Electronic Supplementary Information

Efficient Dyad-based Organic Solar Cells with a Highly Crystalline Donor Group

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Chemicals

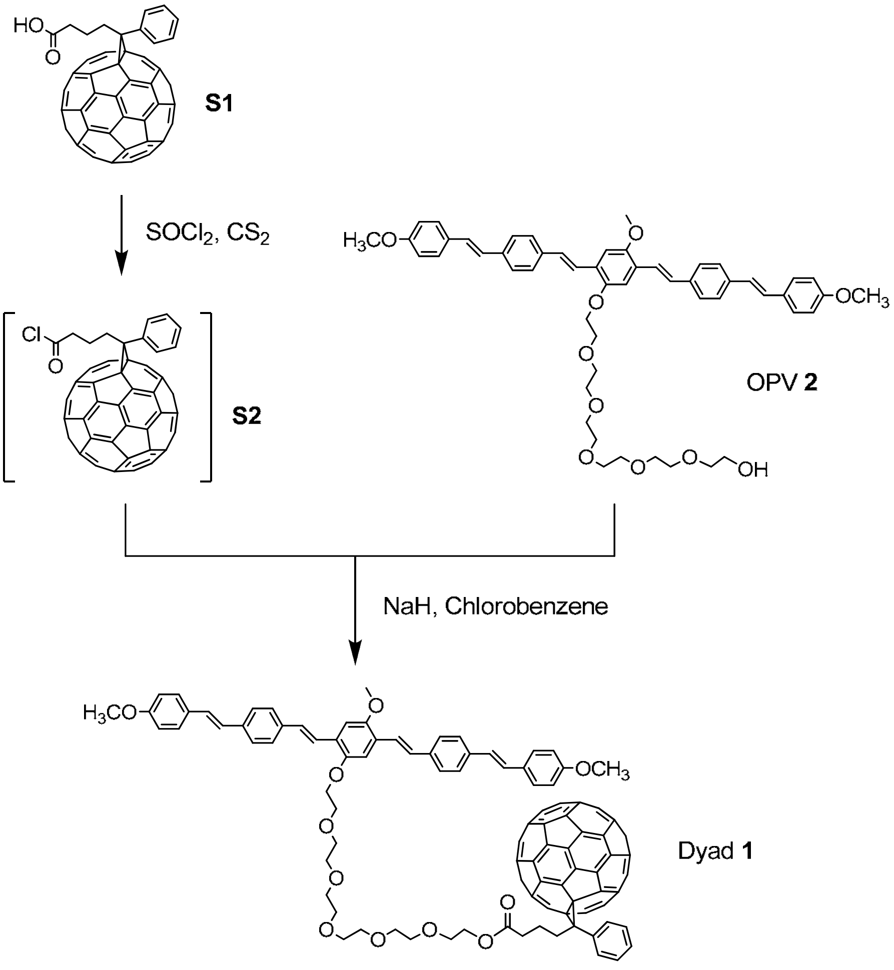
The fullerene derivative PCBM was purchased from Frontier Carbon Corp. The remaining chemicals were purchased from Wako Pure Chemicals Industries, Ltd. All chemicals were used as received.

Instruments

^{1}H NMR spectra were measured in $CDCl_3$ containing 0.03% v/v TMS using an OXFORD Superconducting magnet system (500 MHz). MALDI-TOF MS spectra were measured with dithranol as matrix on an Applied Biosystems BioSpectrometry workstation Model Voyager-DE STR Spectrometer. Powder X-ray diffraction (XRD) patterns were obtained using a RINT 2400 X-ray diffractometer (Rigaku) with an X-ray source of Cu-Kα at 45 kV-200 mA. Differential scanning calorimetry (DSC) traces were obtained using a Rigaku Thermo plus DSC8230. Absorption spectra were measured on a JASCO V-650 spectrophotometer.

Synthesis

OPV **2** and Dya**d 1** were synthesized according to our previous papers [1-3].



Scheme S1. Synthesis of dyad **1**.

