Electronic Supplementary Information

Three-dimensional electron-accepting compounds containing perylene bis(dicarboximide)s as n-type organic photovoltaic materials

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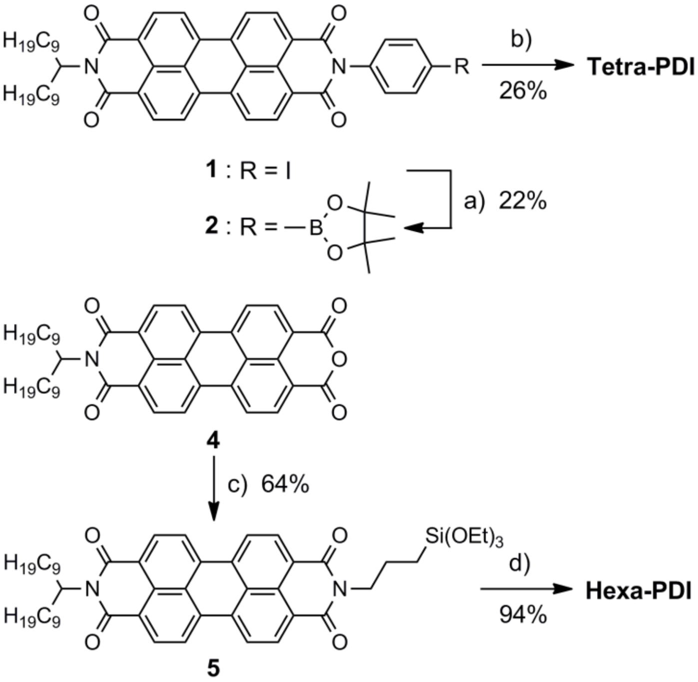
Table of Contents

Scheme and Figures **S2-S4**
General Information **S5**
Materials **S5**
Experimental Procedures **S6–S7**
GPLC Charts **S8**
OFET Device Fabrication **S9**
Photovoltaic Device Fabrication **S10**
Surface Free Energy Estimation **S11**
Charge Extraction Measurement **S12**
References **S13**

Scheme and Figures



Scheme S1. Syntheses of **Tetra-PDI** and **Hexa-PDI**. Reagents and conditions: (a) PdCl$_2$(dppf), KOAc, bis(pinacolato)diboron, DMSO, 110 °C; (b) Pd(PPh$_3$)$_4$, K$_2$CO$_3$, C(C$_6$H$_4$I)$_4$ (**3**), THF/H$_2$O, 90 °C; (c) H$_2$N(CH$_2$)$_3$Si(OEt)$_3$, 150 °C; (d) TBAF, CHCl$_3$, r.t..

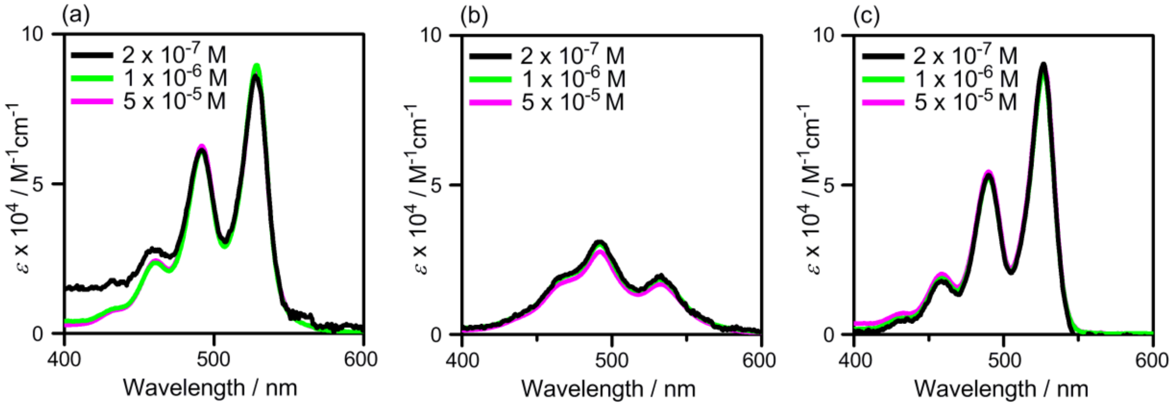


Fig. S1 Concentration-dependent UV-vis spectra of (a) **Tetra-PDI**, (b) **Hexa-PDI**, and (c) **6** in CHCl$_3$. Molar extinction coefficients were normalized by the number of PDI unit.

