Electronic Supplementary Information (ESI)

Enhanced photoelectrochemical performance of composite photovoltaic cells of $Li^+@C_{60}$/sulphonated porphyrin supramolecular nanoclusters

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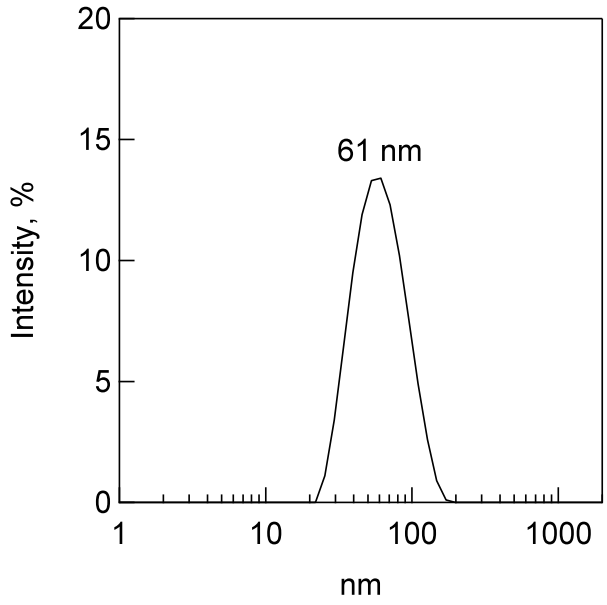

Fig. S1 Dynamic light scattering (DLS) diagram of $(ZnTPPS^{4-}/Li^{+}@C_{60})_n$ in MeCN/PhCN (3:1 v/v).

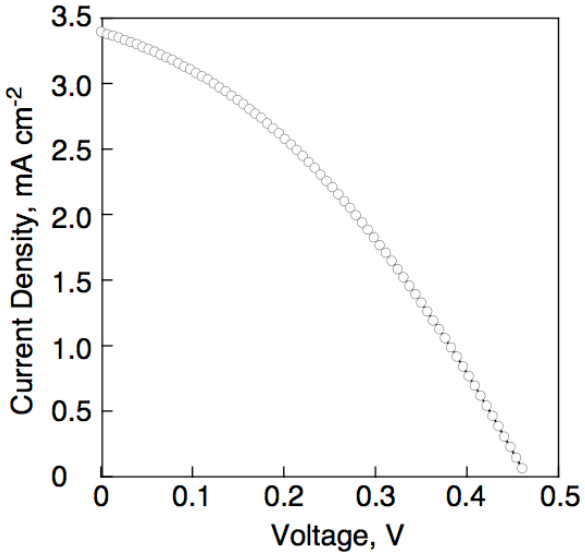

Fig. S2 I-V characteristics of OTE/SnO_2/$(ZnTPPS^{4-}/Li^{+}@C_{60})_n$ electrode under white light illumination (AM 1.5); electrolyte LiI (0.5 M) and I_2 (0.05 M) in MeCN; input power 40 mW cm^{-2}.

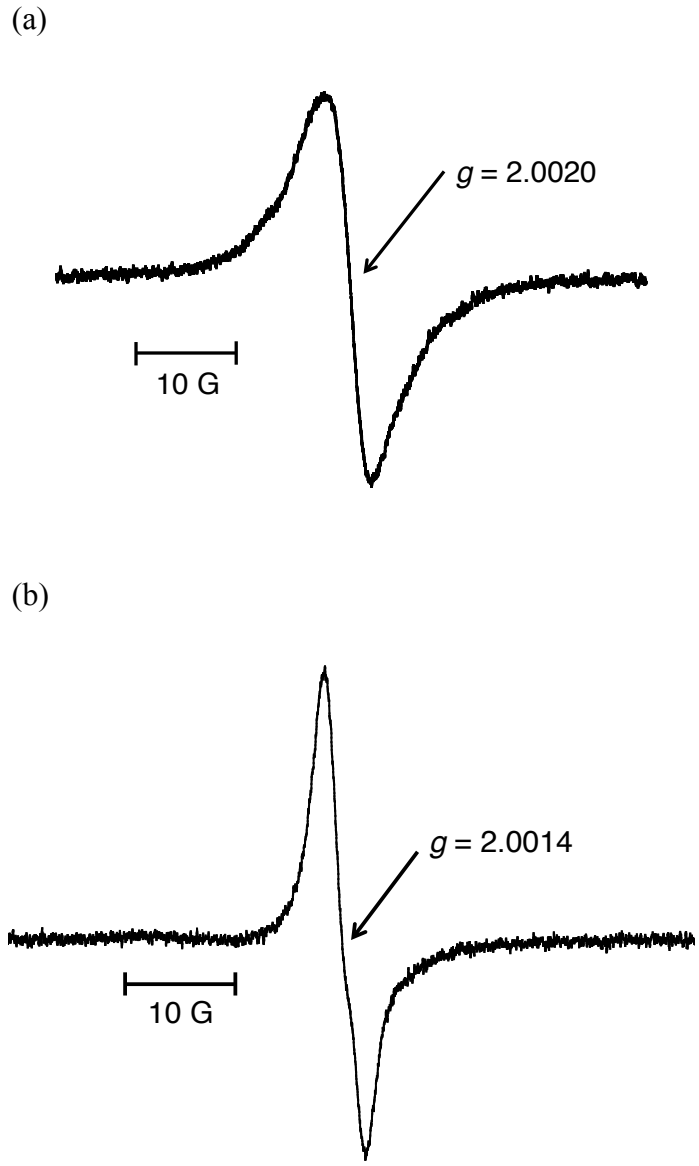

Fig. S3 (a) EPR spectrum of the charge-separated state of $(ZnTPPS^{4-}/Li^{+}@C_{60})_n$ dispersed in deaerated MeCN/PhCN (3:1 v/v) and observed after photoirradiation at 77 K. (b) EPR spectrum of $Li^{+}@C_{60}^{\bullet-}$ generated by the electron-transfer reduction from dimeric 1-benzylnicotinamide to $Li^{+}@C_{60}$ at 100 K.

