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Electron-donor function of methanofullerenes in donor-acceptor bulk heterojunction systems

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LEIPS. Experimental setup of LEIPS is described elsewhere.¹ A quartz glass plate coated with indium tin-oxide (ITO) with the thickness of 10 nm is used as a substrate. The thin films of BCN-HH-BCN were prepared by spin-coating from a chloroform solution (0.1 wt%) on the ITO. The sample specimen was introduced into the vacuum chamber evacuated to 2×10^{-7} Pa and incident to an electron beam. In order to avoid the sample damage, the kinetic energy of incident electrons was restricted to less than 4 eV and the electron current densities ranged between 10^{-6} and 10^{-5} A cm⁻². Under these experimental conditions, the same LEIPS spectra were obtained after several scans confirming the sample damage was negligible. The emitted photons were collected and focused into a photon detector consisting of an optical bandpass filter and a photomultiplier tube. The center wavelength of the bandpass filter was 254 nm. The overall energy resolution was estimated to be 0.29 eV. The vacuum level was determined as the onset energy of the sample current.

In order to precisely determine the onset of the LEIP spectrum, only the energy region between -5.0 and -3.5 eV are accumulated as shown in Fig. S1. The onset is determined as the crossing of the two straight lines fitted to the spectrum.



Fig. S1 The onset region of LEIP spectrum of BCN-HH-BCN.

PESA. Photoelectron spectroscopy was carried out using a Riken Keiki Co. Ltd. AC-3. The measurements were performed under N₂ condition. An irradiation light power was set to be 10 and 20 nW cm⁻² for BCN-HH-BCN and PC₆₁BM, respectively.



Fig. S2 Photoelectron spectra of (a) BCN-HH-BCN and (b) PC₆₁BM.

TRMC and photocurrent measurements. A resonant cavity was used to obtain a high degree of sensitivity in the conductivity measurement. The resonant frequency and microwave power were set at ca. 9.1 GHz and 3 mW, respectively, so that the electric field of the microwave was sufficiently small to not disturb the motion of charge carriers. Third harmonic generation (THG; 355 nm) of a Nd:YAG laser (Spectra Physics Inc., INDI, 5-8 ns pulse duration, 10 Hz).² The photoconductivity $\Delta\sigma$ was obtained by $\Delta P_r/(AP_r)$, where ΔP_r , A, and P_r are the transient power change of reflected microwave from a cavity, the sensitivity factor, and the reflected microwave power, respectively. The nanosecond laser intensity was set

at 9.1×10^{15} photons cm⁻² pulse⁻¹. The samples were drop-casted on a quartz plate from tetrahydrofuran solutions of PC₆₁BM and TCNE and dried in a vacuum oven. After the preparation of thin films, the films were thermally annealed on a hot plate. The TRMC experiments were performed under ambient conditions at room temperature.

An interdigitated comb-type gold electrode with 5 μ m gaps, 50 nm height, and 2 mm width fabricated by lithographic process in the laboratory was used for photocurrent experiments. The details are described in our previous report.³ After casting the sample on the electrode, it was exposed to THG (355 nm) of a Nd:YAG laser (Spectra Physics Inc. GCR-100, 5–8 ns pulse duration) from the bottom side through a glass substrate. The applied bias was controlled by an Advantest Corp. model R8252 digital electrometer. The transient photocurrent was measured by a Tektronix model TDS3052B digital oscilloscope equipped with termination resistance (10 k Ω). The experiments were carried out at room temperature.



Fig. S3 (a) FP-TRMC transients of $PC_{61}BM$ films without (red) and with TCNE (black) prepared from THF solutions. The transients were recorded upon exposure to a 355 nm laser pulse. The mixing ratio of $PC_{61}BM$ and TCNE was 1:0.1 by weight. (b) Photocurrent transients of the corresponding films measured with a 5 µm-gap interdigitated Au electrode on glass under the applied bias of 2×10^4 V cm⁻¹.