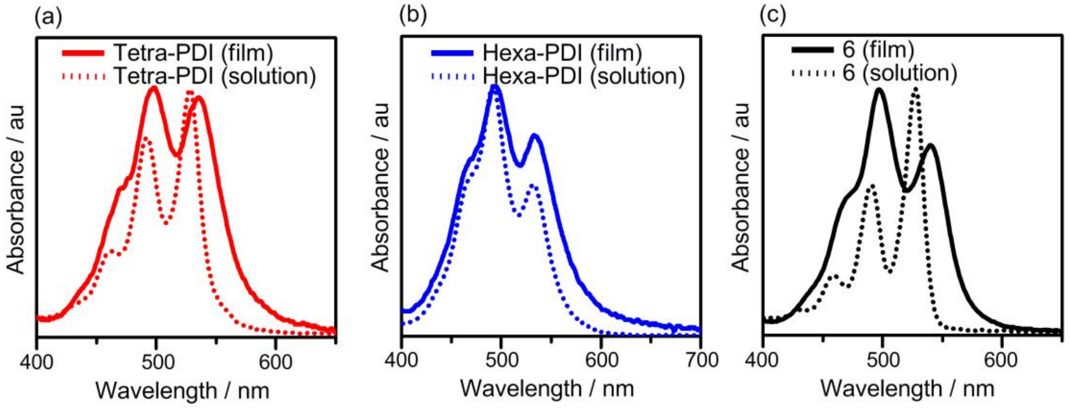


Fig. S2 UV-vis spectra of (a) **Tetra-PDI**, (b) **Hexa-PDI**, and (c) **6** in films.

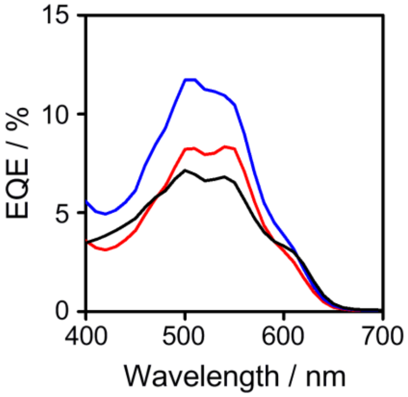


Fig. S3 EQE spectra of the OPV devices based on blend of P3HT:**Tetra-PDI** (red solid line), P3HT:**Hexa-PDI** (blue solid line), and P3HT:**6** (black solid line).

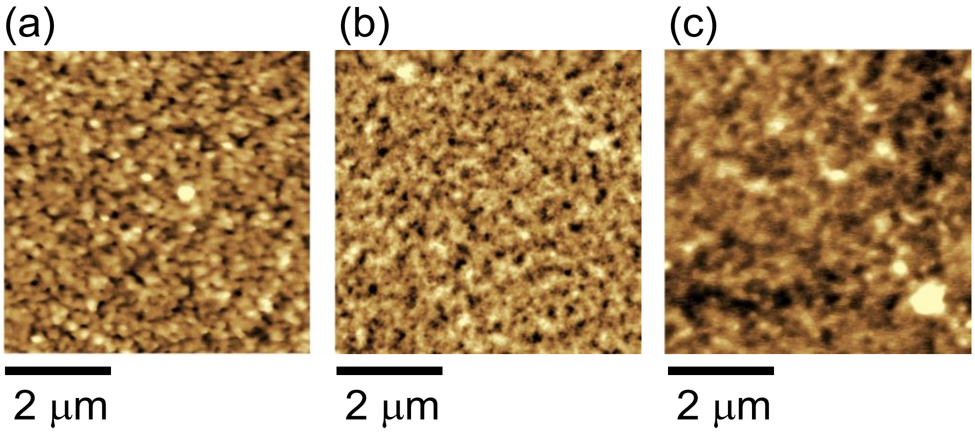


Fig. S4 AFM images of (a) **Tetra-PDI**, (b) **Hexa-PDI**, and (c) **6**.