Dyad 1

Thionyl chloride (4.9 g, 41 mmol) was added to a solution of **S1**[1] (300 mg, 0.34 mmol) in 80 mL of freshly distilled CS_2, and the solution was heated to reflux for 17 h. After all the volatile components were removed in vacuo, sodium hydride (8 mg, 0.33 mmol) and chlorobenzene (50 mL) were added to the residue (**S2**). Then, a separately prepared solution of **OPV 2**[3] (150 mg, 0.18 mmol) dissolved in 100 mL of chlorobenzene was added to the reaction mixture. After the reaction mixture was stirred at 60 ºC for 5 days, the solution was filtered, and the solvent was removed by evaporation. The crude product was purified by silica column chromatography twice; first eluting with chloroform/ethyl acetate (1:1), then with chloroform/ethyl acetate (7:1). The obtained product was further purified by HPLC with chloroform/ethyl acetate (9:1) as eluant to afford the pure product (81 mg, 26.3%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ : 7.89 (d, 2H, J = 7.5 Hz, *o-H*PhC(C60)), 7.54 – 7.44 (m, 17H, Ph-H(OPV), *m-H*PhC(C60), *p-H*PhC(C60)), 7.19-6.96 (m, 8H, -*CH*=*CH*- x 4), 6.91 (d, 4H, J = 8.5 Hz, -CH_2O-*H*Ph, Ph*H*-OCH_2-), 4.24 (t, 2H, J = 5.0 Hz, -Ph-O$C\mathit{H}_2$$CH_2$O-), 4.21 (t, 2H, J = 4.8 Hz, -$C\mathit{H}_2$OCOCH2-), 3.94-3.93 (m, 5H, CH_3O-Ph-$OCH_2$$C\mathit{H}_2$O-), 3.84 (s, 6H, C$\mathit{H}_3$O-Ph-CH=CH-, -CH=CH-Ph-OCH_3), 3.79-3.61 (m, 18H, -(O$C\mathit{H}_2$$C\mathit{H}_2$O)$_4$$C\mathit{H}_2$$CH_2$OCO), 2.89 (m, 2H, PhC(C60)$C\mathit{H}_2$), 2.52 (t, 2H, J = 7.8 Hz, $C\mathit{H}_2$COO), 2.16 (m, 2H, $C\mathit{H}_2$$CH_2$COO). Molecular weight (calc. for $C_{124}H_{70}O_{11}$, 1735.88). MALDI TOF-MS m / z: (found [M]$^{2-}$ 1733.44).

