

# Photoconversion Mechanism at the *pn*-Homojunction Interface in Single Organic Semiconductor

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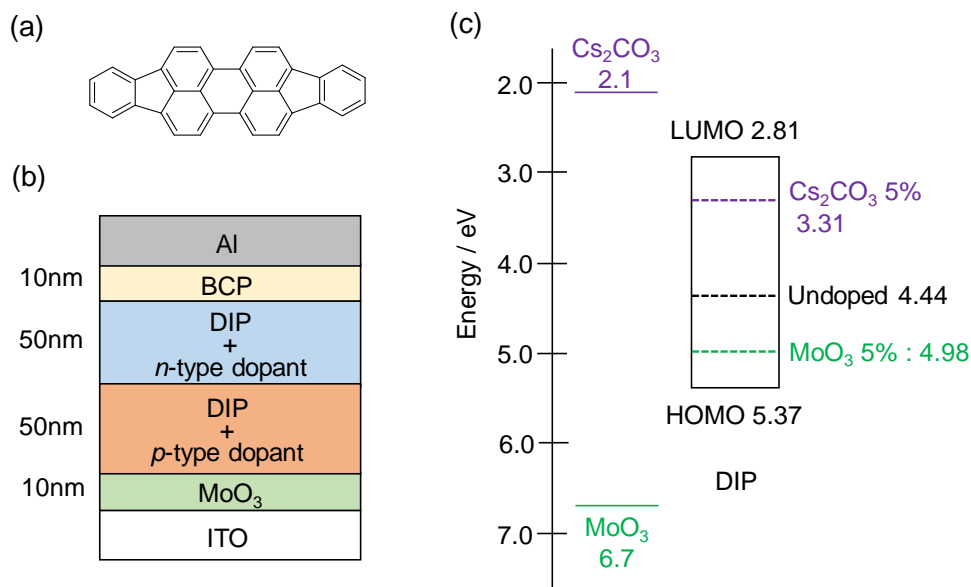
## Methods

The organic SC devices were fabricated on ITO-coated glass substrates (ITO thickness: 150 nm; sheet resistance: 10.3  $\Omega$  sq<sup>-1</sup>; Techno Print, Fujimino, Japan). MoO<sub>3</sub> (Alfa Aesar, Haverhill, MA, USA), DIP (Lumtec, New Taipei City, Taiwan), Cs<sub>2</sub>CO<sub>3</sub> (Sigma-Aldrich, St. Louis, MO, USA), BCP (Tokyo Chemical Industry, Tokyo, Japan) were used without further purification.

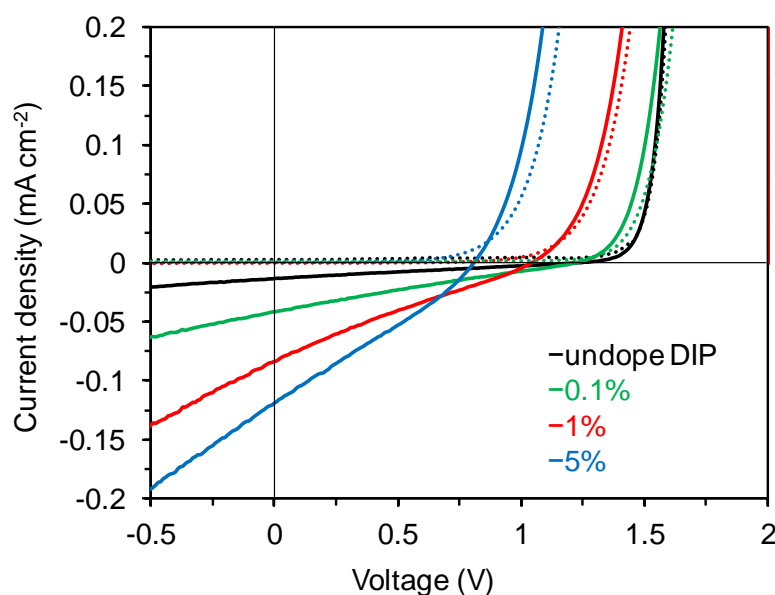
The MoO<sub>3</sub> hole-transporting layer (10 nm, 0.1 nm s<sup>-1</sup>), doped DIP layer (100 nm, 0.1 nm s<sup>-1</sup>), BCP electron-transport layer (15 nm, 0.1 nm s<sup>-1</sup>), and Al electrodes (60 nm, 0.4 nm s<sup>-1</sup>) were deposited via thermal evaporation under high vacuum ( $\sim 10^{-5}$  Pa) in a vacuum evaporation system (VTS-350M, ULVAC, Kanagawa, Japan) housed in a glove box (UNICO, Suite E Dayton, NJ, USA). The MoO<sub>3</sub> and Cs<sub>2</sub>CO<sub>3</sub> as the dopants were introduced by co-deposition with DIP.