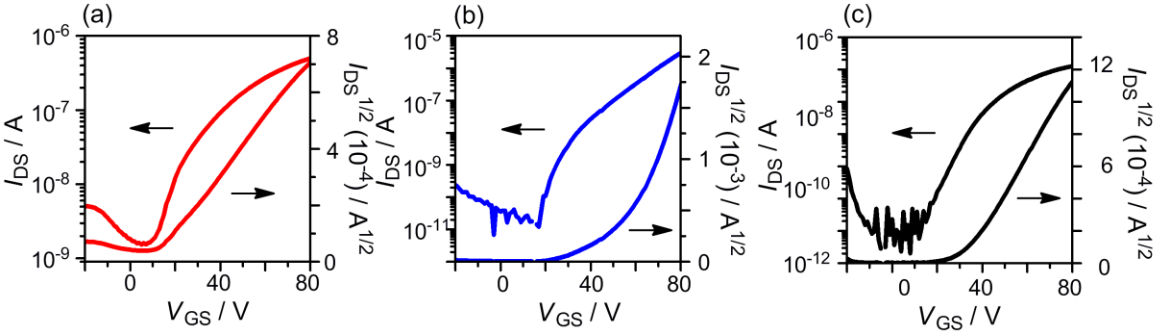


Fig. S5 Transfer characteristics of OFETs based on (a) **Tetra-PDI**, (b) **Hexa-PDI**, and (c) **6** at a drain voltage of 80 V.

Table S1. OFET characteristics

Compounds	μ_e/cm^2 V^{-1} s^{-1}	on/off ratio	V_{th}/V
Tetra-PDI	1.8×10^{-6}	10^3	10
Hexa-PDI	1.2×10^{-4}	10^5	59
6	1.0×10^{-5}	10^6	33

General Information. Column chromatography was performed on silica gel, KANTO Chemical silica gel 60 N (40–50 μm). Thin-layer chromatography (TLC) plates were visualized with UV light. Preparative gel-permeation chromatography (GPC) was performed on Japan Analytical Industry LC-918 equipped with JAI-GEL 1H/2H column. Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL ECS-400 and ECA-600 spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. Data are reported as follows: chemical shift in ppm (δ), multiplicity (d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad), coupling constant (Hz), and integration. Mass spectra were obtained on a Shimadzu AXIMA-TOF. Analytical gel permeation liquid chromatography (GPLC) was performed on a Hitachi High-Technologies Corporation L-2420/L-2130 equipped with a shodex K-803L. UV-vis spectra were recorded on a Shimadzu UV-3100PC spectrophotometer. Fluorescence spectra were recorded using a Fluoromax-2 spectrometer in the photo-counting mode equipped with a Hamamatsu R928 photomultiplier. The bandpass for the emission spectra was 1.0 nm. All spectra were obtained in spectrograde solvents. Cyclic voltammetry was carried out on a BAS CV-620C voltammetric analyzer. Elemental analyses were performed on Perkin Elmer LS-50B by the Elemental Analysis Section of Comprehensive Analysis Center (CAC), ISIR, Osaka University.

Materials. All reactions were carried out under a nitrogen atmosphere. Solvents of the highest purity grade were used as received. Unless stated otherwise, all reagents were purchased from commercial sources and used without purification. **1** was prepared by our previously reported procedure.[1] Tetrakis(4-iodophenyl)methane (**3**)[2] and *N*-(10-nonadecyl)-3,4,9,10-perylenetetracarboxylic acid 3,4-anhydride-9,10-imide (**4**)[3] were prepared by the reported procedure. ^{1}H NMR data of these compounds were in agreement with those previously reported.