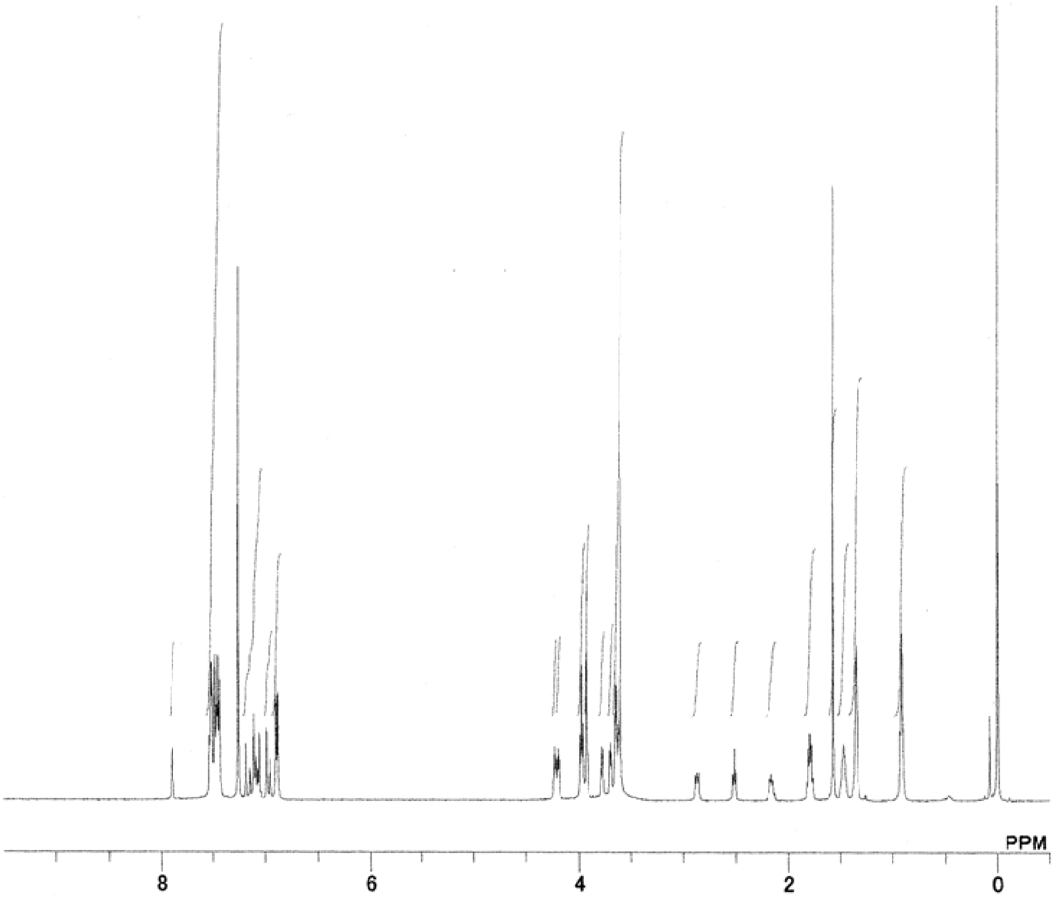


Figure S1. NMR spectrum of dyad **1**.

DSC measurement

The DSC trace of dyad **1** was obtained at a scan rate of 10 ºC min^{-1} after an initial heating process to eliminate the thermal history of the sample.

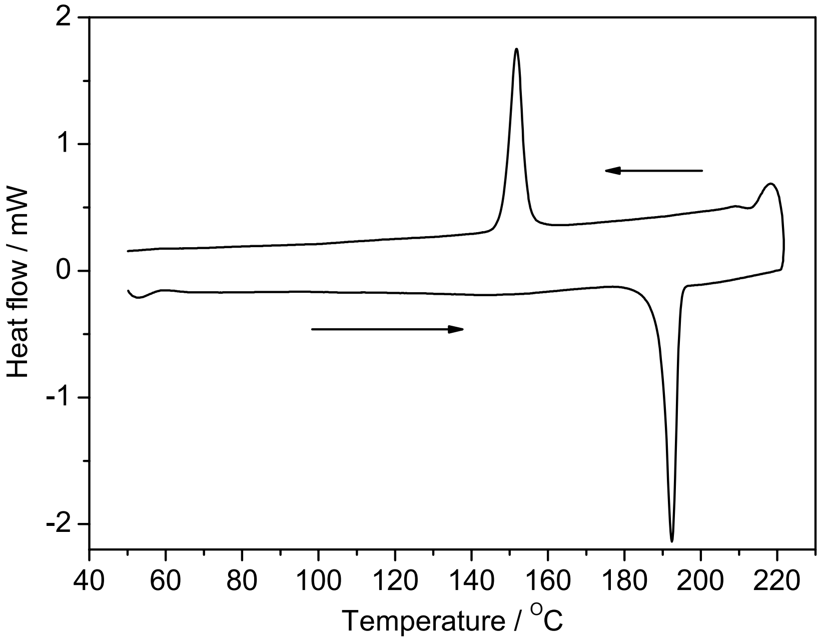


Figure S2. DSC trace of dyad **1**.

Solar cell fabrication and measurement

Solar cells were fabricated as follows. Indium tin oxide (ITO) coated glass substrates (sheet resistance: 10 Ω sq^{-1}, Geomatech, Japan) were cleaned by ultra-sonication in detergent, H_2O, acetone, and 2-propanol. The PEDOT:PSS layer was applied to the ITO substrates by spin-coating (4000 rpm, 30s), followed by drying at 140 ºC for 15 minutes. The organic layer was applied by spin-coating (1000 rpm, 30s) $CHCl_3$ solutions containing 10 mg mL^{-1} of dyad **1**, and 0.4 mg mL^{-1} of poly(dimethyl siloxane-*b*-methyl methacrylate) (PDMS-*b*-PMMA) (M_n = 8000 for PDMS and M_n = 4000 for PMMA, M_w/M_n = 1.09, Polymer Source, Canada). Note that PDMS-b-PMMA spontaneously forms a buffer layer over the organic layer[4]. Finally, an Al cathode electrode (80 nm) was deposited onto the organic layer under a high vacuum (3×10^{-4} Pa).

