Supplementary Information

The Effect of Atomic Nitrogen on the C\textsubscript{60} Cage

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Experimental details.

Figure S1. (a) HPLC profile of the sublimed soot containing N@C\textsubscript{60} and (b) its expanded view. (c) EPR spectra of the soot and each fraction (I-IV) after separation by HPLC in toluene.

Figure S2. EPR spectra of N@C\textsubscript{60} in toluene.

Figure S3. Decay profiles of N@C\textsubscript{60} (red line), a mixture of N@C\textsubscript{60}/C\textsubscript{60} (6:4) (blue line), and C\textsubscript{60} (black line) at 750 nm in Ar-saturated toluene at room temperature.

Figure S4. Decay profiles of N@C\textsubscript{60} at 750 nm in Ar-saturated toluene at room temperature. The inset shows first-order plots.

Figure S5. Decay profiles of a mixture of N@C\textsubscript{60}/C\textsubscript{60} (6:4) at 750 nm in Ar-saturated toluene at room temperature. The inset shows first-order plots.

Figure S6. Decay profiles of C\textsubscript{60} at 750 nm in Ar-saturated toluene at room temperature. The inset shows first-order plots.

Figure S7. Decay profiles of N@C\textsubscript{60} at 750 nm with different laser power in deaerated toluene at room temperature. The inset shows pseudo-first-order plots.

Figure S8. Decay profiles of C\textsubscript{60} at 750 nm with different laser power in deaerated toluene at room temperature. The inset shows pseudo-first-order plots.

Figure S9. ^1O\textsubscript{2} phosphorescence emission spectra in the near-IR region observed by the 400 nm laser irradiation of N@C\textsubscript{60} (filled circles) and C\textsubscript{60} (open circles) in O\textsubscript{2}-saturated toluene.
Experimental details

N@C$_{60}$ was prepared by the nitrogen bombardment method and successfully isolated from a crude mixture of N@C$_{60}$, C$_{60}$, C$_{60}$O, and so on using a multi-step and recycling HPLC system. HPLC was performed by a Cosmosil Buckyprep column (φ 20 x 250 mm) and toluene as eluent at a flow rate of 9.9 mL/min at room temperature (Figure S1a, b). To clarify the location of N@C$_{60}$ in the chromatogram, the C$_{60}$ peak was divided into four fractions and each fraction was measured by electron paramagnetic resonance (EPR) measurements using φ5mm quartz tube (Figure S1c). The volume of EPR sample and concentration of C$_{60}$ for each fraction was 200 μL and 1g/L, respectively. Figure S1a shows the HPLC diagram of our fullerene sample after preparation by nitrogen bombardment method. The vertical lines define the different fractions in which the C$_{60}$ peak was divided (Figure S1b). In Figure S1c, the EPR spectra of the fractions I to IV are displayed. The triplet seen in the lower three spectra is the fingerprint of N@C$_{60}$; the intensity (peak-to-peak height) is a direct measure of the amount of N@C$_{60}$ in the sample. The highest intensity is found in the third fraction, i.e., at the upper tail of the C$_{60}$ peak. Thus N@C$_{60}$ is clearly delayed in our column, compared to C$_{60}$, and enrichment is possible. Consequently, this preparative HPLC was repeated tens of times for the enrichment of N@C$_{60}$. Finally, several tens of μg N@C$_{60}$ was isolated by recycling HPLC system.

The EPR measurements were performed with a conventional continuous wave spectrometer in the X band (about 9.4 GHz). Figure 2 shows the three characteristic $^{14}$N EPR lines ($g = 2.0028$, $hfc = 5.67$ G) of the sample irradiated with $^{14}$N atom (nuclear spin $I = 1$, NA = 99.634%) and the doublet $^{15}$N EPR lines ($g = 2.0028$, $hfc = 7.96$ G) from the sample irradiated with $^{15}$N atom (nuclear spin $I = 1/2$, NA = 0.366%). The line splitting is due to the hyperfine interaction with the nuclear spin.

Figure S3-S6 show the decay kinetics of exited states of Ar-saturated toluene solutions of N@C$_{60}$, N@C$_{60}$/C$_{60}$(3:2), and C$_{60}$ at room temperature. These spectra demonstrated that the presence of the N atom enhances the intrinsic first order decay of (N@C$_{60}$)$^*$. Meanwhile, these decay times are influenced a great deal by the concentration of residual oxygen in the solution, beccase these exited species are quenched by oxygen. To shed undoubtedly light on the effect of the N atom on C$_{60}$ cage in the exited state, we have performed laser flash photolysis of the deoxygenated toluene solutions of N@C$_{60}$ and C$_{60}$ (Figure S7-S8). The decay rates of the exited states were strongly affected by the laser power as shown in Figure S7 and S8. The decay time profiles are composed of mixed-order kinetics of first- and second-order, in which the former is the intrinsic decay rate of the exited state and the latter is due to the annihilation process among the exited species such as triplet-triplet annihilation in the case of C$_{60}$. The decay rates of the exited states were strongly affected by the laser power as shown in Figure S7 and S8. The decay time profiles are composed of mixed-order kinetics of first- and second-order, in which the former is the intrinsic decay rate of the exited state and the latter is due to the annihilation process among the exited species such as triplet-triplet annihilation in the case of C$_{60}$. As shown in an inset of Figure S7 and S8, plot of Δk$_{l}$ to ΔA$_{l}$ shows a linear correlation. From this slope, an intrinsic first-order decay rate (Δk$_{f}$) of the exited state was estimated.

