

Improvements in Photoconductive Characteristics of Organic Device Using Silole Derivative

Takeshi FUKUDA*, Ryohei KOBAYASHI, Norihiko KAMATA, Satoshi AIHARA¹, Hokuto SEO¹, Ken HATANO, and Daiyo TERUNUMA

Graduate School of Science and Engineering, Saitama University, 255 Shimo-Ohkubo, Sakura, Saitama, Saitama 338-8570, Japan

¹*NHK Science and Technical Research Laboratories, 1-10-11 Kinuta, Setagaya, Tokyo 157-8510, Japan*

Poly[9,9-dioctylfluorenyl-2,7-diyl]-co-1,4-benzo-(2,1,3)-thiadiazole (F8BT) is one of the suitable materials for color-selective organic photoconductive devices owing to its high carrier mobility and absorption coefficient against only the blue light. We investigated a mixing method using a silole derivative, 1,1-dimethyl-2,3,4,5-tetraphenylsilole (DMTPS), in F8BT to improve the ratio between photocurrent and dark current (ON/OFF ratio), which is an important parameter for practical organic photoconductive devices. These organic materials can be coated by a solution process, which leads us to realize a low fabrication cost and a large device area in the future. By adding DMTPS into F8BT, the maximum improvement in ON/OFF ratio of 5 times was achieved compared with the reference device with F8BT only; however, the external quantum efficiency was independent of the concentration of DMTPS less than 50 wt%. In addition, the wavelength selectivity of DMTPS:F8BT in the visible wavelength region was almost the same as that of F8BT only. This result indicates that the DMTPS:F8BT layer can absorb only the blue light, indicating the possibility of a color separation without a prism for high-resolution cameras by combining the green- and red-sensitive devices.

1. Introduction

In recent years, organic devices have attracted considerable attention for flat panel/flexible displays,¹⁻³⁾ general lightings,⁴⁾ light sources for optical communications,⁵⁻⁷⁾ and solar cells^{8,9)} owing to their several special advantages over inorganic devices, such as a large substrate selectivity, mechanical flexibility, and an easy process at a low cost. In particular, organic photoconductive devices have attracted much attention from viewpoints of lightweight and thinness compared with other conventional semiconductor image sensors, complementary metal-oxide-semiconductor sensors, and charge-coupled devices.¹⁰⁻¹⁴⁾ This is because several organic materials have selective absorption only for blue, green, and red lights.^{11,14)}

For larger photoconductive devices with a lower cost, we should develop solution-processed organic photoconductive devices. However, one serious problem of solution processes is the

*E-mail address: fukuda@fms.saitama-u.ac.jp

dissolution of the underlayer, and it makes difficult to prepare multilayer structures formed by different polymer layers using a conventional wet process. Since most photo-excited carriers recombine in an organic layer without reaching electrodes as a photocurrent in the case of a single layer device, the single-layer device has lower photoconductive characteristics than a multilayer device.^{11,14)} One possible approach to improving the photoconductive characteristics is the use of a bulk heterojunction structure, which realizes the dislocation of photoinduced carriers in an organic layer.^{15,16)} The fabrication cost of the single-layer device is lower than that of the multilayer device; therefore, single-layer devices with high performance characteristics have been required for practical applications.

To realize high photoconductive performance characteristics of organic photoconductive devices, the large absorption coefficient and high carrier mobility of an organic material are necessary. We selected poly[9,9-dioctylfluorenyl-2,7-diy]-co-1,4-benzo-(2,1,3)-thiadiazole (F8BT) as an organic photoconductive material owing to its high hole mobility and absorption coefficient in the blue wavelength region,¹⁷⁾ and a blue-sensitive organic photoconductive device with F8BT was already reported in our previous paper.¹⁴⁾ In addition, one silole derivative, 1,1-dimethyl-2,3,4,5-tetraphenylsilole (DMTPS),^{18,19)} is considered to form the electron transport path to the cathode in the F8BT layer with a low recombination probability because of its high ionization potential and high electron mobility.