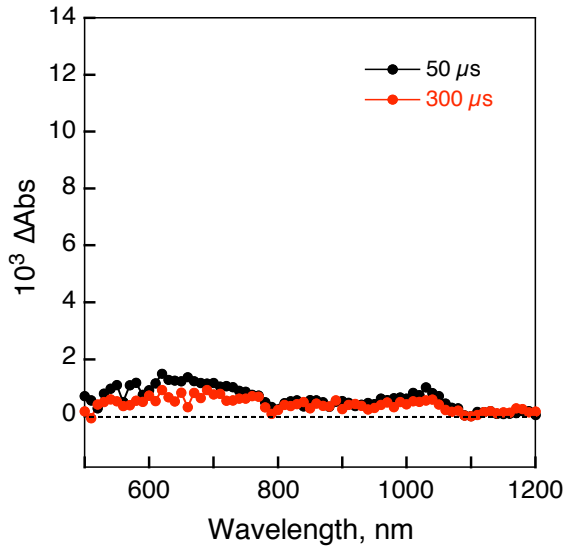

Fig. S4 (a) Transient absorption spectrum of H_2TPPS^{4-} (3.2×10^{-5} M) with $Li^+@C_{60}$ (3.2×10^{-5} M) in deaerated MeCN/PhCN (3:1 v/v) taken at 50 μs (black) and 300 μs (red) after laser excitation at 520 nm.

Experimental

Materials. Chemicals were purchased from commercial sources and used without further purification, unless otherwise noted. Lithium ion-encapsulated fullerene hexafluorophosphate salt ($Li^+@C_{60}$ PF_6^-: 96%) was obtained from Daiichi Jitsugyo Co. Ltd, Japan. $(Bu_4N^+)_4MTPPS^{4-}$ (M = Zn, H_2) were synthesized by the neutralization of tetrasulphonated porphyrin (Tokyo Chemical Industry Co. Ltd.) with 4 equiv. of tetrabutylammonium hydroxide in MeOH. Benzonitrile (PhCN) used as a solvent was distilled over phosphorus pentoxide. Acetonitrile (MeCN) was purchased from WAKO pure chemical and used as received.

UV-vis absorption and fluorescence spectral measurements. UV-vis absorption spectra were recorded on a Hewlett-Packard 8453 diode array spectrophotometer at room temperature. Fluorescence spectra were measured on a Horiba FluoroMax-4 spectrofluorophotometer.

Photoelectrochemical measurements. Electrophoretic deposition was performed using a Power Pac HV (Bio-Rad). Photoelectrochemical measurements were carried out in a standard two-compartment cell consisting of a working electrode, a Pt wire gauze counter electrode. A KEITHLEY 2400 was used for recording *I-V* characteristics and photocurrent generation density under an AM 1.5 simulated light source (OTENTO-SUN II, Bunkoh Keiki Co., LTD). For the IPCE measurements, a monochromator (SM-25, Bunkoh Keiki Co., LTD) was introduced into the path of the excitation beam (150 W xenon lamp, Bunkoh Keiki Co., LTD) for the selected wavelength. The lamp intensity at each wavelength was determined using a Si photodiode (Hamamatsu Photonics S1337-1010BQ) and corrected.

TEM measurements. Transmission electron micrograph (TEM) measurements were recorded on Tecnai spirit (FEI company) by applying a drop of the sample to a copper grid. TEM images were recorded on a transmission electron microscope an accelerating voltage of 120 kV for imaging.

Dynamic light scattering (DLS) measurements. The particle size and distribution were measured in MeCN/PhCN (3:1 v/v) using light-scattering equipment (Zetasizer nano ZS).

Time-resolved transient absorption measurements. Nanosecond transient absorption spectral measurements were made according to the following procedure. A deaerated MeCN/PhCN solution (3:1 v/v) containing $(Li^+@C_{60}/MTPPS^{4-})_n$ was excited by a Panther OPO pumped Nd:YAG laser (Continuum, SLII-10, 4-6 ns fwhm) at 450 nm. The resulting time resolved transient absorption spectra were measured by using a continuous Xe-lamp (150 W) and a photodiode (Hamamatsu 2949) as the probe light and detector, respectively. The output from the photodiode and the photomultiplier tube was recorded using a digitizing oscilloscope (Tektronix, TDS3032, 300 MHz). The solutions were deoxygenated by N_2 purging for 10 min prior to measurements. Rates of charge recombination in $(Li^+@C_{60}/MTPPS^{4-})_n$ were monitored by the decay of the absorption band due to the $Li^+@C_{60}$ radical anion at 1035 nm. First-order rate constants were determined by a least-squares curve fit. All experiments were performed at 298 K.