I-*V* characteristics of the devices were measured under the irradiation of simulated solar light (AM 1.5, 100 mW cm^{-2}) from a 150 W xenon lamp (PEC-L11, Peccell Technologies, Inc., Japan) with an AM 1.5 filter. The light intensity was calibrated with a standard silicon solar cell (BS520, Bunkoh-Keiki, Japan). The active area of the devices was defined by a photo mask as 0.06 cm^2. The external quantum efficiency (EQE) of the devices was measured on a Hypermonolight System SM-250F (Bunkoh-Keiki, Japan).

EQE spectrum

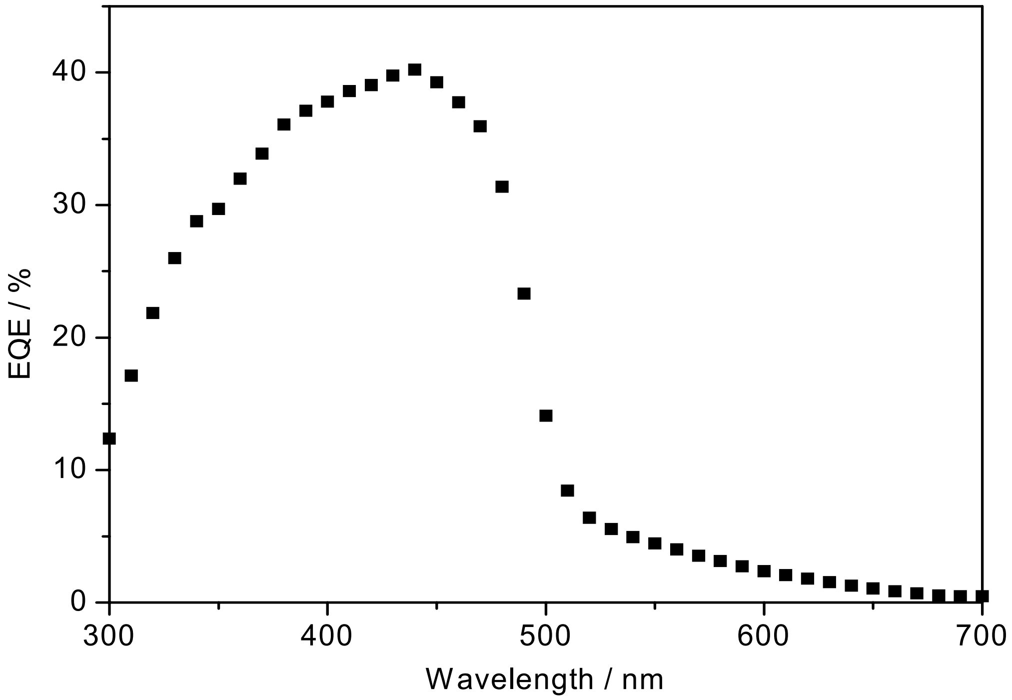


Figure S3. EQE spectrum of the dyad **1** device annealed at 150 ºC for 1 min.

Reference

1. T. Nishizawa, K. Tajima and K. Hashimoto, *J. Mater. Chem.*, 2007, **17**, 2440-2445.
2. T. Nishizawa, K. Tajima and K. Hashimoto, *Nanotechnology*, 2008, **19**, 424017.
3. T. Nishizawa, H. K. Lim, K. Tajima and K. Hashimoto, *J. Am. Chem. Soc.*, 2009, **131**, 2464-2465.
4. S. Yamakawa, K. Tajima and K. Hashimoto, *Org. Electron.*, in press.