

Electronic supplementary information (ESI)

Singlet oxygen generation from $\text{Li}^+\text{@C}_{60}$ nano-aggregates dispersed by laser pulse irradiation in aqueous solution

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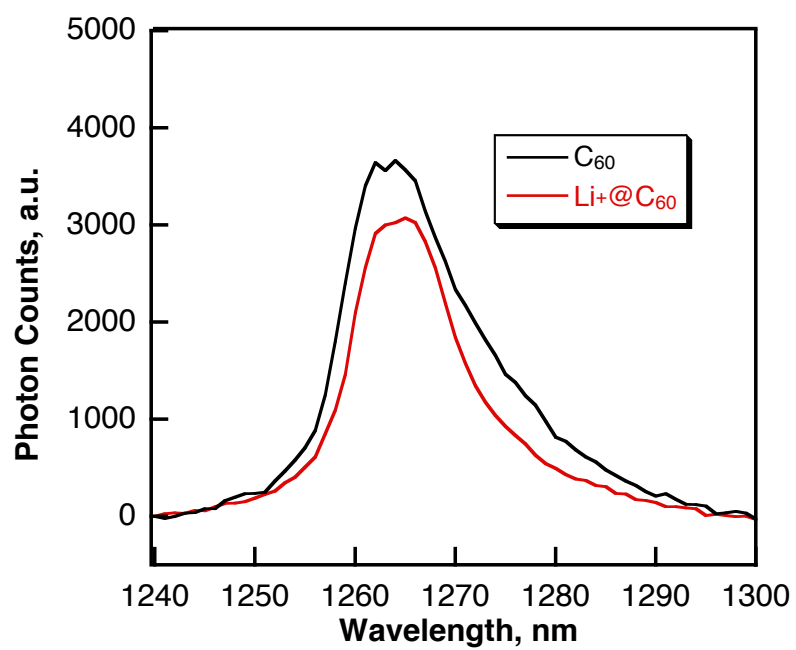


Fig. S1 Emission spectrum of $^1\text{O}_2$ sensitised by irradiation of $\text{Li}^+\text{@C}_{60}$ and C_{60} at 532 nm in O_2 -saturated $\text{C}_6\text{D}_6/\text{C}_6\text{H}_5\text{CN}$ (1:1 v/v) at 298 K.

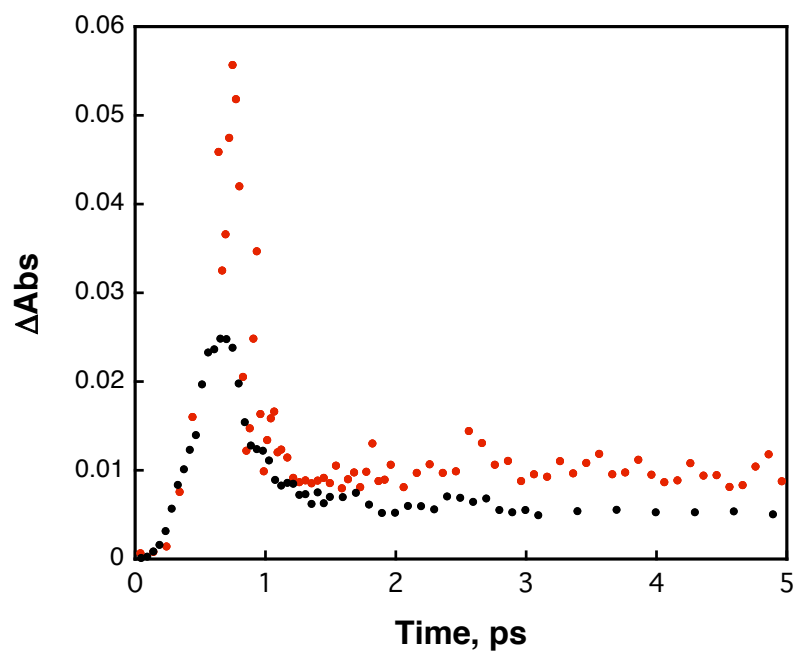


Fig. S2 Decay time profiles at 900 nm of the transient absorption spectra of f $(\text{Li}^+@C_{60})_n$ in deaerated distilled water obtained by femtosecond laser excitation at 393 nm with the different laser excitation power intensities ($8 \mu\text{J pulse}^{-1}$ (black) and $32 \mu\text{J pulse}^{-1}$ (red)).

