# Photooxidation of Olefins Sensitized by Bisazafullerene $(C_{59}N)_2$ and Hydroazafullerene $C_{59}HN$: Product Analysis, Emission of Singlet Oxygen, and Transient Absorption Spectroscopy

Nikos Tagmatarchis and Hisanori Shinohara*

*Department of Chemistry, Nagoya University, Nagoya 464-8602, Japan*

Mamoru Fujitsuka and Osamu Ito*

*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Katahira,*
*Aoba-ku, Sendai 980-8577, Japan*

*nori@nano.chem.nagoya-u.ac.jp*

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The photooxidation reactions of olefins sensitized by the excited triplet states of bisazafullerene $(C_{59}N)_2$ and hydroazafullerene $C_{59}HN$ have been studied. Oxidation yields were compared with those of pristine $C_{60}$. The singlet oxygen yields are also determined directly from the emission intensities, which are in good agreement with the oxidation yields. The triplet states of $(C_{59}N)_2$ and $C_{59}HN$ have been identified by the time-resolved spectroscopic method by observing the triplet−triplet absorption spectra, which decay in the presence of oxygen. It has been proven that $(C_{59}N)_2$ and $C_{59}HN$ have the ability to sensitize the reactions via singlet oxygen in about half of the efficiency of that of pristine $C_{60}$. For both azafullerenes, the triplet lifetimes are shorter than that of pristine $C_{60}$, which may be related to the nitrogen atom embedded in the $C_{60}$ moiety.

## Introduction

The incorporation of a nitrogen atom into the fullerene skeleton strongly perturbs not only the structural character of the parent molecule but also its electronic and physical properties.[1,2] The macroscopic synthesis of the simplest azafullerene, namely, $C_{59}N$, was achieved by a three-step organic reaction sequence starting from $C_{60}$.[3,4] The resulting azafullerenyl radical $C_{59}N^{\bullet}$, a product of the difference in valence between a tetravalent carbon atom and a trivalent nitrogen, is a highly reactive species. Consequently, the radical dimerizes yielding bisazafullerene $(C_{59}N)_2$.[5] If the synthetic procedure is slightly modified, hydroazafullerene $C_{59}HN$ is formed (Figure 1).[6,7]

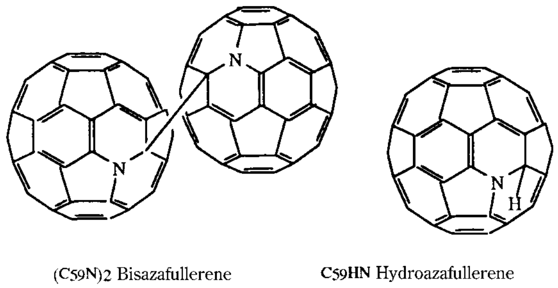

**Figure 1.** Molecular structures of bisazafullerene $(C_{59}N)_2$ and hydroazafullerene $C_{59}HN$.

The studies on the photochemical and physical properties of fullerenes shed light on their electronic structures and photoexcited states and can lead to their potential applications in materials science ranging from superconductivity to nanostructured devices.[8−10] Although such studies have been performed for various fullerenes and their derivatives,[11,12] only a few preliminary results have been reported so far for the family of the azafullerene analogues,[13] mainly because of the difficulty in their synthesis. Also, detailed photochemical and physical studies on the dimeric structures of $(C_{60})_2$ and $(C_{60})_2O$ have already appeared in the literature.[14,15]

Very recently, we showed from the product analysis of the reaction mixture that both $(C_{59}N)_2$ and $C_{59}HN$ photosensitize the reaction of olefins with oxygen.[16] In that study, however, the generation of singlet oxygen upon

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* Corresponding authors. H. Shinohara: fax, +81-52-789-3660. O. Ito: fax, +81-22-217-5608; e-mail, ito@tagen.tohoku.ac.jp.

