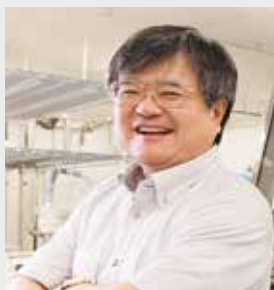


# Organic Solar Cells

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### Awards

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2004 Editor Award, Japanese Journal of Applied Physics

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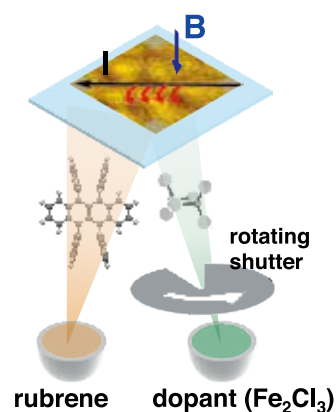
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Organic solar cells have been intensively studied due to many advantages like flexible, printable, light, low-cost, fashionable, etc. We have been focused on the research on the ppm-Level doping effects in organic semiconductor films and organic single crystals for organic solar cells. We believe that the following features are indispensable. (i) A ppm-doping strategy should be performed on sub-ppm purified organic semiconductors together with the total removal of oxygen from the air, which acts as an external dopant. (ii) Perfect *pn*-control, namely, any single or blended organic semiconductors should exhibit either *n* or *p*-type behavior only by impurity doping. (iii) To precisely clarify the nature of the doping effects, ppm doping in the bulk of organic semiconductor single crystals with few grain boundaries should be performed.

So far, we have reported complete *pn*-control, doping sensitization, ppm-level doping effects using an extremely low-speed deposition technique reaching  $10^{-9}$  nm s<sup>-1</sup> (Figure 1), in organic single crystals measured by the Hall effect, which shows a doping efficiency of 24%, and enhancement of

open-circuit voltage of organic solar cells by doping. These results can be regarded as a foundation for the construction of high efficient organic solar cells.



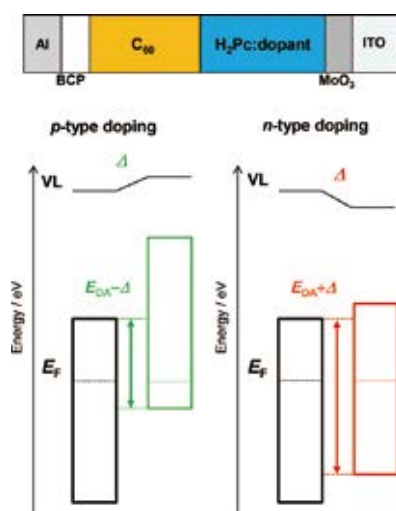
**Figure 1.** Ultra-slow co-deposition technique to produce the doped rubrene single crystal for Hall effect measurements.

### Selected Publications

- M. Hiramoto, M. Kikuchi and S. Izawa, "Parts-per-Million-Level Doping Effects in Organic Semiconductor Films and Organic Single Crystals," *Adv. Mater.* 1801236 (15 pages) (2018). [Invited Progress Report]
- S. Izawa, N. Shintaku and M. Hiramoto, "Effect of Band Bending and Energy Level Alignment at the Donor/Acceptor Interface on Open-Circuit Voltage in Organic Solar Cells," *J. Phys. Chem. Lett.* **9**, 2914–2918 (2018).
- C. Ohashi, S. Izawa, Y. Shinmura, M. Kikuchi, S. Watase, M. Izaki, H. Naito and M. Hiramoto, "Hall Effect in Bulk-Doped Organic Single Crystal," *Adv. Mater.* **29**, 1605619 (6 pages) (2017).

## 1. Controlling Open-Circuit Voltage in Organic Solar Cells by Impurity Doping<sup>1)</sup>

Doping, addition of trace amount of *p*-type and *n*-type impurities, to form the *pn* junction is the central technology in inorganic solar cells. However, the doping effect on the energy-level alignment and the performance in organic solar cells (OSCs) are still unclear. Here, we report that the addition of *p*-type ( $\text{MoO}_3$ ) and *n*-type ( $\text{Cs}_2\text{CO}_3$ ) dopants into a donor layer in phthalocyanine/fullerene planar heterojunction OSCs controls the open-circuit voltage ( $V_{\text{OC}}$ ). The  $V_{\text{OC}}$  decreased to 0.36 V when a *p*-type dopant was added to the donor layer, whereas it increased to 0.52 V with an *n*-type dopant. In contrast to the previous reports where *p*-type dopants were usually added to the donor layer, the *n*-type dopant was found to increase the  $V_{\text{OC}}$ . Energy-level mapping revealed that the origin of the  $V_{\text{OC}}$  change was the vacuum level shifts occurring near the donor/acceptor (D/A) interface because of the Fermi-level alignment (Figure 2). The results demonstrated that the  $V_{\text{OC}}$ s in OSCs are largely affected by the energy-level shift near the D/A interface that could be controlled by *p*-type and *n*-type doping.

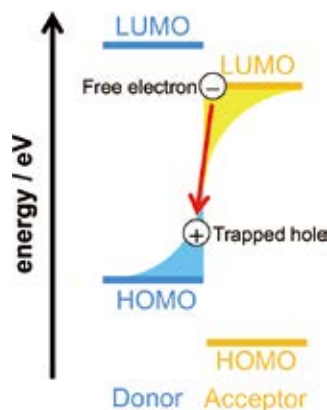


**Figure 2.** Schematic of the Fermi level alignment at the D/A interface when the phthalocyanine layer is doped with *p*-type and *n*-type dopants.

## 2. Effect of Trap-Assisted Recombination on Open-Circuit Voltage Loss in Phthalocyanine/Fullerene Solar Cells<sup>2)</sup>

Large energy losses in  $V_{\text{OC}}$  are still an issue for the photo-conversion efficiency of OSCs. We clarify the relationship between charge recombination and  $V_{\text{OC}}$  loss for phthalocyanine/fullerene planar heterojunction OSCs. We quantify the  $V_{\text{OC}}$  loss relative to the charge-transfer state energy by the temperature dependence of  $V_{\text{OC}}$ . The charge recombination order obtained from impedance measurements indicates the presence of trap-assisted recombination (Figure 3). Our results suggest that the  $V_{\text{OC}}$  losses are caused by the broad distribution of the tail state near the D/A interface. Thus, reducing the number of trap states near the D/A interface could lead to an increase in  $V_{\text{OC}}$ .

The present results offer the method to increase the open-circuit voltage of organic solar cells.



**Figure 3.** Schematics of the charge recombination process. Trapped holes recombining with free electrons.

### References

- 1) N. Shintaku, M. Hiramoto and S. Izawa, *J. Phys. Chem. C* **122**, 5248–5253 (2018).
- 2) N. Shintaku, M. Hiramoto and S. Izawa, *Org. Electron.* **55**, 69–74 (2018).