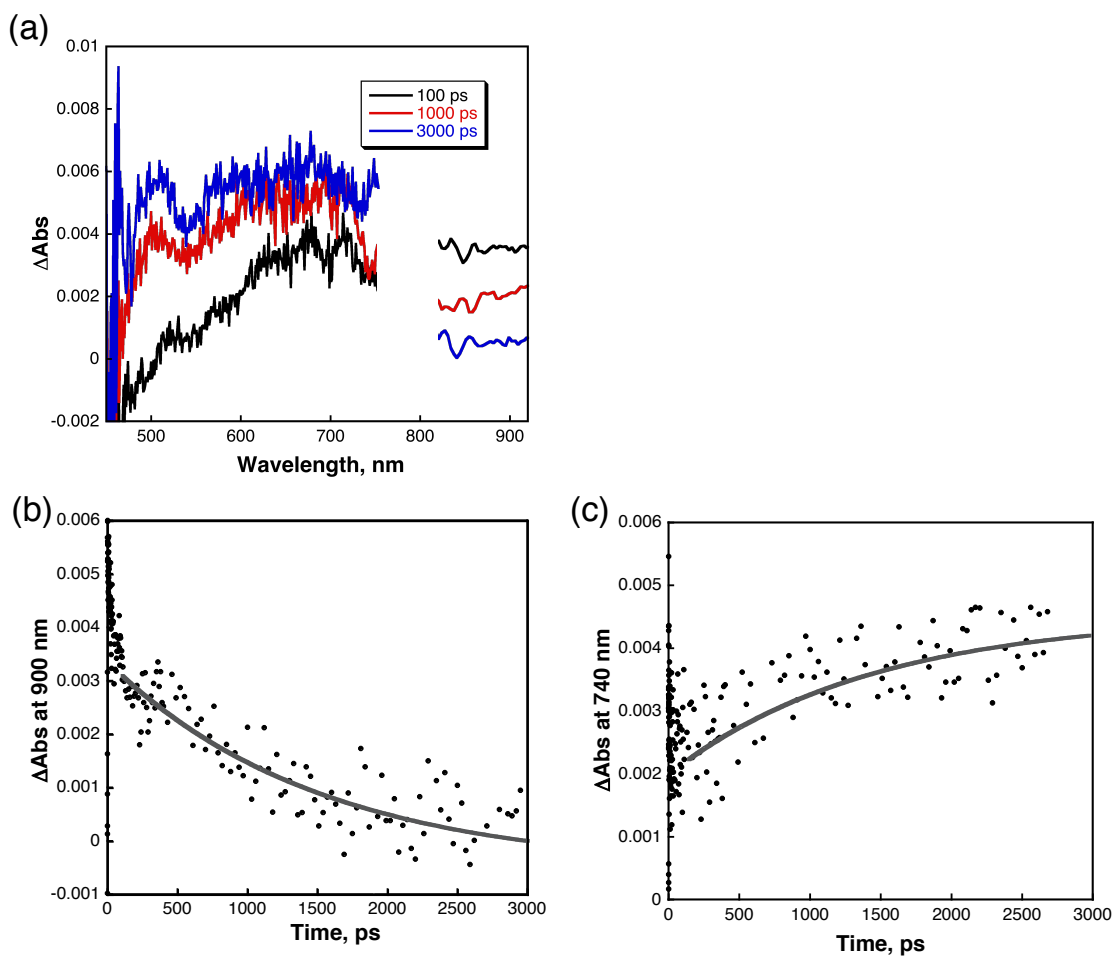


Fig. S3 (a) Transient absorption spectra of $(\text{Li}^+@\text{C}_{60})_n$ in deaerated distilled water obtained by femtosecond laser excitation at 393 nm; (b) Decay time profile at 900 nm. (c) Rise time profile at 740 nm.