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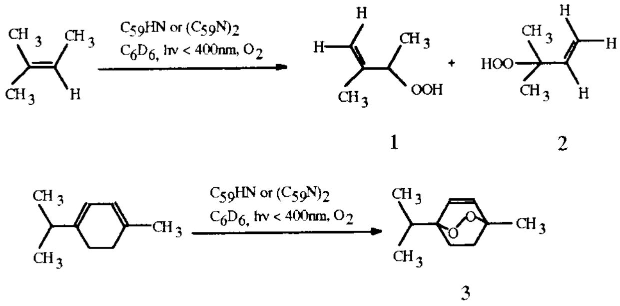

**Figure 2.** Ene and Diels–Alder photooxygenations of 2-methyl-2-butene and α-terpinene in the presence of $(C_{59}N)_2$ or $C_{59}HN$ as a sensitizer.

UV irradiation of azafullerenes was presumed only by the formation and subsequent identification of the corresponding products in the examined photochemical reactions (Figure 2). In this article, we present for the first time direct experimental evidence for the formation of singlet oxygen based on the transient absorption spectroscopy of these azafullerenes. From the transient absorption spectra in the visible and near-IR regions, the triplet-state formations were identified and their lifetimes were estimated as well as their quenching rates by oxygen. These spectroscopic data were compared with those of pristine $C_{60}$. In addition, the observation of luminescence in the near-IR region further confirms the generation of singlet oxygen. Hydroperoxides **1** and **2** as well as endoperoxide **3** were formed upon UV irradiation of 2-methyl-2-butene and α-terpinene, respectively, in the presence of azafullerenes. The yields of conversion of these photooxygenations were compared with those obtained when $C_{60}$ was used as the photosensitizer, and the results were discussed in terms of the efficiency of the singlet oxygen production between the azafullerenes and $C_{60}$. Finally, steady-state absorption measurements were performed before and after the laser irradiation of these azafullerenes to see whether or not transformation to different species occurred during the light irradiation measurements.

## Experimental Section

**Materials.** The synthesis of bisazafullerene $(C_{59}N)_2$ and hydroazafullerene $C_{59}HN$ was accomplished in a three-step sequence starting from $C_{60}$ and has already been reported.[5–7] The materials were purified by high-performance liquid chromatography (5PYE column, toluene as the eluent, 10 mL/min flow rate) and characterized by elemental methods. Soot containing pristine $C_{60}$ was obtained by direct-current arc discharge of graphite/metal composite rods that were used for the production of various endohedral metallofullerenes, which was followed by Soxhlet extraction and HPLC purification, as previously described.[17] The photooxygenations of 2-methyl-2-butene and α-terpinene were performed with a UV lamp equipped with a Kapton filter (cutoff wavelength < 400 nm), as described previously.[16] All other commercial materials were used as received and were of the best commercial grade available.

**Spectroscopic Measurements.** All measured samples were placed in a quartz cell (1 × 1 cm) and deaerated by bubbling Ar through the solution for 15 min. Transient absorption spectra in the near-IR region (600–1600 nm) were measured by using the third-harmonic generation (THG, 355 nm) of a Nd:YAG laser (Spectra-Physics, Quanta-Ray GCR-130, 6 ns fwhm) as an excitation source. Probing light from a pulsed Xe lamp was detected with a Ge avalanche photodiode (Hamamatsu Photonics, B2834). For the measurements in the visible region (400–800 nm), a Si–PIN photodiode (Hamamatsu Photonics, S1722–02) was used as the detector.

**Luminescence Measurements.** Emission of singlet oxygen was observed by the laser excitation of 514 nm of azafullerenes in the $O_2$-saturated toluene solution. An Ar-ion laser (Spectra-Physics, BeamLok 2060-10-AS, ca. 200 mW) was used as the excitation source. InGaAs, a PIN photodiode (New Focus, 2153) was used as a detector in the near-IR region.

**Steady-State Absorption Spectra.** Absorption spectra in the visible and the near-IR regions were measured with a JASCO V-570DS spectrometer at room temperature.

