Transparent Image Sensors Using an Organic Multilayer Photodiode

By Hideyuki Tanaka, Takeshi Yasuda, Katsuhiko Fujita, and Tetsuo Tsutsui*

The most fascinating advantages of organic photodiodes in the context of information-conversion applications are their ability for large-area surface light detection, the potentially wide selection of materials that allows color tuning, and the possibility for low-cost fabrication of flexible devices. The photosensitivity of organic photodiodes, either multilayer-heterojunction type or bulk-heterojunction type, is quite high, and internal photon-to-electron conversion quantum efficiency in some cases approaches unity. Thus, we have a good opportunity to utilize organic photodiodes for high-performance photosensors, even though power-conversion efficiency of organic photovoltaic solar cells under solar light irradiation remains less than 5%. Fabrications of organic photodiodes with good photoresponse, such as fast-response photodetectors, full-color image sensors, and position-sensitive photodetectors, have been reported. The use of anisotropy of optical absorption results from molecular orientation is one of the most fascinating advantages of organic photodiodes. The combination of transparent electrodes and polarized light detection that results from optical anisotropy of molecules provides unique image-sensing devices that capture images under light illumination behind them.

Figure 1 demonstrates the basic concept for reading a black and white picture using our transparent photodiodes with polarization-detection capability. Let us assume that white light or monochromatic light is transmitted through a linear polarizer to the polarization-sensitive photodetector. At present, for simplicity, we assume that the photodetector is composed of oriented molecules with large optical anisotropy. When polarized light perpendicular to the transition moments of the oriented molecules irradiates the photodetector, light passes through the detector with little optical absorption. Thus, a very small photocurrent is detected by the photodiode when the incident light is perpendicularly polarized. The transmitted polarized light is reflected back according to the reflectivity of the object. When white paper is used, a large fraction of the light is reflected back and depolarized by scattering. Thus, the light component with parallel polarization reaches the photodetector and a large photocurrent signal is detected. On the other hand, when the transmitted polarized light reaches a black object, all the light is absorbed and no photocurrent is detected. Thus, the transparent and polarization-sensitive photodetectors are useful for the detection of reflectivity of objects. We note that this principle is applicable to grayscale sensing as well as simple black and white detection. When addressable crossed-array photodiodes are used or 2D scanning of incident light is available, 2D picture images are obtainable.

We have successfully developed polarization-sensitive photodiodes using a pn-heterojunction-type structure composed of 3,4,9,10-perylenetetracarboxylic-bis-benzimidazole (PTCBI) for the n-type layer and titanyl phthalocyanine (TiOPc) for the p-type layer. In this report, we demonstrate the feasibility of our transparent photodetector composed of a well-aligned PTCBI and a non-aligned TiOPc layer for image sensing.