The devices were characterized in a vacuum container for optical measurements (Epitech, Kyoto, Japan) without exposure to air. The *J*-*V* characteristics of the devices were measured under simulated solar illumination (AM 1.5, 100 mW cm<sup>-2</sup>) from a solar simulator based on a 300-W Xe lamp (HAL-320, Asahi Spectra, Torrance, CA, United States) using a source meter (R6243, Advantest, Tokyo, Japan). The light intensity was calibrated with a standard silicon solar cell (CS-20, Asahi Spectra, Torrance, CA, United States) and controlled by neutral density filter (SIGMAKOKI, Tokyo, Japan). The active area of the devices was defined using a 0.04 cm<sup>2</sup> photomask. The EQE values of the devices were measured using a monochromator (SPG-100 ST, Shimadzu, Kyoto, Japan), a 500W Xe lamp (UI-502Q, Ushio Lighting, Tokyo, Japan), and a silicon photodiode (Hamamatsu Photonics, Hamamatsu, Japan). The *J*-*V* characteristics of the devices at various temperatures were measured in a cryostat (Janis, Woburn, MA, USA) without exposure to air.

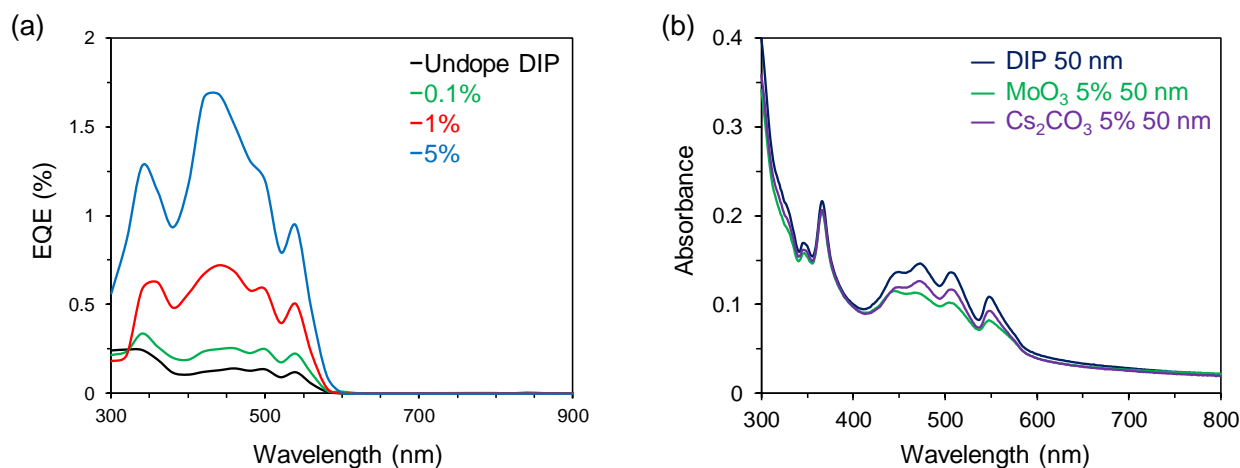
The UV-vis absorption spectra were measured on a spectrometer (V-570, JASCO, Tokyo, Japan). The PYS spectra were measured using an (AC-2, Riken-Keiki, Tokyo, Japan). The WF was determined using a Kelvin probe (FAC-1, Riken-Keiki, Tokyo, Japan) without exposure to air. The Kelvin probe was housed in a glove box with N<sub>2</sub> gas (H<sub>2</sub>O < 1 ppm, O<sub>2</sub> < 1 ppm).