**Table 1. Sensitized Photooxidation Yields of 2-Methyl-2-butene and α-Terpinene and Excited Triplet-State Properties of Hydroazafullerene $C_{59}HN$ and Bisazafullerene $(C_{59}N)_2$ As Compared with Those of Pristine $C_{60}$**

| | $C_{59}HN$ | $(C_{59}N)_2$ | $C_{60}$ |
|---|---|---|---|
| sensitized oxidation yield of 2-methyl-2-butene (%)[a] | 90 | 85 | 95 |
| sensitized oxidation yield of α-terpinene (%)[a] | 80 | 70 | 95 |
| triplet-state lifetime $\tau_T$ (μs)[b] | 5 | 10 | 40 |
| quenching rate constant $k_{O2}$ ($M^{-1}$ $s^{-1}$)[c] | $2.0 \times 10^9$ | $2.0 \times 10^9$ | $1.9 \times 10^9$ |
| singlet oxygen yield $\Phi_{IO2}$[d] | $0.48 \pm 0.05$ | $0.48 \pm 0.05$ | $0.96 \pm 0.02$ |
| triplet–triplet absorption (nm) | 750 | 680 | 740 |

[a] Yields were determined by integrating the appropriate area of the corresponding olefinic protons on the $^1H$ NMR spectrum of the reaction mixture of the sensitized photooxidation, and they were optimized regarding the molecular concentration of the azafullerene photosensitizer (1 order of magnitude higher as compared to those of $C_{60}$). [b] In deaerated toluene solution, $\tau_T = 1/k_T$. [c] In oxygenated toluene solution. [d] From luminescence measurements $\Phi_{isc} \approx \Phi_{IO2}$.

## Results and Discussion

**Photosensitization of Olefins.** When a deuterated benzene solution of 2-methyl-2-butene or α-terpinene was irradiated under a stream of pure oxygen in the presence of either bisazafullerene $(C_{59}N)_2$ or hydroazafullerene $C_{59}HN$, the identification of the corresponding peroxygenated products was carried out by means of $^1H$ NMR analysis of the reaction mixture (Figure 2). The ene photosensitization reaction of 2-methyl-2-butene with singlet oxygen afforded hydroperoxides **1** and **2** in the presence of both azafullerenes. As expected, the secondary and tertiary hydroperoxides were formed in an almost 1:1 ratio, which means that there is no Markovnikov-type effect upon the oxygen addition, as with the case when conventional sensitizers were used. The total yields of **1** and **2** are summarized in Table 1, in which the yield obtained via $^3(C_{59}HN)^*$ is slightly higher than that via $^3[(C_{59}N)_2]^*$, although they are both slightly lower than those obtained when $C_{60}$ was used as the photosensitizer (see footnote *a* in Table 1). Importantly, a considerable amount of $(C_{59}N)_2$ was found to be transformed into monomeric hydroazafullerene species as well as oxygenated adducts under the applied UV irradiation conditions, as revealed by HPLC analysis, denoting the ease of the C–C interdimer bond disruption. This is not surprising as we already expected that, as soon as the first excited singlet state was populated, some fractions of $(C_{59}N)_2$ could intersystem-cross to the triplet state and subsequently generate singlet oxygen while some others might follow the pathway that leads to the breakage of the dimeric structure (competitive process, see discussion below).

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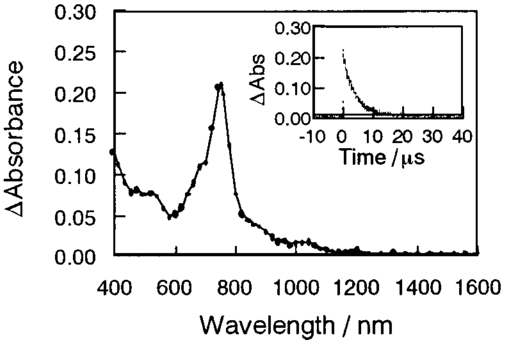

**Figure 3.** Transient absorption spectrum of $C_{59}HN$ in toluene solution observed by 355 nm laser irradiation. Inset: absorption-time profile of a transient absorption band at 750 nm of $^3[C_{59}HN]^*$.

