Bull. Chem. Soc. Jpn., ***68***, *738—743(1995)*

Photovoltaic Properties of Triphenodioxazine and Dichlorotriphenodioxazine

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(Received May 31, 1994)

Photovoltaic behaviors of evaporated thin films of triphenodioxazine (TPDO) and 6,13-dichlorotriphenodioxazine (DClTPDO) were investigated with sandwich-type cells, the configurations of which were Ag/TPDO/Al and Al/DClTPDO/indium–tin oxide (ITO). The action spectra of the short-circuit photocurrent suggest that only the photons absorbed by pigments near the Ag/TPDO interface or the DClTPDO/ITO interface are effective to produce carriers for external circuits. These results mean that Schottky barriers are formed at these interfaces, and that both pigment layers act as n-type semiconductors. Observed effects of oxygen and/or hydrogen gas on the dark conductivity of these pigment films also reflect the n-type semiconducting behavior. The observed electrical behaviors are consistent with the proposed band structures for these two cells, which are estimated from the spectroscopic data.

Recently, we reported the photogenerated carrier mobilities in thin films of phenothiazine derivatives, and also the photovoltaic properties of thin film organic photocells about similar compounds.[1,2] The pigments used in our previous work were observed to be p-type semiconductors with rather low power conversion efficiency.[2] It is known that many of the organic semiconductors ever reported are p-type, and a small number of them are n-type.[3—7] In this paper, we would like to present photovoltaic properties of thin films of triphenodioxazine (TPDO) and 6,13-dichlorotriphenodioxazine (DClTPDO), both of which act as n-type semiconductors.

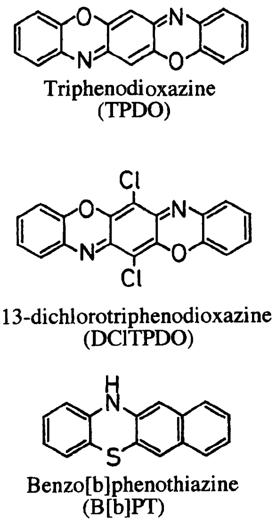


Chart 1. Molecular structures of the compounds used.

Experimental

Materials. Structural formula of the materials used in this work are shown in Chart 1. Benzo[*b*]phenothiazine (B[*b*]PT), a typical p-type semiconductor,[2] was used to compare its electrical properties with those of TPDO and DClTPDO. They were prepared as described in the literature, and purified by vacuum sublimation repeated more than three times.[8—10] Their purity was checked by thin-layer chromatography (Merck No. 5554). Indium–tin oxide (ITO)-coated glass plates (Nippon Electric Glass Co.) were used for transparent electrodes, and their sheet resistance value was obtained as an average of 8×10 Ω with 1 cm^2 sample pieces observed with a Kyowa-Riken sheet-resistance-meter model K-705RD-B. Purity of the Al, Ag, and Au metals, used as electrodes of cells, is higher than 99.95%.

UP Spectra. The work function of ITO was estimated by ultraviolet photoelectron spectroscopy (UPS). The apparatus used for measurement was as improved version of that reported in detail previously.[11] Experimental error for the measured value is about ±0.1 eV.

Absorption Spectra. Electronic absorption spectra of organic pigment films, sublimed on glass plates, were observed on a Hitachi 330 spectrometer.

Device Fabrication. Figure 1 shows the cell structure used in this work. The configuration of the sandwich-type cells, used in this study, is Ag (170 Å)/TPDO (2300 Å)/Al (170 Å), Al (250 Å)/DClTPDO (1900 Å)/ITO, Au (140 Å)/TPDO (1000 Å)/Au (140 Å), Au (110 Å)/DClTPDO (1000 Å)/Au (110 Å), and Au/B[*b*]PT/Au. The order from left to right of films in the above notation corresponds to the order from top to bottom on the glass substrate. Thin films of Au, Ag, Al, and organic pigments were vacuum deposited onto substrates through a mask with a ULVAC EBH-6 at a base pressure of 10^{-5} Torr (1 Torr=133.322 Pa). ITO-coated glass was etched with hydrochloric acid to prepare