Experimental Procedures

*Synthesis of **2***: **1** (1.00 g, 1.16 mmol), bis(pinacolato)diboron (769 mg, 2.33 mmol), KOAc (342 mg, 3.49 mmol), and $PdCl_2$(dppf) (128 mg, 0.18 mmol) were placed in a test tube with screw cap and dissolved in DMSO (12 mL). The reacion mixture was stirred at 110 °C for 12 h. After being cooled to room temperature, the mixture is diluted with $CHCl_3$ and washed with water. After removal of the solvent under reduced pressure, the residue was filtered over silica gel with $CHCl_3$ as eluent, followed by isolation with preparative GPC to give **2** (759 mg, 79%). Red solid; m.p. = 262-263 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.76-8.67 (m, 8H), 8.03 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.3 Hz, 2H), 5.19 (m, 1H), 2.26 (m, 2H), 1.88 (m, 2H), 1.37 (s, 12H), 1.34-1.198 (m, 28 H), 0.83 (t, *J* = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 164.56, 163.41, 137.69, 135.93, 135.06, 134.27, 131.77, 131.09, 129.79, 129.50, 127.91, 126.63, 126.36, 124.10, 123.25, 123.02, 83.99, 54.81, 40.99, 31.84, 29.52, 29.25, 26.96, 24.86, 22.63, 14.07; MS (MALDI-TOF,1,8,9-trihydroxyanthracene matrix) *m/z* 858.48 (M^+, Calcd. 858.48); Anal. Calcd. for $C_{55}H_{63}BN_2O_6$: C, 76.91; H, 7.39; N, 3.26. Found: C, 76.63; H, 7.34; N, 3.23.

*Synthesis of **Tetra-PDI***: **2** (130 mg, 0.15 mmol), **3** (28 mg, 0.03 mmol), K_2CO_3 (42 mg, 0.00 mmol), and $Pd(PPh_3)_4$ (7 mg, 6 μmol) were placed in a test tube with screw cap and dissolved in THF/H_2O (1.5/0.3 mL). The reaction mixture was stirred at 90 °C for 12 h. After being cooled to room temperature, the mixture is extracted with $CHCl_3$. After removal of the solvent under reduced pressure, the residue was filtered over silica gel with $CHCl_3$ as eluent, followed by purification with preparative GPC to give **Tetra-PDI** (26 mg, 26%). Red solid; m.p. > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.80-7.40 (br, 64H), 5.20-5.00 (br, 4H), 3.60-3.40 (br, 16H), 2.20-0.60 (br, 136H); MS (MALDI-TOF,1,8,9-trihydroxyanthracene matrix) *m/z* 3243.67 (M^+, Calcd. 3243.67);

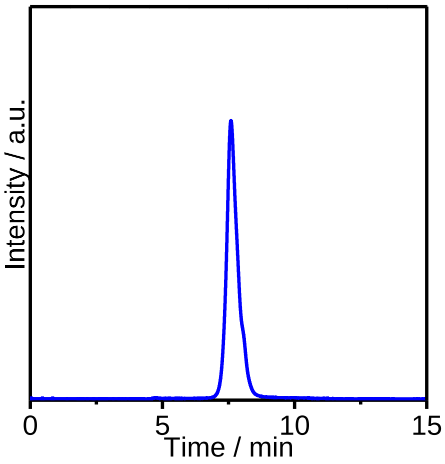
*Synthesis of **5***: **4** (258 mg, 0.39 mmol), 3-triethoxysilyl-1-propylamine (1 mL) were placed in a test tube with screw cap and stirred at 150 °C for 12 h. After removal of the solvent under reduced pressure, the residue was filtered over silica gel with $CHCl_3$ as eluent, followed by isolation with preparative GPC to give **5** (217 mg, 64%). Red solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.70-8.60 (m, 8H), 5.17 (m, 1H), 4.21 (t, *J* = 7.5 Hz, 2H), 3.82 (q, *J* = 6.8 Hz, 6H), 2.27-2.23 (m, 2H), 1.92-1.85 (m, 4H), 1.32-1.21 (m, 26H) , 1.22 (t, *J* = 6.8 Hz, 9H), 0.88 (t, *J* = 7.5 Hz, 2H), 0.83 (t, *J* = 7.5 Hz, 6H), 0.77 (t, *J* = 8.2 Hz, 2H); ^{13}C

NMR (100 MHz, $CDCl_3$, TMS): δ 163.52, 163.05, 134.13, 131.13, 131.05, 129.09, 129.05, 126.00, 123.15, 123.13, 122.80, 77.230, 58.42, 44.31, 43.04, 37.95, 30.75, 28.69, 24.07, 23.07, 21.50, 18.28, 14.10, 10.61, 8.03; MS (MALDI-TOF,1,8,9-trihydroxyanthracene matrix) *m/z* 860.15 (M^+, Calcd. 860.48).