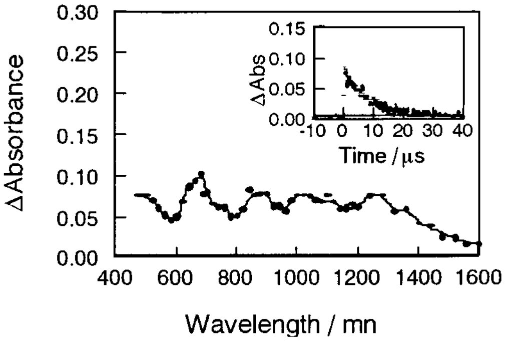

**Figure 4.** Transient absorption spectrum of $(C_{59}N)_2$ in toluene solution observed by 355 nm laser irradiation. Inset: absorption-time profile of a transient absorption band at 680 nm of $^3[(C_{59}N)_2]^*$.

Similarly, the Diels–Alder photooxygenation of α-terpinene did not proceed smoothly. Only after prolonged irradiation periods (i.e., 1 h) and/or higher molecular concentrations of the azafullerenes (i.e., 0.01 mol %) was the formation of endoperoxide **3** achieved in relatively high yield and decreased in the order of $C_{60} > C_{59}HN > (C_{59}N)_2$ (Table 1). However, optimum conversion of the examined alkenes to the corresponding peroxygenated products was achieved when the molecular concentration of azafullerenes was at least 1 order of magnitude higher than that of $C_{60}$. Finally, when we repeated the ene and Diels–Alder photoxygenations in the presence of a catalytic amount of 1,4-diazabicyclo[2.2.2]octane (DABCO),[18] we hardly observed any progress of the reactions. This further verifies that singlet oxygen is the species responsible for the photooxygenations of these alkenes because DABCO is well-known as a singlet oxygen quencher.[18] In contrast, when $C_{60}$ was used as the photosensitizer, both 2-methyl-2-butene and α-terpinene were transformed quantitatively into the corresponding products; more importantly, not only was a smaller amount of sensitizer used for the transformation but a shorter reaction time was also applied (Table 1).[19,20] This is consistent with our experimental findings from the transient absorption spectroscopy study regarding the lower yields of singlet oxygen production of azafullerenes compared to that of $C_{60}$ (see results below).

**Excited Triplet States.** Irradiation of a toluene solution of hydroazafullerene $C_{59}HN$ with the nanosecond laser light at 355 nm generated transient absorption bands at 750 nm along with a shoulder at 1050 nm (Figure 3). By the photoexcitation, the lowest singlet excited state was generated first, followed by intersystem crossing to the corresponding triplet excited state. Since the transient absorption bands were observed in the microsecond range (inset in Figure 3), they can be assigned to the triplet–triplet absorption bands. In deaerated toluene solutions, the lifetime of the triplet state was estimated to be 5 μs. In the presence of oxygen, all these transient bands were quenched, and therefore it was confirmed that these bands are attributable to the triplet excited state of hydroazafullerene, namely, $^3[C_{59}HN]^*$. The rate of the quenching was subsequently calculated to be $2 \times 10^9\ M^{-1}\ s^{-1}$. The overall transient spectrum is very similar to that of the triplet–triplet absorption of $C_{60}$, indicating that the presence of nitrogen in the fullerene skeleton has little effect on the triplet absorption spectrum. Moreover, oxygen quenches the triplet excited state of $C_{60}$ as well as the triplet states of other structurally related iminofullerenes with similar rate constants.[21,22]