As shown in Figure 2a, the device configuration was indium tin oxide (ITO)/indium/aligned PTCBI/TiOPc/poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS)/Au. A well-aligned PTCBI layer with the optical axis parallel to the rubbing direction was grown. A large dichroic ratio of optical absorption was obtained at the peak wavelength of 540 nm. Figure 2b shows absorption spectra of both aligned PTCBI and non-aligned TiOPc films. An aligned PTCBI showed a dichroic ratio of 4.7:1 at the peak wavelength of 540 nm, while non-aligned TiOPc showed isotropic absorp-
and a 20 nm thick Au layer (dotted line). Light irradiation to the molecular orientation axis of PTCBI (solid line), (ITO/In/aligned PTCBI/TiOPc/PEDOT:PSS) for perpendicularly polarized aligned TiOPc (dotted line); and c) transmittance spectra of a multilayer perpendicular to the molecular orientation axis (solid lines), and non-absorption spectra of aligned PTCBI when light is polarized parallel and perpendicularly relative to the rubbing direction. It should be noted here that linear polarization of incident light changes to elliptic polarization when linearly polarized light passes through a uniaxially aligned PTCBI layer. This effect, however, is assumed to be small, because the thickness of the PTCBI layer is 20 nm. Figure 3a and b shows IPCE spectra when light is irradiated from the ITO side and the Au side, respectively. Large photocurrent anisotropy was detected in both cases of incident light, although the IPCE values in the case from the Au side is about 20 % smaller than in the case from the ITO side, due to lower transmittance of the Au electrode. The photocurrent anisotropic ratios at 540 nm, where the aligned PTCBI showed a dichroic ratio of 4.7, were 2.58 and 3.00 under photoradiation from the ITO and Au sides, respectively. Decrease in the photocurrent ratio compared with the dichroic ratio of the aligned PTCBI film (Fig 2b) can be interpreted as follows: We can ascribe the origin of that phenomenon to the degradation in molecular orientation of the aligned PTCBI in the active region located at the p/n interface, which contributes to photocarrier generation. We can point out at least two reasons for the degradation of the orientation the PTCBI at the p/n interface region. The anchoring effect on the rubbed surface may be decreased gradually as the thickness of the PTCBI layer is increased, even though PTCBI molecules are carefully deposited at a very slow deposition rate. In addition, the orientation of the PTCBI near the p/n interfaces may be relaxed by the thermal energy of evaporated TiOPc molecules acting on the aligned PTCBI. Thus, for the purpose of minimizing the effect of the orientation degradation at the p/n interface, we used thin, aligned PTCBI 20 nm thick, comparatively thinner than that used in conventional organic photovoltaic devices. The use of the thin PTCBI layer is also effective for avoiding the self-absorption effect. When we adopted a thick aligned PTCBI layer, a much lower photocurrent ratio was obtained. The different polarization sensitivity and spectral shapes between the two IPCE spectra in Figure 3a and b are interpreted in terms of optical self-absorption effect and filtering effect. At around 540 nm, no optical absorption due to the TiOPc layer is present, and photocurrent generation takes place at the PTCBI/TiOPc interface region. Thus, neither a filtering effect nor a self-absorption effect is involved when monochromatic light at 540 nm is introduced from the Au side, and the largest photocurrent anisotropy is realized. In contrast, self-absorption at around 540 nm and filtering at 600–700 nm by the PTCBI layer brings about a large photocurrent anisotropy at the wide wavelength region of 500–700 nm when light is introduced from the ITO side.

Using our polarization-sensitive detector with good transparency, we verified our concept of reading a black and white picture mentioned above. The transparent photodetector was placed on black or white paper with the ITO electrode side touching the paper. Figure 4 shows the photoresponse spectra when the perpendicularly polarized (Fig. 4a) or parallel-polarized light (Fig. 4b) was irradiated. When we used a perpendicular configuration, white paper gave a photoresponse more than twice that of black paper, over a wide spectral region. In contrast, the difference in black or white responses in the parallel configuration was quite small even at around 540 nm, where the spectral anisotropy due to the aligned PTCBI layer.

Figure 2. a) Device structure of a transparent organic photodiode; b) absorption spectra of aligned PTCBI when light is polarized parallel and perpendicular to the molecular orientation axis (solid lines), and non-aligned TiOPc (dotted line); and c) transmittance spectra of a multilayer (ITO/In/aligned PTCBI/TiOPc/PEDOT:PSS) for perpendicularly polarized light irradiation to the molecular orientation axis of PTCBI (solid line), and a 20 nm thick Au layer (dotted line).

The polarization sensitivity of transparent organic photodetectors was investigated. Figure 3 shows the incident photon-to-current conversion efficiency (IPCE) plotted against wavelength, under light that was parallel or perpendicularly polarized relative to the rubbing direction. It should be noted here that linear polarization of incident light changes to elliptic polarization when linearly polarized light passes through a uniaxially aligned PTCBI layer. This effect, however, is assumed to be small, because the thickness of the PTCBI layer is 20 nm. Figure 3a and b shows IPCE spectra when light is irradiated from the ITO side and the Au side, respectively. Large photocurrent anisotropy was detected in both cases of incident light, although the IPCE values in the case from the Au side is about 20 % smaller than in the case from the ITO side, due to lower transmittance of the Au electrode. The photocurrent anisotropic ratios at 540 nm, where the aligned PTCBI showed a dichroic ratio of 4.7, were 2.58 and 3.00 under photoradiation from the ITO and Au sides, respectively. Decrease in the photocurrent ratio compared with the dichroic ratio of the aligned PTCBI film (Fig 2b) can be interpreted as follows: We can ascribe the origin of that phenomenon to the degradation in molecular orientation of the aligned PTCBI in the active region located at the p/n interface, which contributes to photocarrier generation. We can point out at least two reasons for the degradation of the orientation the PTCBI at the p/n interface region. The anchoring effect on the rubbed surface may be decreased gradually as the thickness of the PTCBI layer is increased, even though PTCBI molecules are carefully deposited at a very slow deposition rate. In addition, the orientation of the PTCBI near the p/n interfaces may be relaxed by the thermal energy of evaporated TiOPc molecules acting on the aligned PTCBI. Thus, for the purpose of minimizing the effect of the orientation degradation at the p/n interface, we used thin, aligned PTCBI 20 nm thick, comparatively thinner than that used in conventional organic photovoltaic devices. The use of the thin PTCBI layer is also effective for avoiding the self-absorption effect. When we adopted a thick aligned PTCBI layer, a much lower photocurrent ratio was obtained. The different polarization sensitivity and spectral shapes between the two IPCE spectra in Figure 3a and b are interpreted in terms of optical self-absorption effect and filtering effect. At around 540 nm, no optical absorption due to the TiOPc layer is present, and photocurrent generation takes place at the PTCBI/TiOPc interface region. Thus, neither a filtering effect nor a self-absorption effect is involved when monochromatic light at 540 nm is introduced from the Au side, and the largest photocurrent anisotropy is realized. In contrast, self-absorption at around 540 nm and filtering at 600–700 nm by the PTCBI layer brings about a large photocurrent anisotropy at the wide wavelength region of 500–700 nm when light is introduced from the ITO side. Using our polarization-sensitive detector with good transparency, we verified our concept of reading a black and white picture mentioned above. The transparent photodetector was placed on black or white paper with the ITO electrode side touching the paper. Figure 4 shows the photoresponse spectra when the perpendicularly polarized (Fig. 4a) or parallel-polarized light (Fig. 4b) was irradiated. When we used a perpendicular configuration, white paper gave a photoresponse more than twice that of black paper, over a wide spectral region. In contrast, the difference in black or white responses in the parallel configuration was quite small even at around 540 nm, where the spectral anisotropy due to the aligned PTCBI layer.