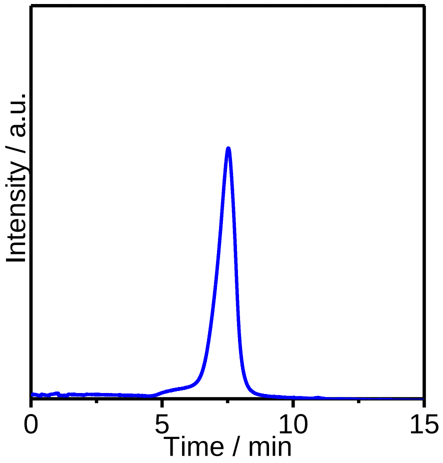
*Synthesis of **Hexa-PDI***: **5** (217 mg, 0.252 mmol), TBAF (1 mol/L in THF, 0.1 mL) were placed in round-bottomed flask and dissolved in $CHCl_3$ (3 mL). The reaction mixture was stirred at room temperature for 24 h. The mixture is diluted with $CHCl_3$ and washed with water. After removal of the solvent under reduced pressure, the residue was filtered over silica gel with $CHCl_3$ as eluent, followed by isolation with preparative GPC to give **Hexa-PDI** (177 mg, 93%). Red solid; m.p. > 300 ºC; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 8.80-7.40 (br, 64H), 5.20-4.80 (br, 24H), 4.40-4.00 (br, 32H), 3.60-3.20 (br, 16H), 2.40-2.00 (br, 48H), 1.60-1.00 (br, 192H), 0.75 (br, 48H); MS (MALDI-TOF,1,8,9-trihydroxyanthracene matrix) *m/z* 5997.97 (M^+, Calcd. 5997.97).

GPLC Charts

Chromatogram of **Tetra-PDI**



Chromatogram of **Hexa-PDI**



OFET Device Fabrication: The field-effect mobility was measured using bottom-contact thin-film field-effect transistor (FET) geometry. The p-doped silicon substrate functions as the gate electrode. A thermally grown silicon oxide dielectric layer on the gate substrate was 300 nm thick with a capacitance of 10.0 nF cm^{-2}. Interdigital source and drain electrodes were constructed with gold (30 nm) that were formed on the SiO_2 layer. The channel width (W) and channel length (L) were 294 mm and 25 μm, respectively. The silicon oxide surface was washed with toluene, acetone, water, and 2-propanol. The silicon oxide surface was then activated by ozone treatment and pretreated with hexamethyldisilazane (HMDS). The semiconductor layer was spin-coated on the Si/SiO_2 substrate at 1000 rpm from 1.0 wt% copolymer solution in chloroform. The characteristics of the OFET devices were measured at room temperature under a pressure of 10^{-3} Pa. The field-effect electron mobility (μ_e) was calculated in the saturated region at the V_{DS} of 80 V and the current on/off ratio was determined from the I_{DS} at V_{GS} = –40 V (I_{off}) and V_{GS} = 80 V (I_{on}) by the following equation.

$$I_{DS} = \frac{W}{2L} C_i \mu (V_{GS} - V_{th})^2$$

Photovoltaic Device Fabrication: Organic photovoltaic devices were prepared with a structure of ITO/PEDOT:PSS/active layer/LiF/Al. ITO-coated glass substrates were first cleaned by ultrasonication in toluene, acetone, H_2O, and 2-propanol for 10 min, respectively, followed by O_2 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 fabricated from their chlorobenzene solutions. The concentration of blend solutions and the donor–acceptor ratio were fixed at 1.0 wt% and 1:1, respectively. The active layers were then prepared by spin-coating on the ITO/PEDOT:PSS electrode at 1000 rpm for 2 min in a glove box. The typical thickness of the active layer was 90–110 nm. LiF and Al electrode were evaporated on the top of active layer through a shadow mask to define the active area of the devices (0.09 cm^2) under a vacuum of 10^{-5} Pa to a thickness of 1.0, 100 nm determined by a quartz crystal monitor. Thermal annealing was performed at 80 °C for 10 min. 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.