For $(C_{59}N)_2$, the transient absorption spectrum is much different from that of $C_{59}HN$. There is a maximum transient absorption band at 680 nm (Figure 4). This absorption maximum was blue-shifted with respect to those of $C_{60}$ and hydroazafullerene, as previously described. In addition, the appearance of other absorption bands and shoulders at 500, 850, 1020, and 1230 nm strongly supports the hypothesis that interactions exist between azafullerenyl $C_{59}N$ cages in the triplet states. There are 61 π-electrons in each $C_{59}N$ radical (i.e., this radical combines in pairs to form bisazafullerene $(C_{59}N)_2$), and consequently, it is isoelectronic to the π-radical anion of $C_{60}$. Moreover, the replacement of a carbon atom with a nitrogen atom resulted in the reduction of a [6, 6] double bond in the parent $C_{60}$ skeleton and, therefore, in a smaller conjugated area. Thus, interaction between two $C_{59}N$ moieties may shift the triplet absorption to longer wavelengths.

The lifetime of $(C_{59}N)_2$ at the 680 nm band was estimated to be twice as long as that of $C_{59}HN$ and decays in 10 μs in the absence of oxygen. In oxygenated toluene solution, the second-order rate constant was calculated to be identical to that of $C_{59}HN$, $2 \times 10^9\ M^{-1}\ s^{-1}$ (inset in Figure 4), a value typical for the triplet excited states of aromatic hydrocarbons. For both azafullerenes, the triplet lifetimes are shorter than that of $C_{60}$ or even some fulleropyrrolidene derivatives.[23]

As mentioned previously, the triplet states of both azafullerenes, namely, $^3[(C_{59}N)_2]^*$ and $^3[C_{59}HN]^*$, were efficiently quenched by molecular oxygen. Generation of the singlet oxygen was further confirmed by the observation of the luminescence in the near-IR region (Figure 5). The luminescence intensity of the singlet oxygen derived from either $^3[(C_{59}N)_2]^*$ or $^3[C_{59}HN]^*$ is less than

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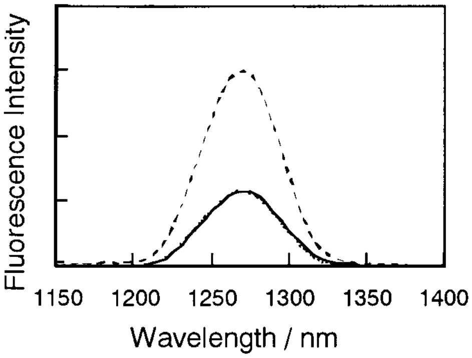

**Figure 5.** Luminescence spectra of singlet oxygen in oxygen-saturated toluene solution generated by Ar ion-laser excitation (matched at 514 nm) of $(C_{59}N)_2$ (solid line), $C_{59}HN$ (dotted line), and pristine $C_{60}$ (dashed line) as a standard.

half than that derived from pristine $C_{60}$ (the absorbance was matched at the excitation wavelength at 514 nm). Subsequently, the quantum yield of singlet oxygen ($\Phi_{1O2}$) was estimated to be 0.48 for both $C_{59}HN$ and $(C_{59}N)_2$, taking $\Phi_{1O2} = 0.96$ for $C_{60}$ as a standard.[22]

The quantum yield for the singlet oxygen generation $\Phi_{1O2}$ can be expressed with the following equation:

