Supporting Information

Femtosecond excited-state dynamics of fullerene-C$_{60}$ nanoparticles in water

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1. **Time-resolved fluorescence spectra of nC\textsubscript{60} in water.**

The experimental setup for time-correlated single-photon-counting measurement was described below. Light source for the picosecond time-resolved fluorescence (TRF) spectroscopy was the second harmonic (400 nm) of Ti:sapphire laser (Spectra Physics, Tsunami) generated in a type I BBO crystal (2-mm thickness) and the repetition rate was 82 MHz. This pump light was guided into the inverted optical microscope (Olympus, IX71), and focused into the sample cell with the objective lens (x60, NA 0.7). The emission was collimated with the same objective lens and guided to the photodetector. An avalanche photodiode (PDM, MPD) and a counting board (SPC-130, Becker & Hickl GmbH) were used for signal detection. A band pass filter in 10-nm fwhm (Asahi spectra) was placed in front of the avalanche photodiode to select monitoring wavelength and avoid the scattering of excitation light. The instrumental response function (IRF) was 30 ps, which was determined by the fluorescence decay from Malachit Green in water with very short lifetime of less than 10 ps. The fluorescence time profile was measured at different wavelengths, 700, 730 750 770 and 800 nm by changing a bandpass filter. The reconstruction of the time-resolved fluorescence spectrum was based on a method similar to that reported by Tamai et al.\textsuperscript{1} It was assumed that the relative integrated intensity of the fluorescence decay at each wavelength corresponds to that of the steady state fluorescence spectrum. The number of photons was counted up to delay of 3 ns with a step size of 1.22 ps and it was averaged over certain intervals (±10 ps) to obtain a TRF spectrum with higher S/N ratio.

Figure S1 shows the time-resolved fluorescence spectra of nC\textsubscript{60} in water. At 0 ns, the peak at 730 nm due to the free exciton appeared, red-shifted by 40 nm in 100 ps, and the broad band originated from the self-trapped excition (excimer) appeared. After 100 ps, the excimer emission decayed with a slight spectral change. Considering two lifetimes of excimers (120 ps and 360 ps in figure 2), this spectral change indicated that at least two trapped sites existed in nC\textsubscript{60}.
Figure S1. Time-resolved fluorescence spectra of nC₆₀ in water measured at various time delays, 20 ps, 100 ps, 200 ps, 300 ps, 400 ps, and 500 ps, respectively. Solid grey line was the steady-state fluorescence spectrum, excited at 400 nm.
2. Laser fluence dependence of transient absorption spectra.

Figure S2 shows the transient absorption spectra of nC\textsubscript{60} in water at four laser fluence of 0.14, 0.57, 1.1 and 1.4 mJ/cm\textsuperscript{2}\textsuperscript{-pulse\textsuperscript{-1}}. At 0.57 mJ/cm\textsuperscript{2}\textsuperscript{-pulse\textsuperscript{-1}} in Figure S2(C), a negative signal around 460 nm due to the bleaching of the ground state and broad positive transient absorption band with a peak at 550 nm due to the intermolecular CT excited state appeared at 0.1 ps. Although this spectral band shape around 550 nm was similar to that at the low laser fluence of 0.14 mJ/cm\textsuperscript{2}\textsuperscript{-pulse\textsuperscript{-1}} as shown in Figure S2(D), the band around 700 nm due to the electronic interaction between neighboring excited C\textsubscript{60} molecules was slightly observed. On the other hand, at 1.1 mJ/cm\textsuperscript{2}\textsuperscript{-pulse\textsuperscript{-1}}, the transient absorption spectrum at 0.1 ps resembled that at 1.4 mJ/cm\textsuperscript{2}\textsuperscript{-pulse\textsuperscript{-1}}, and the difference of the band shape around 750 nm was remarkable as compared to that at 0.14 mJ/cm\textsuperscript{2}\textsuperscript{-pulse\textsuperscript{-1}}. At any laser fluences, after 1.5 ps, the transient absorption decreased monotonously with a slight change in the spectral shape. The spectra in the time range of 10 ps to 500 ps could be ascribed to excimer. The transient absorption spectrum at 500 ps in was different from the spectral band shape of the triplet excited state of C\textsubscript{60}. Figure S3 shows the time profiles of the transient absorbance recorded at 550 nm at four laser fluences of 0.14, 0.57, 1.1 and 1.4 mJ/cm\textsuperscript{2}. The time profile at each excitation intensity was normalized by the transient absorbance at 0.1 ps. At 550 nm where the transients were mainly contributed to the intermolecular CT-excited state and S\textsubscript{1} state, the transient signal at any excitation intensities decayed to 10% of the initial amplitude in 200 ps, and remained small amount due to the excimers at 500 ps. These curves were apparently independent of the excitation intensity. The time profiles can be reproduced by the result calculated with a quadruple exponential function, a response function (100 fs fwhm), and a constant value. It was noted that forth time constant was fixed to 120 ps, which was obtained from the fluorescence decay. The obtained results are listed in Table S1. The three time constants (average: 0.36 ps, 3.3 ps, and 16 ps) showed almost the same value at any excitation intensities, and the relative amplitude of each component was also independent of the excitation intensity.
Figure S2. Transient absorption spectra of nC₆₀ in water at four laser fluences of (A) 1.4 (B) 1.1, (C) 0.57 and (D) 0.14 mJ cm⁻² pulse⁻¹.