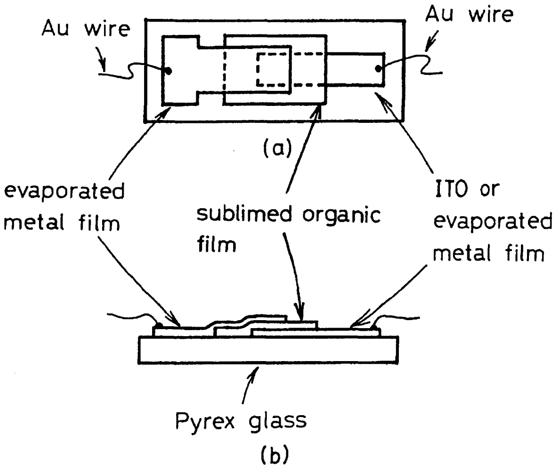


Fig. 1. Cell structure. (a) Top view, (b) Side view.

an electrode with adequate size. Thickness of the evaporated films was monitored by an ULVAC Model CRTM-5000 quartz crystal oscillator. Metal electrodes were deposited from tungsten filaments, and their deposition rates were controlled at 0.1 Å s^{-1}, 3 Å s^{-1}, and 1—2 Å s^{-1} for Au, Ag, and Al, respectively. TPDO, DClTPDO, and B[*b*]PT were deposited at rates of 1—2 Å s^{-1} from a glass crucible. The substrates were kept at room temperature during sublimation, and the vacuum was broken after each deposition. The area in which all the two electrodes and a pigment film entirely overlapped, was designed to be about 0.1 cm^2 for all the cells.

Measurements. The electrical properties were estimated for Ag/TPDO/Al and Al/DClTPDO/ITO cells in vacuo (10^{-5} Torr). Measurements of the current–voltage characteristics (J_d-V: in dark, and J_p-V: irradiated), and the action spectra of the cells were done with the same method described in our previous report.[2]

For the measurements of oxygen and/or hydrogen effects on dark conductivity, the Au/TPDO/Au, Au/DClTPDO/Au, and Au/B[*b*]PT/Au cells were used. After evacuation for 2 h, O_2 and/or H_2 gas was introduced to the cell at about ambient pressure. Then, the electrical resistance of the organic films was measured at regular times.

Results and Discussion

Dark Current. The typical J_d-V characteristics in the dark for an Ag/TPDO/Al and an Al/DClTPDO/ITO cells are shown in Figs. 2 and 3, respectively. In the forward bias mode, the Ag or ITO electrode was positively charged with respect to the Al electrode. The Ag/TPDO/Al cell clearly has a rectifying effect, indicating that a Schottky barrier has been formed. On the other hand, for the Al/DClTPDO/ITO cell, the observed reverse current is larger than the forward current. At present, we can not make a reasonable interpretation for this reverse rectifying behavior. Misoh et al. also reported a similar reverse rectifying behavior about the Cu/poly(thio-*p*-phenylene)/Al cell, and they did not give a clear explanation of this phenomenon, either.[7]

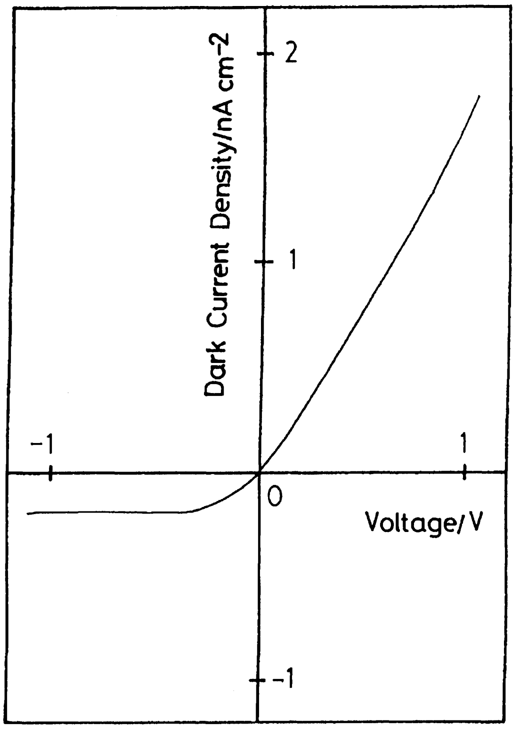


Fig. 2. Dark current density–voltage characteristic of the Ag/TPDO/Al cell.