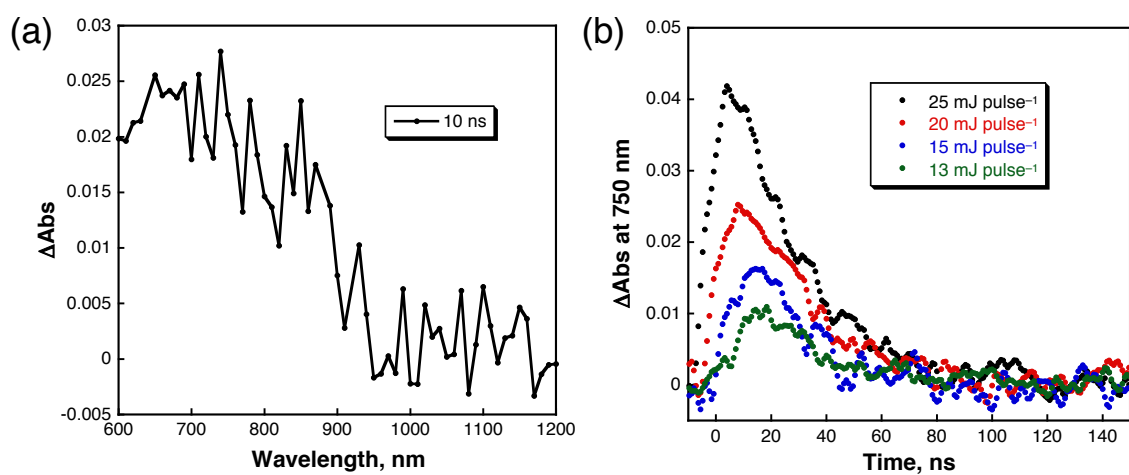


Fig. S4 (a) Transient absorption spectra of $(\text{Li}^+@\text{C}_{60})_n$ in deaerated H_2O taken after nanosecond laser excitation at 355 nm with the power of 20 mJ pulse^{-1} ; (b) Decay time profiles at 750 nm in the absence of O_2 with a single-exponential decay curve with different laser power intensities ($13\text{-}25 \text{ mJ pulse}^{-1}$).

Experimental and instrumental details

Materials. Chemicals were purchased from commercial source and used without purification. Lithium ion-encapsulated fullerene hexafluorophosphate salt ($\text{Li}^+@C_{60}\text{PF}_6^-$ from Idea International Co. Ltd.) was commercially obtained from Wako Pure Chemicals, Japan. Deuterium oxide (D_2O : 99.9%) was obtained from Cambridge Isotope Laboratories, Inc., and used as received. Purification of water ($18.2\text{ M}\Omega\text{ cm}$) was performed with a Milli-Q system (Millipore, Direct-Q3 UV).

Generation of fullerene nano-aggregates. H_2O or D_2O solutions (2.5 cm^3) containing fullerene ($\text{Li}^+@C_{60}\text{PF}_6^-$, C_{60} and C_{70} ; 1.0 mg) in a square quartz cuvette (10 mm i.d.) sealed with a rubber septum was deaerated by bubbling with nitrogen through a stainless steel needle for 10 min. The solution was then irradiated with a Nd:YAG laser (LOTIS TII, LS2134UTF) at $\lambda = 355\text{ nm}$ with the power of 20 mJ pulse^{-1} at room temperature for 1 h with vigorous stirring. The solutions were centrifugated with 15000 rpm for 10 min to remove remained large particles. Size of the fullerene nano-aggregates was monitored by DLS measurements {Zetasizer Nano ZS instrument (Malvern Instruments Ltd., USA)}. UV-vis spectra were recorded on a Hewlett Packard 8453 diode array spectrophotometer at 298 K. Transmission electron microscope (TEM) images of $(\text{Li}^+@C_{60})_n$ were measured using a JEOL JEM 2100 operating at 200 kV. MALDI-TOF-MS measurements were performed on a Kratos Compact MALDI I (Shimadzu) using dithranol as a matrix.