Photovoltaic device fabrication and evaluation. The preliminary PC₆₁BM:BCN-HH-BCN-based cell exhibited typical OPV characteristics. However, these devices showed low power conversion efficiencies (PCEs) of around 0.1%. Thus, the device structures including buffer layers and metal electrodes as well as the inverse BHJ solar cell were tested, and we glass/indium determined employ the configuration tin oxide (ITO)/poly(3,4to of ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)/PC₆₁BM:BCN-HH-BCN/Al. The conditions for fabricating the active layer were also examined, including the blend composition, processing solvent, thermal annealing temperature, and additive. It was found that an optimized active layer could be prepared by spin coating an o-dichlorobenzene solution of the PC₆₁BM/BCN-HH-BCN (2:1 weight ratio) blend in a nitrogen atmosphere without thermally annealing. From the results of fluorescence spectra of blend films, we determined the optimized ratio of blend composition.

Organic photovoltaic devices were prepared with a structure of ITO/PEDOT:PSS/active layer/Al. ITO-coated glass substrates were first cleaned by ultrasonication in toluene, acetone, H₂O, and 2-propanol for 10 min, respectively, followed by O₂ plasma treatment for 10 min. ITO-coated glass substrates were then activated by ozone treatment for 1 h. PEDOT:PSS was spin-coated on the ITO surface at 3000 rpm for 1 min and dried at 135 °C for 10 min. The active layers were then prepared by spin-coating on the ITO/PEDOT:PSS electrode at 600–1000 rpm for 1 min in a glove box. The BHJ layer was spin-coated on this substrate at 1000 rpm for 2 min from 20 mg mL⁻¹ solution PC_xBM (x = 61 or 71)/BCN-HH-BCN (2:1 weight ratio) in *o*-dichlorobenzene. The typical thickness of the active layer was 70–90 nm. The substrates were dried at room temperature for 20 min in a glove box. Finally, Al electrode was evaporated on the top of active layer through a shadow mask to define the active area of the devices (0.09 cm²) under a vacuum of 10⁻⁴ Pa to a thickness of 30 and 100 nm determined by a quartz crystal monitor. After sealing the device from the air, the photovoltaic characteristics were measured in air under simulated AM 1.5G solar irradiation (100 mW cm⁻²) (SAN-EI ELECTRIC, XES-301S). The current-voltage characteristics of photovoltaic devices were measured by using a KEITHLEY 2400 semiconductor parameter analyzer. The EQE spectra were measured by using a Soma Optics Ltd. S-9240. The thickness of active layer was determined by KLA Tencor Alpha-step IQ.

Electronic absorption measurements. Electronic absorption spectra were recorded on a Shimadzu UV-3100PC. Thin films of $PC_{61}BM$, $PC_{71}BM$, and BCN-HH-BCN were spin-coated from their *o*-dichlorobenzene solutions (10 mg mL⁻¹) on glass substrate at 1000 rpm for 2 min, respectively.



Fig. S4 Electronic absorption spectra of (a) $PC_{61}BM$:BCN-HH-BCN (2:1) (red) and $PC_{71}BM$ /BCN-HH-BCN (2:1) (blue) blend films (b) $PC_{61}BM$ (red), $PC_{71}BM$ (blue), and BCN-HH-BCN (black) in the solid state.

SCLC measurements. Hole-only devices were prepared with a structure of ITO/PEDOT:PSS/active layer/Au.⁴ The active layers were prepared from 20 mg mL⁻¹ solution of PC₆₁BM or PC₇₁BM in *o*-dichlorobenzene. The carrier mobilities of these devices were calculated from the equation of $J = 9\varepsilon \varepsilon_0 \mu V^2/d^3$, where $\varepsilon_1 \varepsilon_0$, μ , and *d* are the dielectric constant of the active layer, the permittivity of free space, the carrier mobility, and the thickness of active layer, respectively. The thickness of PC₆₁BM and PC₇₁BM were 54.3 and 54.5 nm, respectively. We used the values of $\varepsilon = 3$, $\varepsilon_0 = 8.8 \times 10^{-12}$.



Fig. S5 $J-V^2 d^{-3}$ characteristics of hole-only device for PC₆₁BM (red) or PC₇₁BM (blue) films under the dark condition.