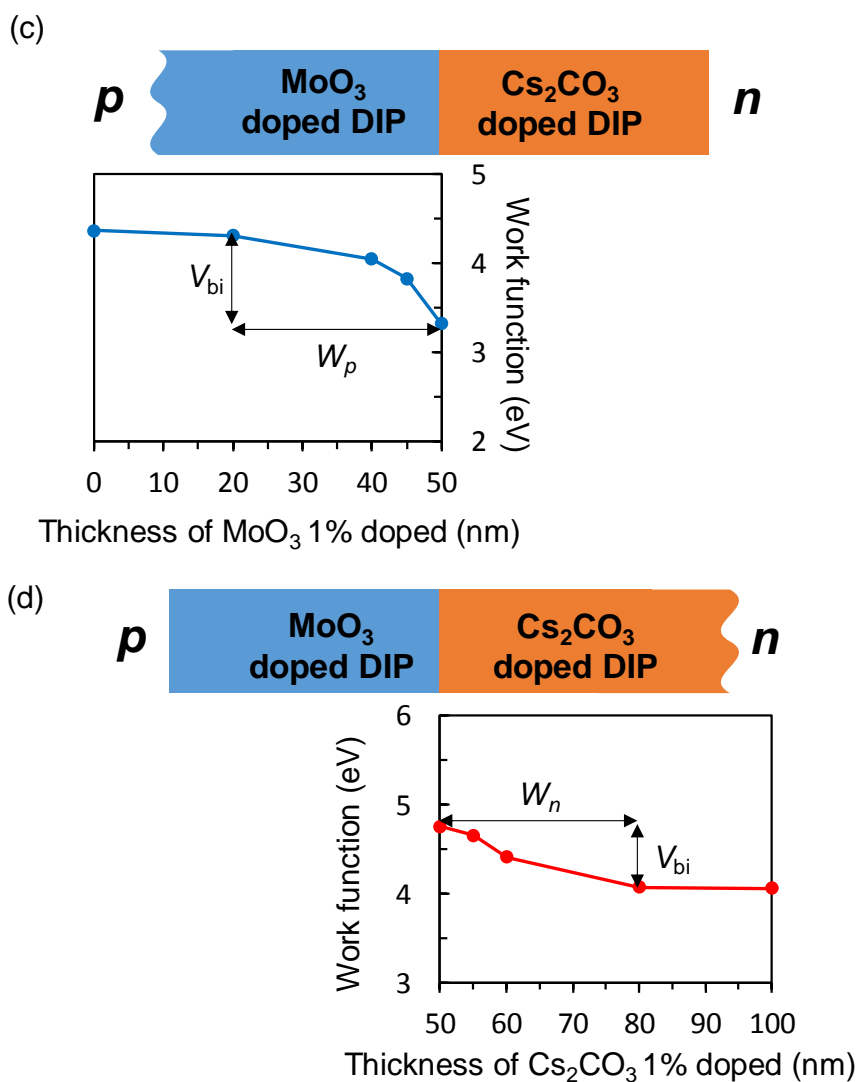
**Figure S1.** (a) Chemical structure of DIP. (b) Schematic of the *pn*-homojunction device. (c) Energy levels of DIP, MoO<sub>3</sub> and Cs<sub>2</sub>CO<sub>3</sub>. The dashed lines indicate the position of *E<sub>F</sub>* of the 50 nm undoped (black), 5% MoO<sub>3</sub> doped (green) and 5% Cs<sub>2</sub>CO<sub>3</sub> doped (purple) films on ITO substrates. The energy level of DIP is cited from Appl. Phys. Lett. 101, 233301 (2012), and HOMO and LUMO are measured by ultraviolet and inverse photoelectron spectroscopy in the paper. Reprinted with permission from S. Izawa et al., *Org. Electron.* **2019**, 71, 45–49. Copyright 2019, Elsevier.



