symmetry and that cycloaddition occurred at the 6,6-ring junction, as for anthracene adducts of C_{60} reported so far.[5–7] The signals of **2** at $\delta = 59.0$, 65.8, 74.9, and 75.8 are reasonably assigned to the bridging sp^3 carbon atoms. The UV/Vis spectrum of **2** in toluene exhibited absorptions at 434 and 702 nm; the former is typical of a 1:1 adduct at the 6,6-ring junction.[6] The LD-TOF mass spectrum of **2** in the negative-ion mode (Figure 1) showed a molecular ion peak at $m/z = 2414.22$ ($C_{141}H_{127}N_{15}O_{24}$ requires $m/z = 2414.62$). As was observed for [4+2] cycloadducts of C_{60},[5a] the fullerodendrimer **2** has a more negative reduction potential ($E^1_{\mathrm{red}} = -1.25$ V) than C_{60} ($E^1_{\mathrm{red}} = -1.12$ V).

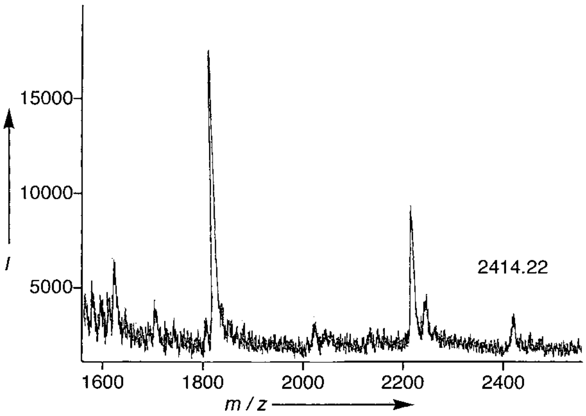

Figure 1. Negative-ion LD-TOF mass spectrum of fullerodendrimer **2**. I = intensity.

It is well known that adducts of C_{60} and anthracene undergo retro-Diels–Alder reactions. To clarify the utility of anthracenyl dendron **1** as a fullerene reservoir, we investigated the possibility of the retroreaction. Heating **2** in methanol at 45 °C for 12 h gave the component molecules C_{60} and dendron **1** in 89 and 87 % yield, respectively. Thus, the reaction is reversible, and there is an equilibrium between bond-forming and dissociation reactions.

It is notable that the fullerodendrimer **2** is readily soluble in acidic water: Saturated concentrations of **2** in H_2O are 20.5 (pH 1.50), 2.19 (pH 5.46), and 0.038 mM (pH 6.51). We investigated photophysical and photochemical properties of **2** in water. The transient spectra observed by laser excitation of **2** in deaerated water are shown in Figure 2A. The absorption peak at 700 nm is assigned to the absorption of the triplet excited state of **2**, because this peak is in good agreement with the triplet–triplet absorption of C_{60} adducts.[12] From the decay at 700 nm, the triplet lifetime was evaluated to be 56 µs. On addition of O_2, the decay rate increased (Figure 2B), and this indicates that energy transfer from the triplet state of **2** to O_2 takes place to produce singlet oxygen. From the decay in O_2-saturated water, the rate constant for energy transfer from the triplet state of **2** to O_2 was found to be 1.3×10^9 mol^{-1} dm^3 s^{-1}. The formation of singlet oxygen was confirmed by the observation of its emission at 1280 nm in D_2O (Figure 2C), from which the quantum yield of singlet oxygen was estimated to be 0.45 after correcting the low O_2 concentration in D_2O by comparison with a standard solution in toluene.[13]

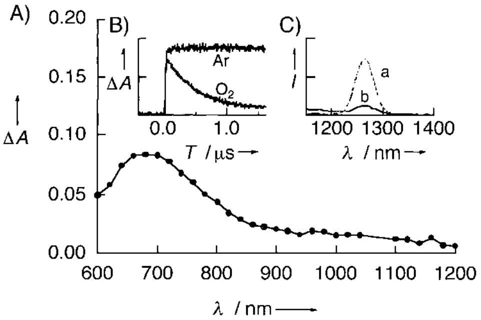

Figure 2. A) Transient absorption spectra observed by nanosecond laser (532 nm) excitation of **2** in deaerated water. B) Time profiles at 700 nm in the absence and presence of O_2. C) Emission spectra in the NIR region; a) C_{60} in toluene; b) **2** in D_2O. A = absorbance.

We have demonstrated the first example of reversible formation of a fullerodendrimer in a Diels–Alder reaction. This system is useful for the synthesis of fullerodendrimers and as a fullerene reservoir. The use of the photoexcited state of this water-soluble fullerodendrimer as a singlet-oxygen sensitizer was also investigated. Potentially important practical applications of this fullerodendrimer are as a removable solubilizing group for fullerenes and as a biologically active agent that releases C_{60} intracellularly. Further work is in progress to explore the applications and advantages of the reversible formation of fullerodendrimers.