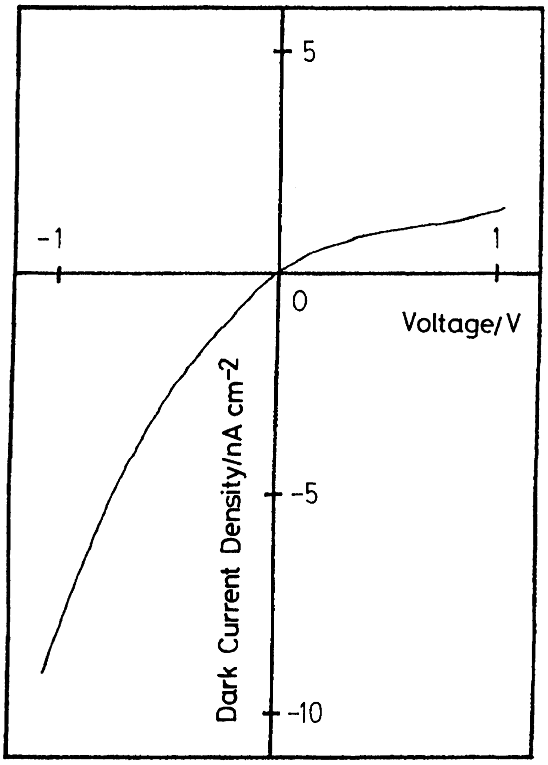


Fig. 3. Dark current density–voltage characteristic of the Al/DClTPDO/ITO cell.

Since Schockley's relation is valid in Schottky barrier devices, the logarithmic plots of the forward-biased dark current must be linearly dependent on the applied voltage in such devices.[12] For the Ag/TPDO/Al cell, the observed forward-biased current varied exponentially with voltage below 0.4 V as shown in Fig. 4. This behavior suggests that the Schottky barrier is formed at the Ag/TPDO interface. Beyond 0.4 V, the plots of log J_d versus applied voltage give another linear relationship with a smaller slope than that in the low voltage region. Such behavior is attributable to the space-charge limited current, and similar behavior was also observed in the In/H_2Pc/Au cell.[3)] If an energy barrier is formed at the TPDO/Al interface, where an insulating layer of Al_2O_3 is sandwiched, log J_d-V plots should have the metal-insulator-semiconductor barrier diode property as reported in many organic photocells, including our previous paper.[2,13—15)]

For the Al/DClTPDO/ITO cell, it could not be decided from the log J_d-V characteristics at which interface the energy barrier was formed, since the Al/DClTPDO/ITO cell did not show the expected rectifying behavior in the dark.

Photocurrent. When the Ag/TPDO/Al and the Al/DClTPDO/ITO cells were irradiated through the Ag or ITO electrode with the white light of 200 mW cm^{-2} intensity, they had photovoltaic behavior as shown in Fig. 5. The Al electrode behaved as an anode in the short-circuit condition in all the cells examined; namely, the photocurrent flowed from Al to Ag (or ITO) through the pigment layers regardless of the direction of irradiation. Since the irradiation on the Ag or ITO side brought a larger photocurrent than that observed when irradiated on the other side, it can be assumed that the Schottky barriers are formed at the Ag/TPDO and the DClTPDO/ITO interfaces.

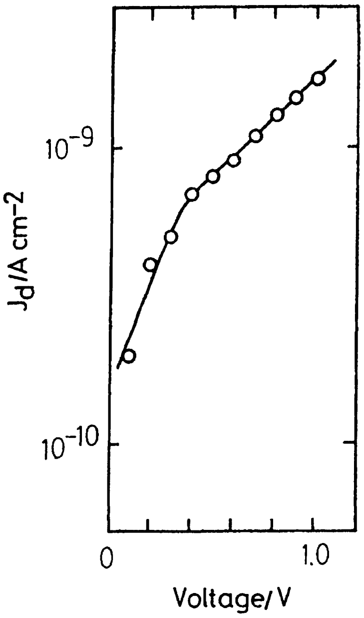


Fig. 4. Forward bias, current density–voltage curves for Ag/TPDO/Al cell.