Surface Free Energy Estimation

The contact angles of compounds were measured by a NiCK LSE-ME1 with distilled water and glycerol. The surface free energy was estimated based on the established theory.[4]

Compounds	Contact angle (˚) (H_2O)	Contact angle (˚) (glycerol)	Surface free energy (mJ/m^2)
Tetra-PDI	98.1	92.2	17.0
Hexa-PDI	102.3	88.8	20.0
6	104.9	92.7	14.7
P3HT	107.2	102.6	9.7
PC$_{61}$BM	80.9	65.9	33.7

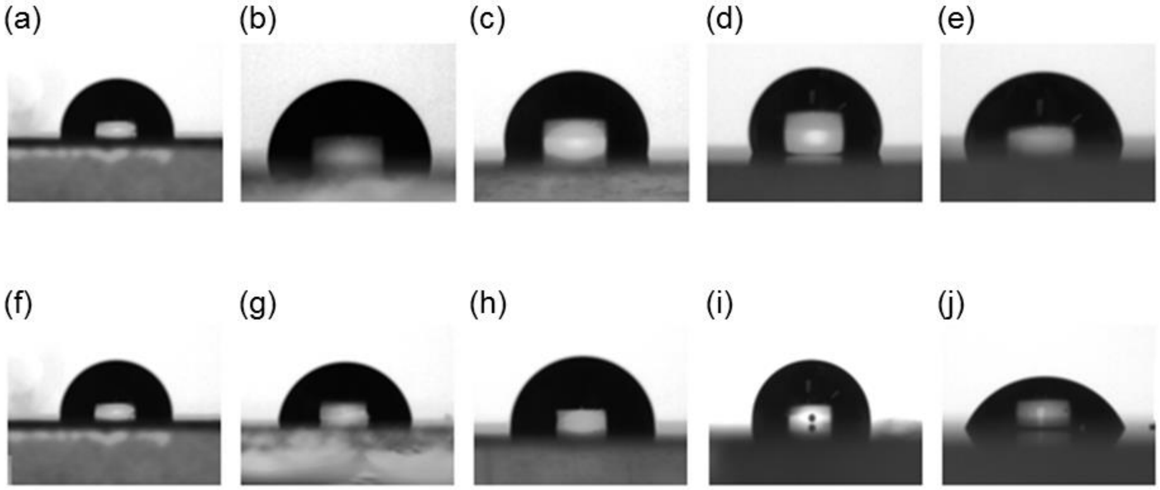


Fig. S4 Contact angle measurements of (a) **Tetra-PDI** (H_2O), (b) **Hexa-PDI** (H_2O), (c) **6** (H_2O), (d) **P3HT** (H_2O), (e) **PC$_{61}$BM** (H_2O), (f) **Tetra-PDI** (glycerol), (g) **Hexa-PDI** (glycerol), (h) **6** (glycerol), (i) **P3HT** (glycerol), (j) **PC$_{61}$BM** (glycerol).

Charge Extraction Measurement: The plots of V_{oc} vs charge density and lifetime vs charge density were measured by charge extraction measurements. The method is similar to that reported by Shuttle et. al,[5] but we modified it so that we were able to apply bias potential during the extraction. The description of the experiments in detail will be published elsewhere. In brief, a solar cell was connected with a fast MOSFET switch and a function generator in series. The cell was irradiated by a CW diode laser (635 nm, 100 mW, CUBE, Coherent) at open circuit conditions and V_{oc} was measured. Then, the laser was turned off and simultaneously the switch was turned off. At dark, transient current originated from the stored charges in the cell under laser irradiation was recorded, and the current was numerically integrated. During the extraction, bias potential was applied to accelerate the time for extraction. This was to avoid charge recombination during the extraction. The measurement was repeated by changing the laser intensity and the V_{oc} was plotted as a function of the integrated charges.

To measure the charge recombination lifetime, the switch was turned off some time after the laser irradiation was turned off. Then, transient current was measured. The measurement was repeated by changing the time to turn off the switch, and integrated charges were plotted as a function of the time. Lifetime was obtained from the slope of the plot.

For the both measurements, bias voltage of 1 V for P3HT/$PC_{61}BM$ cell and that of 4 V for P3HT/**Hexa-PDI** cell was applied.

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