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[11] ^{1}H NMR (400 MHz, [D$_8$]toluene): $\delta = 2.17-2.63$ (m, 24H), 2.32–2.83 (m, 46H), 3.29–3.40 (m, 14H), 3.43 (d, $J = 1.6$ Hz, 2H), 3.48 (s, 24H), 3.48–3.57 (m, 8H), 6.91–7.95 (m, 9H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 32.7$, 33.8, 34.0, 36.1, 37.1, 37.5, 49.2, 49.9, 51.65, 51.67, 52.2, 52.6, 52.9, 55.0, 59.0, 65.9, 74.7, 75.6, 123.7, 125.2, 126.8, 127.8, 128.4, 129.2, 136.5, 137.3, 138.8, 140.1, 141.39, 141.4, 141.6, 141.9, 142.0, 142.1, 142.59, 142.60, 142.62, 142.64, 142.9, 144.5, 144.6, 145.0, 145.18, 145.22, 145.33, 145.37, 145.40, 145.9, 146.1, 146.2, 146.4, 146.5, 152.4, 155.8, 159.52, 159.59, 172.2, 172.4, 173.1; UV/Vis (toluene): $\lambda_{\max}$ (ε) = 434.4 (1500), 702.0 nm (153); LD-TOF MS: C$_{141}$H$_{127}$N$_{15}$O$_{24}$: *m/z* calcd: 2414.62 [*M*]$^-$; found: 2414.22.

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Stereospecific Interconversion between *cis* and *trans* 2,3-Epoxysulfides[**]

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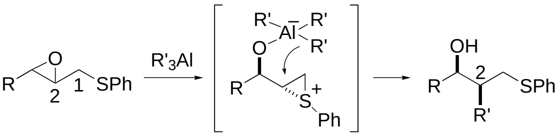
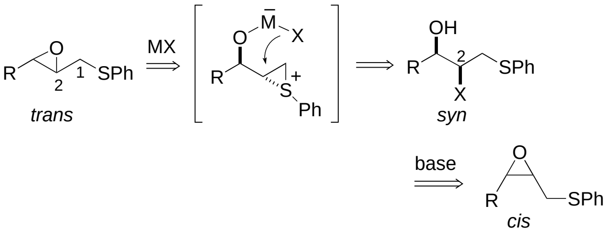
Ring-opening reactions of epoxides with nucleophiles provide a useful method for the stereoselective synthesis of organic compounds.[1] In this type of transformation, the relative stereochemistry of the products reflects that of the parent epoxides, which are usually prepared in the *cis* or *trans* forms from the corresponding *Z* or *E* olefins, respectively.[2] In this connection, however, the interconversion between the *cis* and *trans* epoxides, which contrasts with the configurational isomerization of olefins that is possible by some methods, has not been reported.[3]

Recently, Saigo and co-workers and our group have independently reported that the reaction of a 1-(phenylthio)-2,3-epoxyalkane with an organoaluminum reagent resulted in regio- and stereoselective substitution at C2, with double inversion of configuration (Scheme 1).[4, 5]



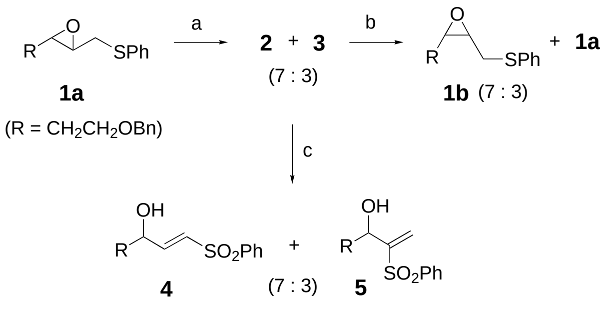
Scheme 1. Proposed reaction mechanism of the alkyl substitution reaction with double inversion of the configuration.

The characteristic stereochemical results, which can be rationalized by assuming an episulfonium ion intermediate, have led us to design a new method for the interconversion between *cis* and *trans* epoxides (Scheme 2): the reaction of a *trans* 2,3-epoxysulfide with a metal halide should afford a *syn* 2-halo-3-alkanol with double inversion of configuration at C2. On treatment with a base, the resulting *syn* halohydrin would undergo an intramolecular S$_N$2 reaction at C2 to yield the corresponding *cis* 2,3-epoxysulfide. The application of a similar procedure to a simple *trans* epoxide merely results in the recovery of the same *trans* epoxide via an *anti* halohydrin intermediate.[6]



Scheme 2. Interconversion between *cis* and *trans* epoxides (X = halogen).

First, *trans*-5-benzyloxy-2,3-epoxy-1-phenylthiopentane (**1a**) was treated with MgBr$_2\cdot$OEt$_2$[7] at 0 °C in toluene, and an inseparable 7:3 mixture of bromohydrins **2** and **3** was obtained (Schemes 3 and 4). The crude product was treated with potassium carbonate in methanol[8] to give a 7:3 mixture of *cis*-epoxide **1b** and *trans*-epoxide **1a**. On the other hand, treatment of the crude bromohydrins **2** and **3** with



Scheme 3. Reagents and conditions: a) MgBr$_2\cdot$OEt$_2$, toluene, 0 °C; b) K$_2$CO$_3$, MeOH; c) 1. MCPBA, 2. DBU. MCPBA = *meta*-chloroperbenzoic acid; DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene.

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