# **Organic Solar Cells**

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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 establishment of "bandgap science for organic solar cells." We believe that the following features are indispensable. (a) Organic semiconductors purified to sub-ppm level, at least seven nines (7N; 0.1 ppm), should be used. (b) A ppm-level doping technique should be developed. (c) Every individual organic semiconductor should be capable of displaying both *n*- and *p*-type characteristics by impurity doping alone, *i.e.*, complete pncontrol should be developed. (d) Unintentional and uncontrollable doping by oxygen and water from air should be completely eliminated. (e) The doping technique should be applicable not only to single organic semiconductor films, but also to codeposited films consisting of two kinds of organic semiconductors since a key element for exciton dissociation in organic solar cells is having a co-deposited films.

Recently, we have showed that in principle, almost all single organic semiconductors can be controlled to both *n*-type and *p*-type by doping alone, similar to the case of inorganic semiconductors (Figure 1). This can be regarded as a foundation for the construction of high efficient organic solar cells.



Figure 1. Energy diagrams of various organic semiconductor films. The black, red, and blue lines show the energetic position of  $E_{\rm F}$  for non-doped, acceptor dopant (MoO<sub>3</sub>)-doped, and donor dopant  $(Cs_2CO_3)$ -doped films. The doping concentration is 3,000 ppm.  $E_F$ values for MoO<sub>3</sub> and Cs<sub>2</sub>CO<sub>3</sub> films (100 nm) are also shown.

#### Selected Publications

- M. Hiramoto, M. Kubo, Y. Shinmura, N. Ishiyama, T. Kaji, K. Sakai, T. Ohno, M. Izaki and M. Hiramoto, "Bandgap Science for Organic Solar Cells," Electronics 3, 351-380 (2014).
- M. Kubo, K. Iketaki, T. Kaji and M. Hiramoto, "Conduction Type Control of Fullerene Films from n- to p-Type by Molybdenum

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• M. Hiramoto, H. Fujiwara and M. Yokoyama, "Three-Layered Organic Solar Cell with a Photoactive Interlayer of Codeposited Pigments," Appl. Phys. Lett. 58, 1062-1064 (1991).

## 1. Effects of ppm-Level Doping in Organic Photovoltaic Cells Based on Minority Carrier Diffusion

The doping of organic semiconductors has mainly been in the concentration range of the order of a few %. We believe that a doping technique for very low concentrations of the order of parts per million should be developed. In this study, we clarified the effects of doping at the ppm-level.

Organic photovoltaic cells with *pn*-homojunctions in  $C_{60}$ :H<sub>2</sub>Pc co-deposited films were fabricated. The donor (Cs<sub>2</sub>CO<sub>3</sub>) doping concentration in the *n*-layer was kept constant at 50 ppm. On the other hand, the acceptor (F<sub>4</sub>-TCNQ) doping concentration in the *p*-layer was varied, *i.e.*, 0, 1, 3, 10, and 100 ppm. Figures 2 and 3 show the current-voltage characteristics and the energy band diagrams for the *pn*-homojunction cells.

# (i) 0-1 ppm region

The fill factor (FF) increases from 0.37 (black solid curve) to 0.47 (blue solid curve) together with an increase of the forward dark current (black and blue broken curves)(Figure 2), *i.e.*, a decrease of the cell resistance ( $R_S$ ) from 15.0 to 9.6  $\Omega cm^2$ . Acceptor doping inevitably introduces majority (hole) and minority carriers (electron) (Figures 3(a)). The increase in the majority carrier concentration causes  $R_S$  to decrease and FF to increase. Thus, the doping effect of extremely low concentrations of the order of 1 ppm was confirmed.

#### (ii) 1-10 ppm region

The short-circuit photocurrent ( $J_{SC}$ ) increases (Figure 2, blue orange red solid curves). One can see that a *pn*-homojunction is formed and the built-in field ( $V_{bi}$ ) increases from a small value at 1 ppm to a much larger value at 10 ppm (Figures 3(a) and 3(b)). One of the reasons for the increase in  $J_{SC}$  is the increase in carrier generation efficiency in a *pn*homojunction with a depletion layer (red shaded regions). Moreover, the depth of the photocurrent generation region ( $\sigma$ ) (blue shaded region) is clearly larger than the width of the depletion layer ( $W_{dep}$ ) (red shaded region)(Figure 3(b)). Photocurrent generation in the region where there is no electric field (green double-headed arrow) occurs by the diffusion of minority carriers (electrons).

### (iii) 10- 100 ppm region

 $J_{SC}$  decreased (Figure 2, red and green solid curves) due to narrower depletion layer and narrower diffusion length of minority carrier by impurity scattering (Figure 3(c)).

We believe that doping at the ppm-level offers a general method for optimizing the design of organic photovoltaic cells and other organic electronic devices.



**Figure 2.** Current-voltage characteristics for the *pn*-homojunction cells. The doping concentrations of the *p*-layer are 0 (black), 1 (blue), 3 (orange), 10 (red), and 100 ppm (green).



**Figure 3.** Energy structures of cells with doping concentrations of 1 (a), 10 (b), and 100 ppm (c).