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Kaku Uehara [a], Tomoaki Ichikawa [b], Takahiro Yamamoto [b], Masahiro Tsunooka [b], Akira Sugimoto [b] & Liyuan Han [c]

[a] Research Institute for Advanced Science and Technology, Osaka Prefecture University, Gakuencho, Sakai, Osaka, 593, Japan

[b] College of Engineering, Osaka Prefecture University, Gakuencho, Sakai, Osaka, 593, Japan

[c] Central Research Laboratories, Sharp Corporation, Ichimotocho, Tenri, Nara, 632, Japan

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VECTOR ELECTRON TRANSFER IN THE REACTION SITE OF ORGANIC TWO-LAYER FILM DIODE

KAKU UEHARA[1], TOMOAKI ICHIKAWA[2], TAKAHIRO YAMAMOTO[2], MASAHIRO TSUNOOKA[2], AKIRA SUGIMOTO[2] AND LIYUAN HAN[3]

[1]*Research Institute for Advanced Science and Technology, Osaka Prefecture University , Gakuencho, Sakai, Osaka 593, Japan*

[2]*College of Engineering, Osaka Prefecture University, Gakuencho, Sakai Osaka 593, Japan*

[3]*Central Research Laboratories, Sharp Corporation, Ichimotocho, Tenri, Nara 632, Japan*

Abstract A possible process for the controle of the electron transfer direction in organic two-layer diodes is proposed from the viewpoint of redox properties of the compounds studied.

INTRODUCTION

An organic two-layer photovoltaic cell has been interested from the viewpoint of an elegant photoelectric energy conversion such as the primary process of a plant photosynthesis. It is very important to controle electron transfer direction to lead an efficient charge separation. Recently, we reported on the highly rectifying organic two-layer cell using the interface between dihydrophenazine derivatives and lightly doped poly(3-methylthiophene) (PMeT)[1,2] and on the control of electron transfer direction in an organic two-layer diode based on a lightly-doped PMeT/9-fluorenone derivatives junction[3] In the present study, vector electron transfer and photovoltaic conversion were studied for an organic two-layer diode based on a junction between two organic dyes using indigo (IG), rhodamine B (RB) and N,N,N',N'-tetrakis(p-diethyl-amino-phenyl)-p-phenylene diamine (TDAPD). The chemical structures of the dye are shown in Fig. 1.

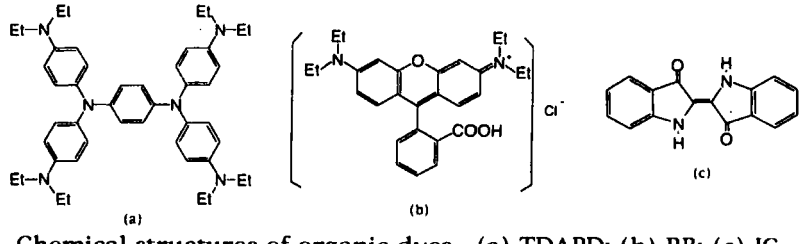

FIGURE 1. Chemical structures of organic dyes. (a) TDAPD; (b) RB; (c) IG

MATERIALS AND METHODS

The organic dye was sublimed under vacuum ($\sim 10^{-4}$ Torr) onto a gold (Au)- or aluminum (Al)-evaporated slide glass. The structure of the organic two-layer film diode Au/Dye 1/Dye 2/Al is depicted in Fig. 2. The thickness of these organic films was 60~120 nm. All the electrical measurements were carried out by the method described in our previous paper.[4] The measurements of cyclic voltammetry (CV) were carried out by means of BAS CV-50W voltammetry analyzer using a platinum plate (1.6 mm diameter) as a working electrode in acetonitrile in the presence of tetraethyl ammonium perchlorate as a supporting electrolyte. An Ag/Ag^+ electrode was used as a reference, and a platinum wire served as a counter electrode.

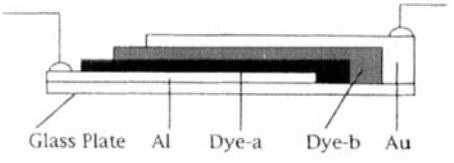

FIGURE 2. Structures of organic two-layer diodes.

RESULTS AND DISCUSSION

A typical dark current-voltage (J-V) characteristics for Au/IG/TDAPD/Al diode and Au/TDAPD/IG/Al are illustrated in Fig. 3a and 3b, respectively. For the former diode, a large forward current was observed when the Au electrode was positively biased with respect to the Al electrode. The direction of rectification is normal and comparable with ordinary p-n junction models. However, for the latter diode, the direction of rectification was reversed. On the other hand, both Au/TDAPD/RB/Al diode and Au/RB /TDAPD/Al gave a normal J-V curve as shown in Fig. 4a and 4b. Whereas, both Au/IG/RB/Al and Au/RB/IG/Al diodes showed a slight reversed rectification (data not shown). With illumination, all the cell exhibited a photovoltaic effect in which the gold electrode always generated a positive photovoltage with respect to the aluminum electrode regardless of the direction of the incident light.