$$\Phi_{IO2} = \Phi_{isc}\times(k_{O2}[O_2]/(k_T + k_{O2}[O_2]))$$

where $\Phi_{isc}$ is the quantum yield for the intersystem crossing, $k_{O2}$ is the bimolecular quenching rate constant of the triplet state by oxygen, $[O_2]$ is the concentration of oxygen, and $k_T$ is the decay rate of the triplet state in the absence of oxygen. Thus, the term $(k_{O2}[O_2]/(k_T + k_{O2}[O_2]))$ corresponds to the efficiency of the singlet oxygen generation. It is worth mentioning at this point that in the nonpolar toluene employed in the present study, any electron-transfer process with oxygen can be neglected for bimolecular reactions. For hydroazafullerene $C_{59}HN$, $k_T$ and $k_{O2}[O_2]$ are $2 \times 10^5$ and $2 \times 10^7$ s$^{-1}$, respectively; then, the term $(k_{O2}[O_2]/(k_T + k_{O2}[O_2]))$ is equal to 0.99. Therefore, $\Phi_{isc}$ was evaluated to be 0.48. As for the case of bisazafullerene $(C_{59}N)_2$, the terms $k_T$ and $k_{O2}[O_2]$ are $1 \times 10^5$ and $2 \times 10^7$ s$^{-1}$, respectively. Therefore, $(k_{O2}[O_2]/(k_T + k_{O2}[O_2]))$ is equal to 0.99, and subsequently, in a similar way as previously performed, the value of $\Phi_{isc}$ for $(C_{59}N)_2$ is equal to 0.48. At this point, it has yet to be considered to what extent the lower intersystem-crossing quantum yield for azafullerenes should be attributed to the introduction of nitrogen into the fullerene skeleton. The resultant perturbation of the electronic structure of the materials and/or a different pathway they follow from their singlet excited states (i.e., formation of azafullerenyl radicals) may contribute independently to the intersystem-crossing quantum yield.

**Photostability.** The UV−vis−NIR absorption spectra of $(C_{59}N)_2$ and $C_{59}HN$ have previously been reported and extensively analyzed.[5−7] We found that under the experimentally applied conditions for the current photochemical studies, the steady-state absorption spectra remain unchanged after the laser irradiation (see Supporting Information). In the transient absorption spectra, it has been presumed that $C_{59}HN$ is quite stable under laser irradiation, as the sharp transient absorption bands were observed. This implies that $(C_{59}N)_2$ was not accumulated by the photolysis of $C_{59}HN$, as $(C_{59}N)_2$ shows broad transient bands (Figure 4). In the case of $(C_{59}N)_2$, on the other hand, it has already been shown by ESR studies that the interdimer C−C bond of bisazafullerene $(C_{59}N)_2$ was broken either photochemically or thermally.[24−26] There are two possible paths for the interdimer C−C bond cleavage of $(C_{59}N)_2$ upon its excitation: the formation of $C_{59}N^\bullet$ takes place via the excited singlet state of $(C_{59}N)_2$ immediately after excitation or via the triplet excited state of $(C_{59}N)_2$ after intersystem crossing from the excited singlet state. Since the $\Phi_{isc}$ value of $(C_{59}N)_2$ was similar to that of $C_{59}HN$, it is reasonable to assume that as soon as the first excited singlet states were populated, some fractions of the species intersystem-crossed to the triplet states while some others followed the pathway that led to the formation of the azafullerenyl radicals $C_{59}N^\bullet$. However, in this context, it is extremely important to mention that most $C_{59}N^\bullet$ radicals return to $(C_{59}N)_2$ by the radical coupling reaction, which implies that the reactivity of $C_{59}N^\bullet$ with a solvent such as toluene is quite low.

## Conclusion

Ene and Diels−Alder photosensitized oxygenations in the presence of the examined azafullerenes were confirmed, although the yields of the photooxygenation reactions of 2-methyl-2-butene and α-terpinene in the presence of azafullerenes are smaller than those obtained when $C_{60}$ was used as the photosensitizer. Excited states of bisazafullerene $(C_{59}N)_2$ and hydroazafullerene $C_{59}HN$ were easily generated upon laser irradiation as identified by transient spectroscopy. The triplet excited azafullerenyl moiety $C_{59}N$ in bisazafullerene was influenced by the adjacent $\pi$-electron system of the neighboring azafullerenyl group. The quantum yield for singlet oxygen photosensitization was estimated from the luminescence spectrum for both azafullerenes to be almost half of that of $C_{60}$, which verified the yields of photosensitized oxidation by azafullerenes and $C_{60}$.[16] As the mechanical and photochemical properties of azafullerenes and fullerenes are rather similar,[27] we expect to use them as building blocks for novel nanostructured architectures in which both the position and the electronic properties of each component could be well specified.

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**Supporting Information Available:** Steady-state absorption spectra before and after laser flash photolysis experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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