In this study, we investigated the combination of DMTPS and F8BT to improve the photoconductive characteristics of a single-layer organic photoconductive device. The relationship between the concentration of DMTPS in F8BT and the photocurrent/dark current was estimated by the irradiation of blue light with a center wavelength of 470 nm. The photocurrent spectrum of devices and the absorption spectra of neat films were also measured to evaluate the color selectivity of organic photoconductive devices.

2. Experimental Procedure

Figure 1(a) shows the cross-sectional view of a fabricated organic photoconductive device with DMTPS:F8BT as a photoconductive layer. When an incident light reaches an organic photoconductive layer through a glass substrate and an indium tin oxide (ITO) anode, it is absorbed by the DMTPS:F8BT layer, resulting in the generation of carriers. The photoinduced carriers are accelerated by an applied electric field, and finally, they are read out from electrodes as a photocurrent. In addition, molecular structures of DMTPS and F8BT are shown in Fig. 1(b).

After dissolving F8BT in chloroform at a concentration of 10 g/l, DMPTS was added into the above-mentioned F8BT solution. Then, the solution was stirred at a rotation speed of 250 rpm over 24 h. The ratios of DMTPS to F8BT were 0, 10, 40, 80, 150, and 200 wt%, which were used to investigate the mixing ratio dependence of photocurrent characteristics. The organic photoconductive device was fabricated on a glass substrates covered with a patterned

indium tin oxide (ITO) anode with a thickness of 150 nm. The prepared glass substrate was cleaned in deionized water and an organic solvent sequentially under ultrasonic waves, and then treated with an ultraviolet ozone for 20 min. Following the cleaning of glass substrates, the mixed solution of DMTPS and F8BT was spin-coated onto a glass substrate at a rotation speed of 1000 rpm for 60 s. Then, chloroform was removed by baking the sample in a nitrogen atmosphere at a temperature of 70 °C for 30 min. Finally, LiF (1 nm) and Al (100 nm) were thermally evaporated successively at a base pressure below 5×10^{-4} Pa. The deposition rates of LiF and Al were fixed at 0.05 and 0.3 nm/s as determined using a quartz crystal monitor, respectively. The receiving areas of all the devices were fixed at 9 mm².

The photocurrent and dark current-voltage characteristics of the devices were measured by a DC voltage current source/monitor (ADCMT, 6241A). A positive bias voltage was applied to the ITO electrode. The center wavelength and optical intensity of irradiated light were 470 nm and 1 mW/cm², respectively. The dark current was also measured as the current density-voltage characteristic without blue light irradiation. The external quantum efficiency (EQE) was defined as the number of output electrons divided by the total number of irradiated photons, and it was estimated from the measured photocurrent (I_p) and the optical intensity of irradiated light (P) as

$$\eta = \frac{I_p}{e} / \frac{P}{h\nu}, \quad (1)$$

Here, e , h , and ν are the elemental charge, Planck's constant, and the frequency of irradiated light, respectively. The ON/OFF ratio was calculated as the photocurrent divided by the dark current. The thickness of the DMTPS:F8BT layer was measured by a surface profile meter (ULVAC, Dektak3), and then, the applied electric field was calculated as the applied voltage divided by the thickness of the DMTPS:F8BT layer.

To estimate the wavelength selectivity of DMTPS:F8BT, the ultraviolet-visible (UV-vis) light absorption spectrum of the organic neat film was recorded with a UV-vis spectrophotometer (JASCO, V-550). Here, the DMTPS:F8BT neat film was spin-coated on a silica glass substrate. The photocurrent spectrum of the organic photoconductive device was estimated by measuring the wavelength dependence of photocurrent density while irradiating the monochromatic light by the fluorescence spectrometer (JASCO, FP-777).