Redox potentials of dyes (V vs Ag/Ag^+) in the solution of propylene carbonate increased as follows: TDAPD (-0.344) < RB (+0.842) < IG (+1.016). Ionic potential of TDAPD (4.56 eV) in the solid state was lower than that of RB (5.61 eV). Indigo has been known to be capable of behaving as a p-type semiconductor,[5] however, we confirmed that its effect is very small.[6] RB has been known to be capable of behaving as an n-type semiconductor.[5] TDAPD might behave as a p-type semiconductor.

A new type of mechanism for the controle of the electron transfer direction in organic two-layer diodes is proposed from the viewpoint of redox properties of the compounds studied. A possible process of the

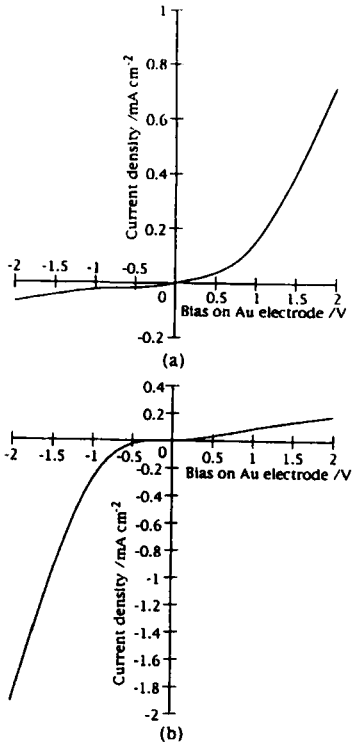

FIGURE. 3 Current-Voltage curves in dark for organic two-layer diodes.
(a) Au/IG/TDAPD/Al
(b) Au/TDAPD/IG/Al

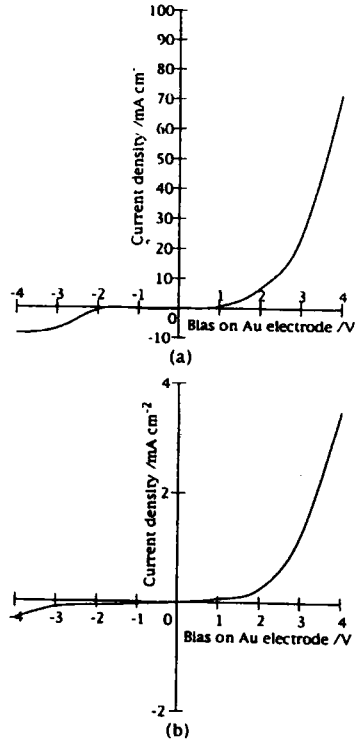

FIGURE. 4. Current-Voltage curves in dark for organic two-layer diodes.
(a) Au/TDAPD/RB/Al
(b) Au/RB/TDAPD/Al

rectification effect for Au/IG/TDAPD/Al diode and that for Au/TDAPD/IG/Al are shown in Fig. 5a and 5b, respectively. For the dark rectification, the direction of electron transfer might be mainly determined by the redox reaction between organic dyes in the reaction site of organic two-layer film diode. The direction of photovoltaic effect might be mostly determined by the difference in the work function of Au and Al electrode, although the efficiency of the charge-separation should be largely affected by the redox property of the dye.

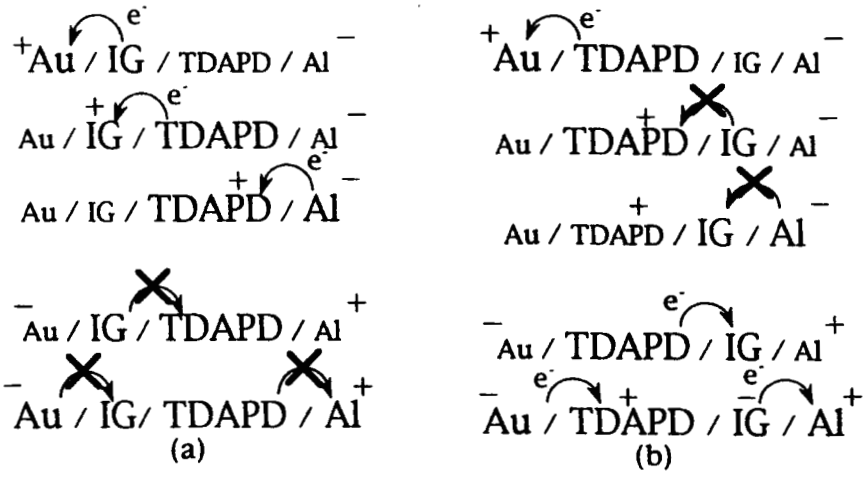

FIGURE. 5. A possible process for the control of the electron transfer direction in organic two-layer diode.
(a) Au/IG/TDAPD/Al (b) Au/TDAPD/IG/Al

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