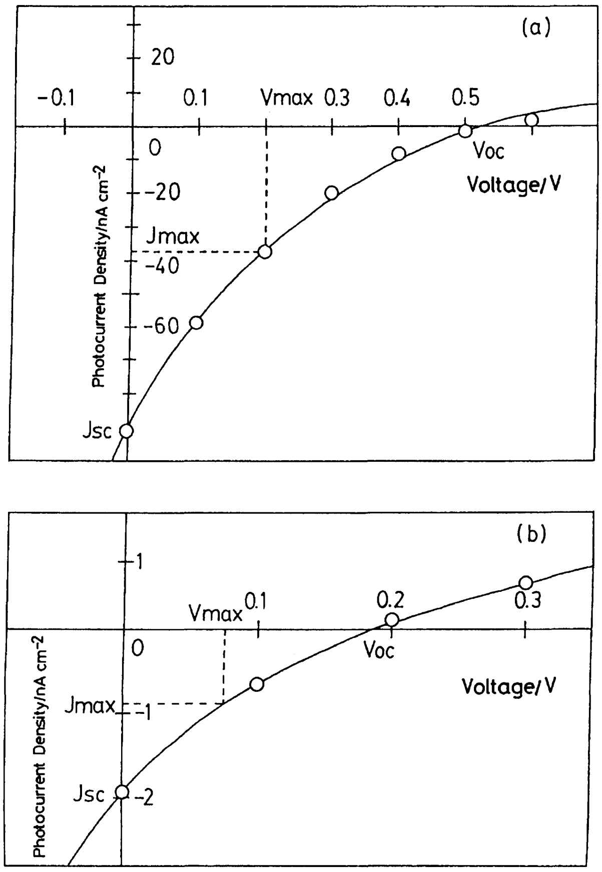


Fig. 5. Photocurrent density–voltage characteristics of (a) Ag/TPDO/Al and (b) Al/DClTPDO/ITO cells under white light. Symbols are explained in the text.

From the J_p-V relationships in the photovoltaic mode, the photovoltaic parameters for the two cells were evaluated, and are presented in Table 1. Judging from the values in the Table 1, it seems to be difficult to use these materials for practical photoelectric conversion devices. These low efficiencies may be attributable to the large resistance and low carrier mobility of these organic films.[16)]

Action Spectra. In Fig. 6, the action spectra of short-circuit photocurrents for the Ag/TPDO/Al and the Al/DClTPDO/ITO cells are shown together with the absorption spectra of the pigment films directly sublimed on a glass plate. The values of photocurrent have been normalized to the relative photon flux over the observed wavelength range.

The action spectrum obtained on illumination through the Ag electrode of the Ag/TPDO/Al cell resembles the absorption spectrum of the TPDO film shown in Fig. 6(a). However, the action spectrum of the

Table 1. Photovoltaic Characteristics of Cells

Cell	V_{oc}/V	J_{sc}/A cm^{-2}	f.f.	η/%
Ag/TPDO/Al	0.52	9.1×10^{-8}	0.16	3.7×10^{-6}
Al/DClTPDO/ITO	0.19	1.9×10^{-9}	0.18	3.4×10^{-8}

V_{oc}: open-circuit photovoltage, J_{sc}: short-circuit photocurrent, f.f.: fill factor, and η: conversion efficiency.

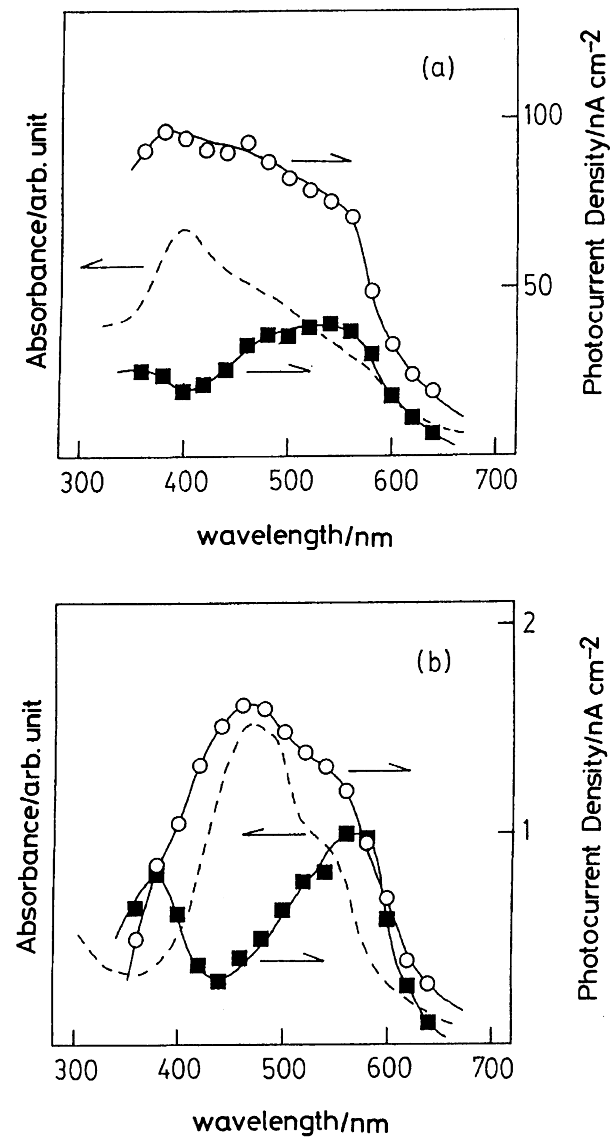


Fig. 6. Action spectra of cells for light incident on Al side (-■-), Ag or ITO side (-O-), and absorption spectra of organic sublimed film (---). (a) Ag/TPDO/Al and (b) Al/DClTPDO/ITO cells.