3. Results and Discussion

Figure 2(a) shows the EQE of the organic photoconductive device as a function of DMTPS:F8BT ratio at the electric fields of 1×10^5 and 2×10^5 V/cm. In addition, the thickness of the organic layer is also shown in Fig. 2(a). The thickness of the organic layer increased with increasing concentration of DMTPS in F8BT; however, the difference in the thickness of the organic layer has a negligible effect on the EQE. The device with the concentration of 200 wt% was broken when the electric field of 2.0×10^5 V/cm was applied to

the device. The EQE was almost independent of the concentration less than 40 wt%, and it decreased with increasing concentration of DMTPS to more than 40 wt%. A maximum EQE of 7.6 % was achieved at the concentration of 40 wt%. The EQE was improved at the high electric field, as shown in Fig. 2(a). This is because the carrier mobility of the organic material increases with increasing electric field,²⁰⁾ resulting in the efficient carrier dislocation with a low carrier recombination probability.¹¹⁾ Therefore, more carriers reach the electrodes without loss in the case of the high electric field. In addition, the photocurrent density-voltage characteristics obtained by irradiating the blue light with an optical intensity of 0.8 mW/cm² are shown in Fig. 2(b). Schottky-type photoconductive characteristics were observed.

The relationship between the concentration of DMTPS:F8BT and the photocurrent/dark current is shown in Fig. 3(a). It is noted that the dark current was rapidly reduced by adding DMTPS into F8BT, and it decreased with increasing concentration of DMTPS. One possible reason of this is that the highest occupied molecular orbital (HOMO) level of DMTPS (6.27 eV) was higher than that of F8BT (6.04 eV), and the HOMO level was determined by photoelectron spectroscopy. The work function of the Al electrode is 4.3 eV; therefore, the holes are blocked in order to inject them into the Al layer by DMTPS due to its HOMO level that is higher than that of F8BT. On the other hand, the most important finding is that the photocurrent remained almost constant at a concentration less than 40 wt%, and it decreased with increasing concentration of DMTPS over 40 wt%. The lowest unoccupied molecular orbital (LUMO) level of DMTPS was 4.0 eV, which exists at the middle of F8BT and ITO. Therefore, the photoinduced electrons in the F8BT layer move to the LUMO level of F8BT easily, resulting in the efficient carrier dislocation in the organic layer. This improves the photocurrent at a concentration less than 40 wt%. However, the photoinduced holes are blocked by DMTPS, and the large amount of DMTPS prevents the hole transport from the organic layer to the Al electrode. Therefore, the photocurrent decreased with the doping of the large amount of DMTPS, as shown in Fig. 3(a).

The ON/OFF ratio was improved by mixing DMTPS:F8BT, as described in Fig. 3(b). In our experimental result, the difference in the thickness of the organic layer has a negligible effect on the ON/OFF ratio. The maximum ON/OFF ratio was 550 at the concentration of 10 wt%, and this value was 5 times higher than that of the reference device with F8BT only. The higher ON/OFF ratio enables us to capture an image using the organic photoconductive device. In addition, the ON/OFF ratio decreased with increasing concentration owing to the low photocurrent in the case of the high concentration. This is because the photocurrent decreased at the high concentration owing to the low carrier mobility of DMTPS compared with F8BT. However, the improvement in ON/OFF ratio was successfully achieved at a concentration of DMTPS less than 150 wt%.

Figure 4(a) shows the absorption spectra of DMTPS:F8BT neat films with different con-

concentrations. The inset of Fig. 4(a) indicates the relationship between the concentration of DMTPS and the absorbance ratio (380 nm/470 nm), which was calculated as the absorbance at 380 nm divided by that at 470 nm. The center wavelength of the absorption spectra was 470 nm, which corresponds to the absorption of F8BT.¹⁴⁾ By increasing the concentration of DMTPS, the relative absorbance at 380 nm was increased. This is because DMTPS exhibits absorption at around 380 nm, and the large amount of DMTPS causes the higher absorbance, as shown in the inset of Fig. 4(a).

To capture images, most of the incident light must be absorbed in the organic photoconductive layer. Figure 4(b) shows the relationship between the concentration of DMTPS:F8BT and the transmittance against the blue light with a wavelength of 470 nm. The relative concentration of F8BT decreased with increasing the concentration of DMTPS, and DMTPS exhibits a negligible absorption against the blue light, and the transmittance increased with increasing concentration of DMTPS. However, the transmittances of all the films were less than 10 %. This result indicates that most of the irradiated blue light was efficiently absorbed in the DMTPS:F8BT layer, resulting in the generation of carriers.