$^1\text{O}_2$ phosphorescence measurements. For the $^1\text{O}_2$ phosphorescence measurements, an O_2 -saturated D_2O solution containing nano-aggregates of $(\text{Li}^+@C_{60})_n$, $(C_{60})_n$ or $(C_{70})_n$ in a quartz cell (optical path length 10 mm) was excited by an LED laser at 532 nm using an Otsuka Electronics Co. Ltd. Vis-near-IR fluorescence spectrometer.

Laser flash photolysis. The measurements of nanosecond transient absorption were performed according to the following procedures. Typically, a nitrogen saturated H₂O solution containing (Li⁺@C₆₀)_n was excited by a Nd:YAG laser (Continuum, SLII-10, 4-6 ns fwhm) at $\lambda = 355$ nm with the powers of 13-25 mJ pulse⁻¹ at 298 K. Photoinduced events were estimated by use of a continuous Xe lamp (150 W) and an InGaAs-PIN photodiode (Hamamatsu 2949) as a probe light and a detector, respectively. The output from the photodiodes and a photomultiplier tube was recorded with a digitizing oscilloscope (Tektronix, TDS3032, 300 MHz).

Femtosecond transient absorption spectroscopy experiments were conducted using an ultrafast source: Integra-C (Quantronix Corp.), an optical parametric amplifier: TOPAS (Light Conversion Ltd.) and a commercially available optical detection system: Helios provided by Ultrafast Systems LLC. The source for the pump and probe pulses were derived from the fundamental output of Integra-C ($\lambda = 786$ nm, 2 mJ pulse⁻¹ and fwhm = 130 fs) at a repetition rate of 1 kHz. 75% of the fundamental output of the laser was introduced into a second harmonic generation (SHG) unit: Apollo (Ultrafast Systems) for excitation light generation at $\lambda = 393$ nm, while the rest of the output was used for white light generation. The laser pulse was focused on a sapphire plate of 3 mm thickness and then white light continuum covering the visible region from $\lambda = 410$ nm to 800 nm was generated via self-phase modulation. A variable neutral density filter, an optical aperture, and a pair of polarizer were inserted in the path in order to generate stable white light continuum. Prior to generating the probe continuum, the laser pulse was fed to a delay line that provides an experimental time window of 3.2 ns with a maximum step resolution of 7 fs. In our experiments, a wavelength at $\lambda = 393$ nm of SHG output was irradiated at the sample cell with a spot size of 1 mm diameter where it passing through the 2 mm sample cell was focused on a fibre optic cable that was connected to a CMOS spectrograph for recording the time-resolved spectra ($\lambda = 410 -$

800 nm). Typically, 1500 excitation pulses were averaged for 3 seconds to obtain the transient spectrum at a set delay time. Kinetic traces at appropriate wavelengths were assembled from the time-resolved spectral data. All measurements were conducted at room temperature, 295 K.

DNA cleavage experiments. Typically, 70 μL of aqueous solution of $(\text{Li}^+@\text{C}_{60})_n$ and 20 μL of aqueous solution of DNA pBR322 ($0.05 \mu\text{g } \mu\text{L}^{-1}$) were mixed in a micro test tube under dark conditions. Samples were incubated under irradiation with a white light ($\lambda > 380 \text{ nm}$) from a Asahi Spectra Max-302 at 298 K. The 9 μL of aqueous solution of DNA pBR322 ($0.01 \mu\text{g } \mu\text{L}^{-1}$) was mixed with 1 μL of loading buffer (0.1% bromophenol blue and 3.75% Ficol in TAE buffer) and loaded onto 1.0% agarose gel. The gel was run at a constant voltage of 130 V for 50 min in TAE buffer using a Nihon Eido electrophoresis kit, then washed with distilled water, soaked into 0.1% ethidium bromide aqueous solution, visualised under a UV transilluminator, and photographed using a digital camera.