same cell illuminated through the Al electrode is characterized by a maximum around 450—580 nm range, which corresponds to the trailing edge of the absorption band of the TPDO film, and its shape can be ascribed to an optical filtering effect of the TPDO phase.[17] These facts suggest that only the light absorbed near the Ag/TPDO interface is effective in producing charge carriers, and that an ohmic contact is formed at the TPDO/Al interface.

Similar results were obtained for the Al/DClTPDO/ITO cell as shown in Fig. 6(b). Namely, the action spectrum obtained on illumination through the ITO electrode resembles the absorption spectrum of the DClTPDO film, but that obtained on illumination through the Al electrode is different in shape from the absorption spectrum of the DClTPDO film.

These results are contrary to those observed for the phenothiazine derivatives that have p-type semiconducting behavior; for example, the B[*b*]PT/Al interface is photoactive in the Au/B[*b*]PT/Al cell.[2] Considering both the action spectrum behaviors and the values of work function of the electrodes, the TPDO and the DClTPDO films are assumed to act as n-type semiconductors.

Effects of Oxygen and Hydrogen. Changes in dark conductivity of organic films with introduction to O_2 and/or H_2 atmosphere can be useful to iden-

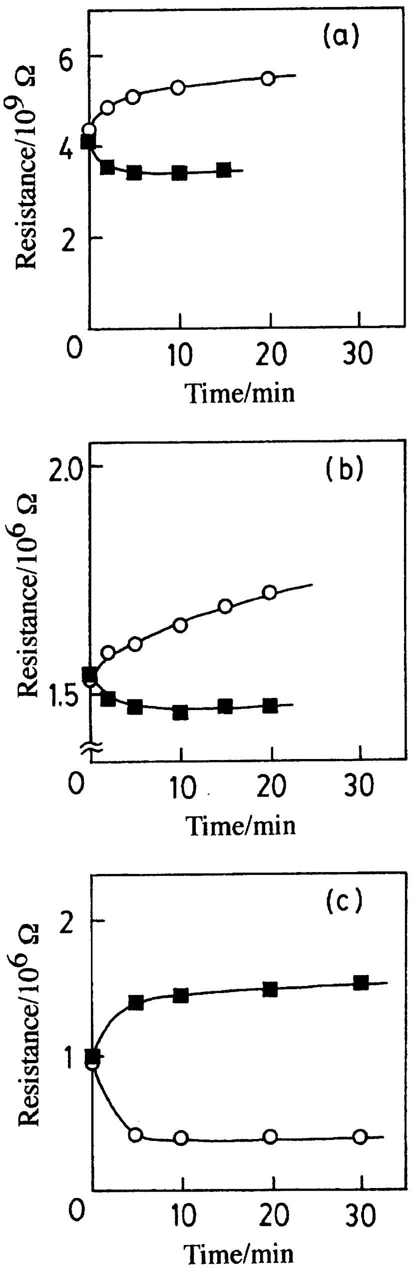


Fig. 7. Time dependence of resistance change of the pigment films by H_2 gas (-■-) and/or O_2 gas (-O-) introduction. (a) Au/TPDO/Au, (b) Au/DClTPDO/Au, and (c) Au/B[*b*]PT/Au cells.