$^1$C$_{60}$$^*$ is well know to be quenched efficiently by molecular oxygen (O$_2$) to generate singlet oxygen ($^1$O$_2$). The quenching of $^1$C$_{60}$$^*$ by molecular oxygen (O$_2$) is generally probed by monitoring the decrease of the triplet-triplet absorption and the increase of the emission from $^1$O$_2$ at 1272 nm. The lifetime of $^1$(N@C$_{60}$)$^*$ decreased in a O$_2$-saturated toluene solution and the emission from $^1$O$_2$ was observed at 1274 nm (Figure S9). This may reveal that $^1$(N@C$_{60}$)$^*$ is quenched by triplet oxygen ($^3$O$_2$) as well as $^1$C$_{60}$$^*$ and the quantum yield (Φ$_{ISC}$) for formation of $^1$(N@C$_{60}$)$^*$ via intersystem crossing from $^3$(N@C$_{60}$)$^*$ was estimated as same as that of $^1$C$_{60}$$^*$ (Φ$_{ISC}$ = 0.96).

The MALDI-TOF MS were measured on a BIFLEXTM III (Bruker, Germany) with 1,1,4,4-tetraphenyl-1,3-butadiene as a matrix. $^{13}$C NMR spectra at 125 MHz were measured on a Bruker AVANCE 500 spectrometer with a CryoProbe system in carbon disulfide with a capillary tube of acetone-$d_6$ as an external lock. UV-vis-NIR spectra were measured on a UV 3150 (Shimadzu, Japan) in toluene. The nanosecond transient absorption spectra were measured by using 532 nm laser light (SHG) of a Nd:YAG laser (Spectra-Physics, Quanta-Ray GCR-130) as an excitation source. A continuous xenon lamp was used as a probe light. A Ge-APD module (Hamamatsu Photonics, B2834) attached to a monochromator (Ritsu MC-10N) was employed as a detector of transient absorption spectra in the visible and near-IR regions (400-1000 nm). Emission spectra of the singlet oxygen ($^1$O$_2$) in the near-IR regions (400-1000 nm). The MALDI-TOF MS were measured on a BIFLEX TM III (Bruker, Germany) with 1,1,4,4-tetraphenyl-1,3-butadiene as a matrix. $^{13}$C NMR spectra at 125 MHz were measured on a Bruker AVANCE 500 spectrometer with a CryoProbe system in carbon disulfide with a capillary tube of acetone-$d_6$ as an external lock. UV-vis-NIR spectra were measured on a UV 3150 (Shimadzu, Japan) in toluene. The nanosecond transient absorption spectra were measured by using 532 nm laser light (SHG) of a Nd:YAG laser (Spectra-Physics, Quanta-Ray GCR-130) as an excitation source. A continuous xenon lamp was used as a probe light. A Ge-APD module (Hamamatsu Photonics, B2834) attached to a monochromator (Ritsu MC-10N) was employed as a detector of transient absorption spectra in the visible and near-IR regions (400-1000 nm). Emission spectra of the singlet oxygen ($^1$O$_2$) in the near-IR regions were detected by using an InGaAs detector. All the spectral measurements were carried out in 1 cm optical cell. All calculations were carried out using the Gaussian 03 program. Geometries were optimized with the hybrid density functional theory at the B3LYP level (a,b) with the 6-31G(d) basis set (a) for C and N,
while the chemical shifts were evaluated with the MPW1K functional\(^1\) and the same basis set and calibrated to the observation.\(^ {1-6} \)


**Figure S1.**

![Figure S1](image1)

**Figure S2.**

![Figure S2](image2)
**Figure S3.**

Normalized intensity vs. time for different samples.

**Figure S4.**

ΔAbsorbance vs. time for N@C₆₀.

**Figure S5.**

ΔAbsorbance vs. time for N@C₆₀/C₆₀ (6:4).
**Figure S6.**

![Graph showing the absorbance changes over time for C60 under 750nm and 532nm laser irradiation.](image)

**Figure S7.**

![Graph showing the absorbance changes over time for N@C60 at 750 nm.](image)

**Figure S8.**

![Graph showing the absorbance changes over time for C60 at 750 nm.](image)
Figure S9.