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was the largest. Thus, we were successful in demonstrating the possibility of reading black and white images using a polarization-sensitive photodetector.

Table 1 summarizes the white/black ratio of photocurrent response under three different incident lights at both 540 and 730 nm. At 540 nm, the white/black ratios are largely dependent on the polarization of the incident light. At 730 nm, on the other hand, the white/black ratios were not sensitive to incident light polarization. This observation is explained by the fact that the photocurrent at 730 nm originates from the optical absorption of the non-aligned TiOPc layer. Even when using organic semiconductors without molecular orientation, white and black detection is possible. It should be noted, however, that detection sensitivity remains small when no polarization sensitivity is used.

In conclusion, we have demonstrated a transparent organic photodiode with polarization-sensitive capabilities using a well-aligned organic semiconductor layer. The difference of reflectivity between black and white objects was detected successfully by using light perpendicularly polarized to the molecular-orientation axis (the rubbing direction). Transparency of less than 20% for the top Au electrode limited the detection sensitivity at longer wavelength regions. Replacement of the semi-transparent Au electrode with a transparent ITO electrode should be tested for further sensitivity enhancement of our photodetectors. It should also be noted that successful white and black detection using both green (540 nm) and red (730 nm) light indicates the possibility of reading color images using our photodiodes when the photosensitivity at blue spectral region could be enhanced.

### Experimental

First, an In metal layer was vacuum-deposited onto a precleaned ITO transparent substrate. A 10 nm thick PTCBI layer was vacuum-deposited, and the surface of the deposited PTCBI was rubbed ten times with a velvet cloth in an ambient atmosphere. The treated substrate was washed with ethanol and dried for the purpose of eliminating dust and PTCBI particles. Then, a 20 nm thick TiOPc layer was formed at a deposition rate of 0.3 nm min$^{-1}$ [9,10]. Following the deposition of the aligned PTCBI, a 20 nm thick TiOPc layer was formed with a deposition rate of 1.2 nm min$^{-1}$. A PEDOT:PSS (Baytron 4083) layer was formed on the TiOPc layer by spin-coating (at 5000 rpm for 30 s) followed by heating at 120 °C for 5 min in a N$_2$ glove box. A top electrode, Au of 20 nm thickness, was deposited through a shadow mask so that the active area of the devices was 2 mm × 2 mm. Photocurrent spectra of the devices were measured using the incident light from a xenon lamp passed through a monochromator and a linear polarizer.

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Table 1. White/black photocurrent-response ratios for the polarized- or unpolarized-light irradiation at 540 nm and 730 nm.

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<tr>
<th>Light</th>
<th>Photocurrent ratio (white/black)</th>
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<tbody>
<tr>
<td></td>
<td>at 540 nm</td>
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<tr>
<td>Perpendicular</td>
<td>2.29</td>
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<tr>
<td>Unpolarized</td>
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