Figure S3. Comparison of the time profiles of the transient absorbance of nC₆₀ in water at four laser fluences of 1.4, 1.1, 0.57 and 0.14 mJ cm⁻² pulse⁻¹. Monitoring wavelength was 550 nm, and the results were normalized by the absorbance at 0.1 ps.
Table S1. Time constants ($\tau_i$) and relative amplitudes (in parentheses) obtained from the analysis of time profiles of transient absorbance at 550 nm in nC$_{60}$.

The time profiles were fitted to: \( f(t) = A_0 + \sum A_i \exp(-t/\tau_i). \) Relative amplitude was calculated by \( A_i / (A_0 + \sum A_i). \) In this calculation, time constant of the fourth component was fixed to be 120 ps.

<table>
<thead>
<tr>
<th>Laser fluence (mJ/cm$^2$)</th>
<th>0.14</th>
<th>0.57</th>
<th>1.06</th>
<th>1.40</th>
<th>0.14 (420 nm exc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau_1$ (ps)</td>
<td>3.2±0.2 (19%)</td>
<td>2.9±0.4 (24%)</td>
<td>3.7±0.5 (29%)</td>
<td>3.2±0.1 (26%)</td>
<td>3.0±0.1 (24%)</td>
</tr>
<tr>
<td>$\tau_2$ (ps)</td>
<td>16±2 (16%)</td>
<td>15±1 (18%)</td>
<td>15±2 (9%)</td>
<td>16±1 (11%)</td>
<td>18±1 (14%)</td>
</tr>
<tr>
<td>$\tau_3$ (ps)</td>
<td>(13%)</td>
<td>(12%)</td>
<td>(13%)</td>
<td>(16%)</td>
<td>(9%)</td>
</tr>
<tr>
<td>$\tau_4 =$ 120 (ps)</td>
<td>(4%)</td>
<td>(5%)</td>
<td>(5%)</td>
<td>(4%)</td>
<td>(2%)</td>
</tr>
</tbody>
</table>

The time profiles were fitted to: \( f(t) = A_0 + \sum A_i \exp(-t/\tau_i). \) Relative amplitude was calculated by \( A_i / (A_0 + \sum A_i). \) In this calculation, time constant of the fourth component was fixed to be 120 ps.
3. Excitation intensity dependence of decay-associated spectra

Additional information on the transient spectral distribution of the time constants is given by the decay associated spectra $A_i(\lambda)$, which obtained from multiexponential global analysis,

$$f(\lambda, t) = A_0 + \sum_i A_i(\lambda) \exp\left(-\frac{t}{\tau_i}\right),$$

Each spectrum, $A_i(\lambda)$ represents the spectroscopic changes caused by the kinetic process with the time constant, $\tau_i$. Here, global analysis of the transient absorption data required the sum of four exponential functions with $0.35 \pm 0.1$ ps ($\tau_1$), $3.2 \pm 1$ ps ($\tau_2$), $16 \pm 5$ ps ($\tau_3$), and $120$ ps (fixed) ($\tau_4$) time constants. The $360$-ps component was omitted because of its small contribution in table 1. The error margin was $30\%$.

The global analysis was performed for the results of time profiles to clarify the interaction between intermolecular CT excited states. The decay-associated spectra of the fastest component ($0.35 \pm 0.15$ ps) at four excitation intensities of $0.14$, $0.57$, $1.1$ and $1.4$ mJ/cm$^2$ were exhibited in figure S4. The negative signal located around $475$ nm at each fluence, while the positive signal around $560$ nm became red-shifted by $50$ nm and the positive band in the wavelength range of $650$-1000 nm increased with increasing in the fluence from $0.14$ to $1.4$ mJcm$^{-2}$pulse$^{-1}$. This spectral broadening will be owing to the electronic interaction between neighbouring CT excited states, ascribed eventually as a “biexciton” state.

![Figure S4. Decay-associated spectra of the 0.35-ps component obtained from the data analysis of the transient absorption spectra in figures 3, 6 and 7.](image)
4. References