Figure 5 shows photocurrent spectra of two devices with F8BT only and 10 wt% DMTPS:F8BT. Both photocurrent spectra were normalized at the wavelength of 470 nm. Since DMTPS exhibits absorption only in the violet wavelength region, the photocurrent was increased by adding DMTPS due to its absorption in this wavelength region. However, DMTPS exhibits a negligible absorption against the visible light, and the photocurrent spectrum showed good spectral selectivity in the blue wavelength region even though DMTPS was added into F8BT.

4. Conclusions

We investigated the ON/OFF ratio of an organic photoconductive device by mixing DMTPS and F8BT, and the maximum improvement of 5 times was achieved by optimizing the concentration of DMTPS without decreasing the EQE. In addition, the wavelength selectivity was sufficiently high for separating the incident light, and the organic photoconductive device can detect only the blue light.

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Figure captions

Figure 1. (a) Cross-sectional view of the organic photoconductive device and (b) molecular structures of F8BT and DMTPS used as photoconductive layers.

Figure 2. (a) EQE obtained by irradiating the blue light with a center wavelength of 470 nm and the thickness of organic layer as a function of the concentration of DMTPS in F8BT. The electric fields were 1×10^5 and 2×10^5 V/cm. (b) Photocurrent-voltage characteristics of two devices with F8BT only and DMTPS:F8BT (10 wt%) obtained by irradiating the blue light of 0.8 mW/cm^2 optical intensity.

Figure 3. (a) Photocurrent and dark current as a function of DMTPS:F8BT at the electric field of 1×10^5 V/cm. (b) Relationship between the concentration of DMTPS:F8BT and the ON/OFF ratio (photocurrent/dark current).

Figure 4. (a) Absorption spectra of DMTPS:F8BT neat films with different concentrations of DMTPS:F8BT. The inset shows the relationship between the absorbance ratio (380 nm/470 nm) and the concentration of DMTPS:F8BT. (b) Transmittance of DMTPS:F8BT neat films as a function of DMTPS:F8BT ratio.

Figure 5. Photocurrent spectra of organic photoconductive devices with F8BT only and 10 wt% DMTPS:F8BT as photoconductive layers.

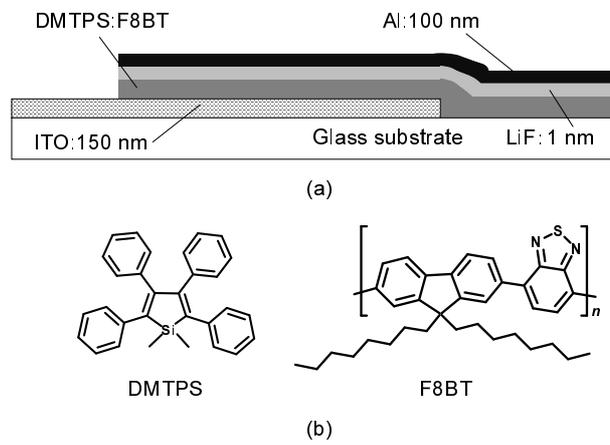
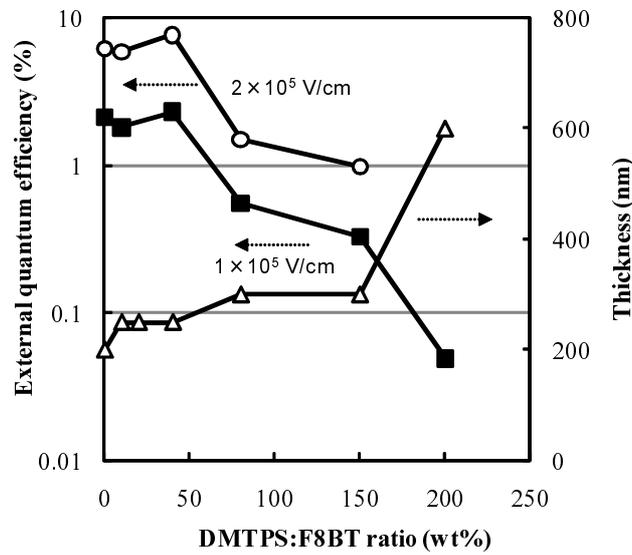
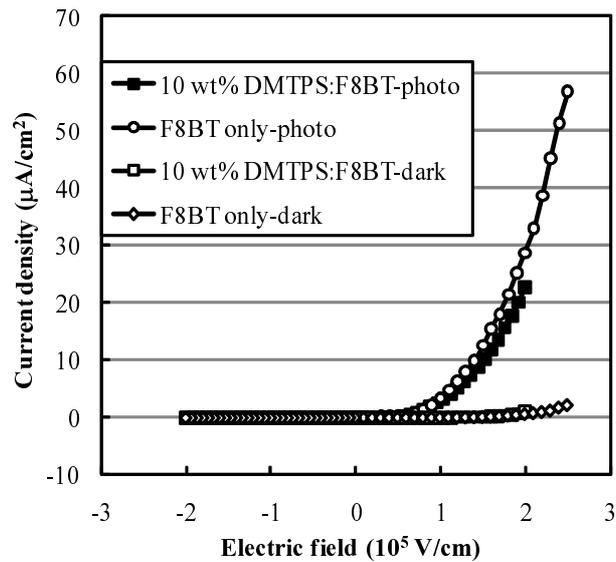