Fluorescence lifetime measurements. The fluorescence lifetime was measured with a time-correlated single-photoncounting (TCSPC) lifetime spectrofluorometer (Horiba, FluoroCube). Prior to the measurement, BCN-HH-BCN was dissolved in chloroform and bubbled in a quartz cuvette by Ar for 15 min. The excitation and detection wavelengths were set at 470 and 750 nm, respectively. As shown in Fig. S6, the emission decayed exponentially with a time constant of $\tau = 0.44$ ns.



Fig. S6 The emission decay kinetics of BCN-HH-BCN in chloroform monitored at 750 nm upon the laser excitation at 470 nm (closed circles). The dotted and broken lines show the instrumental response function and the fitting line by a single exponential function with a time constant of $\tau = 0.44$ ns, respectively.

Transient absorption measurements. Transient absorption data were collected with a pump and probe femtosecond transient spectroscopy system. This system consists of a transient absorption spectrometer (Ultrafast Systems, Helios) and a regenerative amplified Ti:sapphire laser (Spectra-Physics, Hurricane). The amplified Ti:sapphire laser provided 800 nm fundamental pulses at a repetition rate of 1 kHz with an energy of 0.9 mJ and a pulse width of 100 fs (FWHM), which were split into two optical beams with a beam splitter to generate pump and probe pulses. One fundamental beam was converted

into pump pulses at 600 nm with an ultrafast optical parametric amplifier (Spectra-Physics, TOPAS). The other fundamental beam was converted into white light pulses employed as probe pulses in the wavelength region from 400 to 1700 nm. The pump pulses were modulated mechanically with a repetition rate of 500 Hz. The temporal evolution of the probe intensity was recorded with a CMOS linear sensor (Ultrafast Systems, SPEC-VIS) for the visible measurement and with an InGaAs linear diode array sensor (Ultrafast Systems, SPEC-NIR) for the near-IR measurement. Transient absorption spectra and decays were collected over the time range from -5 ps to 3 ns. Typically, 2500 laser shots were averaged on each delay time to obtain a detectable absorbance change as small as $\sim 10^{-4}$. In order to cancel out orientation effects on the dynamics, the polarization direction of the linearly polarized probe pulse was set at a magic angle of 54.7 ° with respect to that of the pump pulse. The sample films were placed in a quartz cuvette purged with N₂ at room temperature. Note that the transient absorption spectra and dynamics were highly reproducible even after the several times measurements. In other words, the laser irradiation had negligible effects on the sample degradation at least under this experimental condition.



Fig. S7 Transient absorption spectra of (a) TMPD and BCN-HH-BCN doped in a PS film and (b) BCN-HH-BCN in an *o*-dichlorobenzene solution at 10 ps (black), 0.5 ns (red), and 2 ns (blue) after the laser excitation at 600 nm. The laser fluence was set at (a) 30 and (b) $15 \,\mu$ J cm⁻².

In order to obtain the absorption bands of BCN-HH-BCN singlet exciton, triplet exciton, and radical anion, we separately measured the transient absorption spectra of N,N,N',N'-tetramethyl-*p*-phenylenediamine (TMPD) and BCN-HH-BCN doped in a polystyrene (PS) film, and BCN-HH-BCN in an *o*-dichlorobenzene solution. As shown in Fig. S7(a), the transient absorption spectrum of TMPD/BCN-HH-BCN doped in a PS film exhibits an absorption peak at 750 nm. This band is assigned to the BCN-HH-BCN radical anion. Note that no distinct absorption of TMPD radical cation (580 nm)⁵ was observed because of the ground-state bleaching signal of BCN-HH-BCN. Fig. S7(b) shows the transient absorption spectra of BCN-HH-BCN in an *o*-dichlorobenzene solution. The absorption band was observed at 950 nm at an early time stage and decayed with a time constant of 0.4 ns. Instead, a new absorption band appeared at 1100 nm with a time constant of 0.4 ns. These rise and decay constants are in good agreement with the fluorescence decay time constant mentioned above. We therefore assign the absorption bands at 950 and 1100nm to the singlet and triplet excitons of BCN-HH-BCN, respectively.

References

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