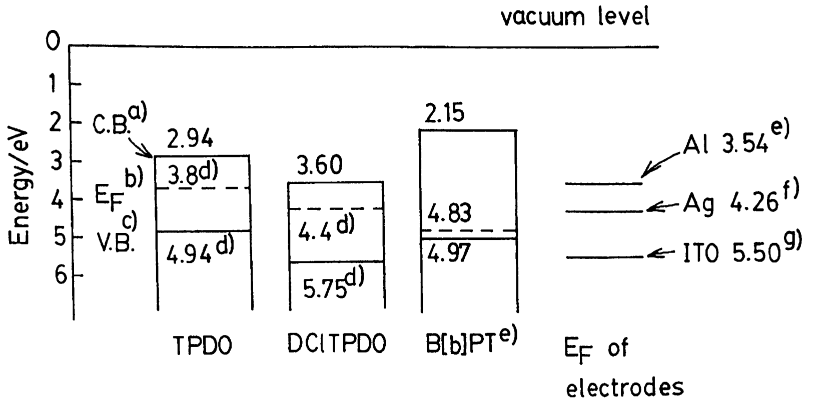


Fig. 8. Energy diagrams of TPDO, DClTPDO, and B[*b*]PT films with metal electrodes. Energy values are presented as depths from the vacuum level. Symbols are defined as follows: a) C.B.: bottom of conduction band, b) E_F: Fermi level, c) V.B.: top of valence band, d) values taken from Ref. 22, e) values taken from Ref. 2, f) value taken from Ref. 23, and g) this work.

tify the type of semiconductivity of pigments; increase (decrease) of the conductivity in H_2 (O_2) indicates n-type conductance.[18,19] The Au/pigment/Au cells are used for the ambient gas-effect measurements to avoid the influence of oxidation of electrode surfaces.

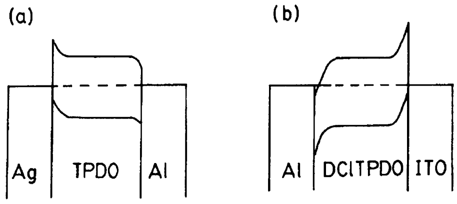
Figure 7 illustrates the effects of O_2 and/or H_2 gas on the resistance for the Au/TPDO/Au, Au/DClTPDO/Au, and Au/B[*b*]PT/Au cells. Resistance of the Au/TPDO/Au, and the Au/DClTPDO/Au cells are increased on exposure to O_2 gas, and decreased on exposure to H_2 gas, as shown in Figs. 7(a) and 7(b). Their behaviors for two ambient gases are completely opposite to those of B[*b*]PT, the results of which are presented in Fig. 7(c).

The O_2 gas has an electron-accepting property and H_2 gas acts as an electron-donating substance.[19,20] Assuming that these electronic properties of the gases simply affect the change in electric conductivities between the two kind of films, the majority of charge carriers can be electrons for the TPDO and DClTPDO films, and holes for B[*b*]PT film. It will therefore be estimated that the TPDO film and the DClTPDO film are n-type semiconductors, and the B[*b*]PT film is a p-type semiconductor. This estimation is consistent with the results of observed *J*–*V* characteristics and action spectra mentioned above. Early, in 1964, Inoue et al. observed the effects of oxygen on the dark- and photo-conductivity of the TPDO film with a surface-type cell, and suggested the n-type conductance for this material.[21] Besides, in an atmosphere of O_2, the Ag/TPDO/Al and the Al/DClTPDO/ITO cells had similar action spectra to those observed in vacuo.

Energy Structures. To explain the results of the electrical measurements, energy structure estimation of the TPDO and the DClTPDO films was attempted on the assumption of the energy band scheme as follows. The observed values of ionization energy and work function were adopted from the literature,[22] and used as the values of the top of the valence band and the Fermi level, respectively. The band-gap energies were estimated from the threshold energy of the action spectra described in the above section. The summarized energy diagrams of the two films are shown in Fig. 8 together with that of the B[*b*]PT film (taken from our previous paper[2]) and the Fermi-level energies of the related electrodes.

The type of conductance for the TPDO and the DClTPDO films is again estimated to be n-type by this energetic consideration, since their Fermi levels are above the centers of band gaps in contrast with the case of p-type B[*b*]PT film. Thus, we propose energy diagrams of the Ag/TPDO/Al and the Al/DClTPDO/ITO cells as shown in Fig. 9. In these diagrams, the conduction and the valence band edges are bent upwards at the Ag/TPDO and the DClTPDO/ITO interfaces. For the Al/DClTPDO/ITO cell, a band bending is also formed at the Al/DClTPDO interface, but this contact is assumed to be ohmic from the location of the top of valence band and the Fermi level. Thus, these diagrams are consistent with the results of action spectra of the Ag/TPDO/Al and the Al/DClTPDO/ITO cells.

We are grateful to Professor Naoki Sato of Kyoto University for the UPS measurements and helpful discussions.



Ag/TPDO/Al Al/DClTPDO/ITO

Fig. 9. Energy diagrams of (a) Ag/TPDO/Al and (b) Al/DClTPDO/ITO cells.

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