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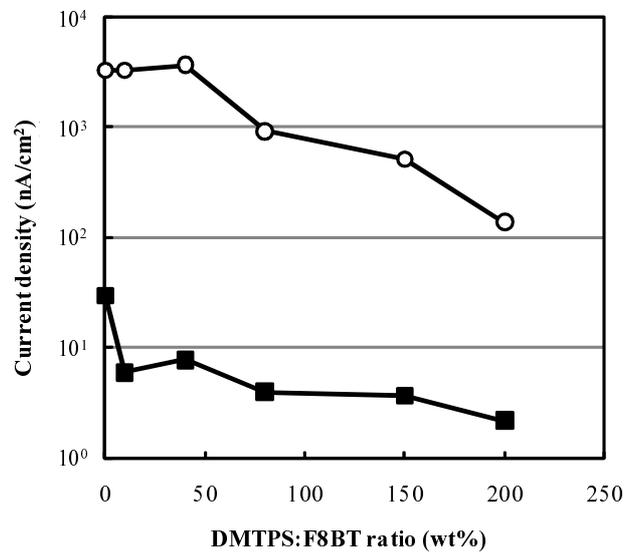


(a)

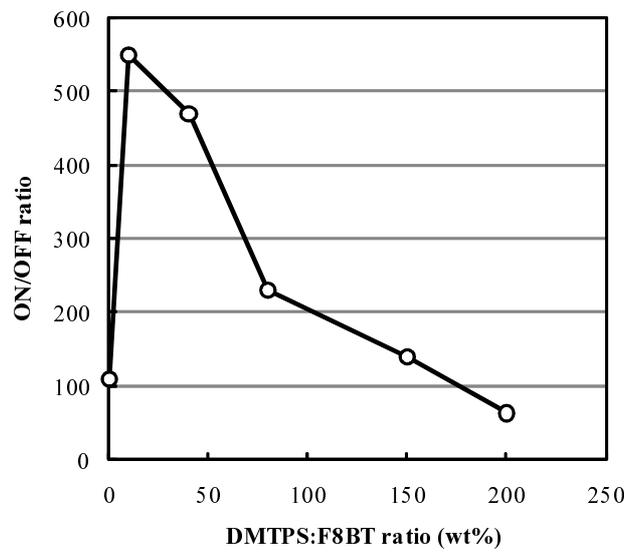


(b)

Fig. 2. (a) EQE obtained by irradiating the blue light with a center wavelength of 470 nm and the thickness of organic layer as a function of the concentration of DMTPS in F8BT. The electric fields were 1×10^5 and 2×10^5 V/cm. (b) Photocurrent-voltage characteristics of two devices with F8BT only and DMTPS:F8BT (10 wt%) obtained by irradiating the blue light of $0.8 \text{ mW}/\text{cm}^2$ optical intensity.



(a)



(b)

Fig. 3. (a) Photocurrent and dark current as a function of DMTPS:F8BT at the electric field of 1×10^5 V/cm. (b) Relationship between the concentration of DMTPS:F8BT and the ON/OFF ratio (photocurrent/dark current).