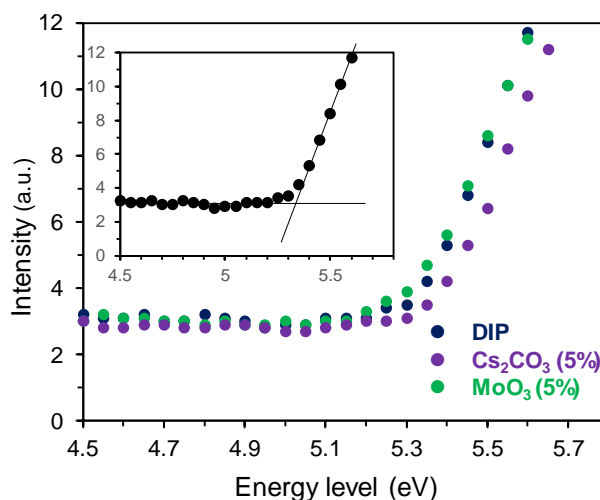
**Figure S2.** *J-V* curves of homojunction devices with 100 nm undoped layer (black) and *pn* doped DIP layers having same MoO<sub>3</sub> and Cs<sub>2</sub>CO<sub>3</sub> concentrations of 0.1% (green), 1% (red) and 5% (blue) using DIP as a host molecule under AM 1.5 irradiation (100 mW cm<sup>-2</sup>, solid lines) or in the dark (dashed lines). The same concentrations of *p*- and *n*-dopants were introduced in the active layers. Reprinted with permission from S. Izawa et al., *Org. Electron.* **2019**, 71, 45–49. Copyright 2019, Elsevier.



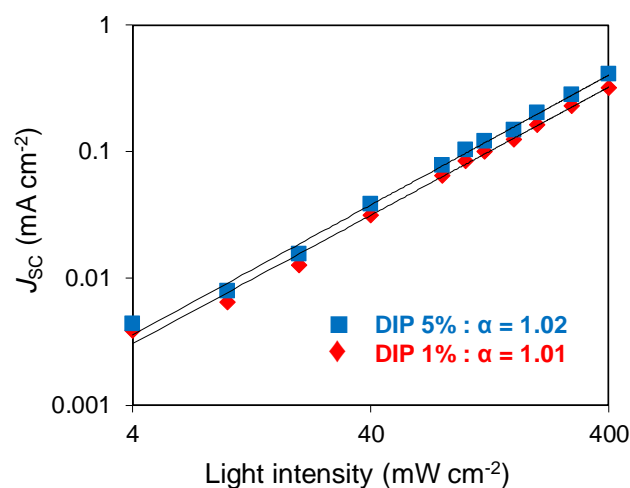
**Figure S3.** (a) EQE spectra of homojunction devices with undoped DIP layer (black), and  $pn$  doped DIP layers with same MoO<sub>3</sub> and Cs<sub>2</sub>CO<sub>3</sub> concentrations of 0.1% (green), 1% (red) and 5% (blue). (b) Absorption spectra of undoped (dark blue), 5% MoO<sub>3</sub> doped (green) and 5% Cs<sub>2</sub>CO<sub>3</sub> doped (purple) DIP films on quartz. The amount of DIP on quartz is equivalent to 50 nm in all the films. Reprinted with permission from S. Izawa et al., *Org. Electron.* **2019**, 71, 45–49. Copyright 2019, Elsevier.



**Figure S4.** WF of (a) 1% MoO<sub>3</sub> doped and (b) 1% Cs<sub>2</sub>CO<sub>3</sub> doped DIP films on the Cs<sub>2</sub>CO<sub>3</sub> doped film and the MoO<sub>3</sub> doped film, respectively, as a function of the thickness.



**Figure S5.** Photoelectron yield spectra of undoped DIP (dark blue), Cs<sub>2</sub>CO<sub>3</sub> 5% doped DIP (purple) and MoO<sub>3</sub> 5% doped DIP (green) thin film. Ionic potential is estimated by approximate line of plot.



**Figure S6.** Light intensity dependence of  $J_{sc}$  of the devices with the 1% (red) and 5% (blue) doped DIP. The value of  $\alpha$  shows the slope of approximate line.

**Table S1.** Summary of the performances of DIP devices with different doping concentrations of MoO<sub>3</sub> and Cs<sub>2</sub>CO<sub>3</sub>. Averaged values are reported. Values inside parentheses are standard deviations. Reprinted with permission from S. Izawa et al., *Org. Electron.* **2019**, 71, 45–49. Copyright 2019, Elsevier.

Concentration (%)	Undoped	0.1	1	5
J <sub>SC</sub> (mA cm <sup>-2</sup> )	0.014 (0.001)	0.056 (0.020)	0.067 (0.017)	0.121 (0.008)
VOC (V)	1.13 (0.14)	1.18 (0.04)	0.98 (0.02)	0.83 (0.10)
FF (%)	25.0 (1.4)	24.4 (0.7)	24.4 (1.6)	29.5 (2.4)
PCE (%)	0.0039 (0.0006)	0.016 (0.006)	0.016 (0.005)	0.026 (0.002)