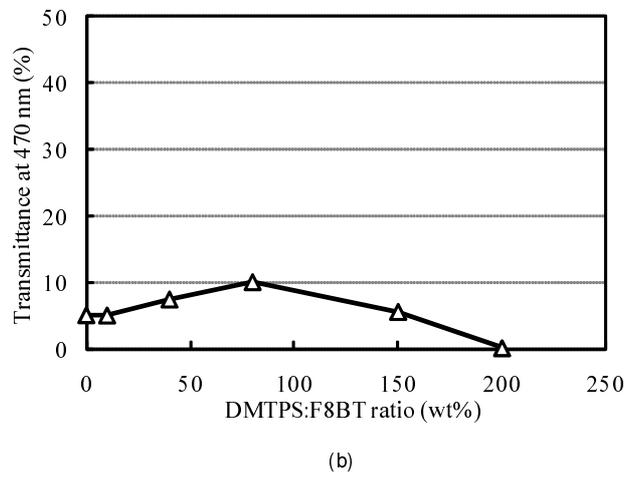
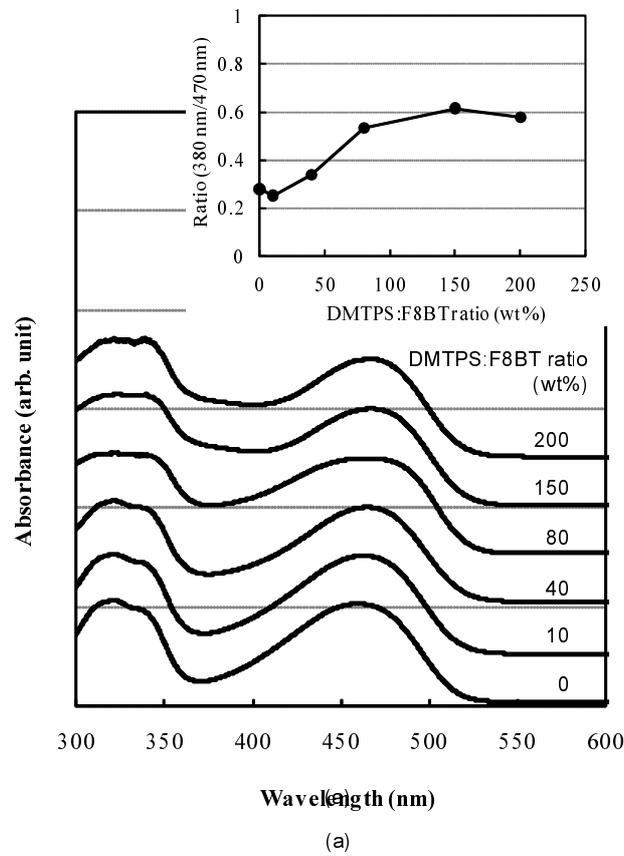


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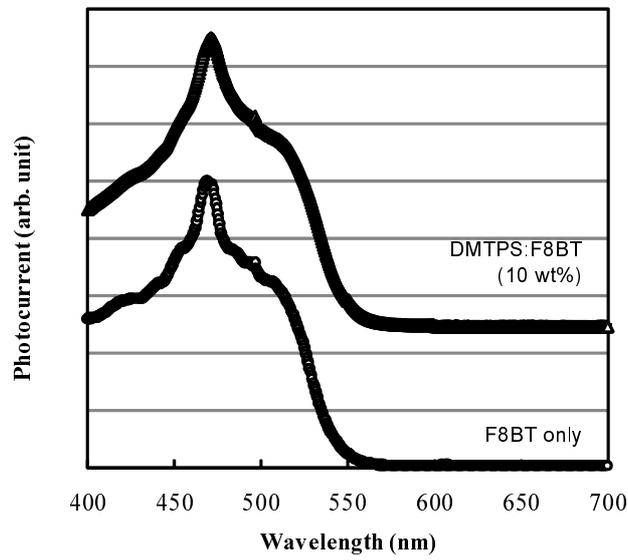


Fig. 5. Photocurrent spectra of organic photoconductive devices with F8BT only and 10 wt% DMTPS:F8BT as photoconductive layers.