

# Red-Sensitive Organic Photoconductive Device Using Soluble Ni-Phthalocyanine

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**SUMMARY** A solution-processed red-sensitive organic photoconductive device was demonstrated by using soluble nickel-phthalocyanine. We found that a ratio of four nickel-phthalocyanine regioisomers was important factor for the high optical-electrical conversion efficiency. A maximum external quantum efficiency of device of 0.83% was achieved by optimizing the device structure.

**Key words:** organic photoconductive device, soluble nickel-phthalocyanines, regioisomer, photoconductive characteristics

## 1. Introduction

Organic photoconductive devices have attracted much attention due to practical and physical points of view [1], [2]. Especially, solution-processed devices have been required because of their advantages in low-fabrication cost and large device area. By now, our research group demonstrated a solution-processed color-selective organic photoconductive device [3], which can separate the incident light into three color components [4]. We reported that Nickel-tetrakis-(*tert*-butyl)phthalocyanine [Ni(*t*-Bu)<sub>4</sub>Pc] has a selective absorption spectrum only at red wavelength region, and the red-sensitive device was obtained by using Ni(*t*-Bu)<sub>4</sub>Pc as a photoconductive layer. However, a reported external quantum efficiency (EQE) of red-sensitive device was much lower than those of blue- and green-sensitive devices [4].

In this study, we investigated the influence of a ratio of four nickel-phthalocyanine regioisomers on the photoconductive characteristics of red-sensitive organic devices.

## 2. Experimental

At first, a glass substrate covered with a patterned indium tin oxide (ITO) was cleaned with solvents and deionized water under ultrasonic wave, and then treated with ultraviolet ozone for 20 minutes. The polymer mixture of poly(3,4-ethylenedioxythiophene) and polystyrenesulfonate [PEDOT:PSS] was spin-coated on the glass substrate at a rotation speed of 2500 rpm for 60 second. After removing the solvent by baking in nitrogen atmosphere at 100 degree centigrade for one hour, Ni(*t*-Bu)<sub>4</sub>Pc as a red-light

sensitive photoconductive material was also spin-coated at a rotation speed of 2000 rpm for 60 second. Then, the solvent was removed by baking at 75 degree centigrade for one hour. [Ni(*t*-Bu)<sub>4</sub>Pc] was dissolved in chloroform as the content of 1 wt% of [Ni(*t*-Bu)<sub>4</sub>Pc]. Finally, LiF and Al were thermally evaporated successively on the top of a [Ni(*t*-Bu)<sub>4</sub>Pc] layer. In addition, we used three samples of Ni(*t*-Bu)<sub>4</sub>Pc-A, B, and C, which were made out of a different ratio of regioisomers. The device structure was ITO(150 nm)/PEDOT:PSS(70 nm)/Ni(*t*-Bu)<sub>4</sub>Pc(70 nm)/LiF(1 nm)/Al(150 nm).

Photocurrent and dark current-voltage characteristics of fabricated 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 the full width at half maximum of the spectrum of the irradiated light-emitting diode were 619 nm and 15 nm, respectively. The red-light was focused on the fabricated sampled with the optical intensity of 1 mW/cm<sup>2</sup>. The dark current was also measured as the current density-voltage characteristic without the red-light irradiation. The 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 and the optical intensity of irradiated light [4]. In the cases of devices A and B, the photocurrent was higher than the dark current density. This result indicates the photo-induced carriers are detected as a current from the electrode.

## 3. Results and Discussion

Figure 1 shows the photocurrent density and dark current density characteristics of devices A, B, and C with different Ni(*t*-Bu)<sub>4</sub>Pc as an organic photoconductive material. In the cases of devices A and B, the current density was improved by irradiating the red-light. This fact indicates the photo-induced carriers were detected from the electrode without the recombination of the electron-hole pair. On other hand, little photocurrent was observed for the device C, and the dark current density of the device C was much higher than those of other devices. In addition, the signal-to-noise ratios were 3.1, 2.6, and 1.0 for devices A, B, and C, respectively. The signal-to-noise ratio was calculated as the photocurrent density divided by the dark current density.

Figure 2 represents the EQE of photoconductive devices A and B which consisted of Ni(*t*-Bu)<sub>4</sub>Pc-A and B. The EQEs increased constantly with increasing the applied

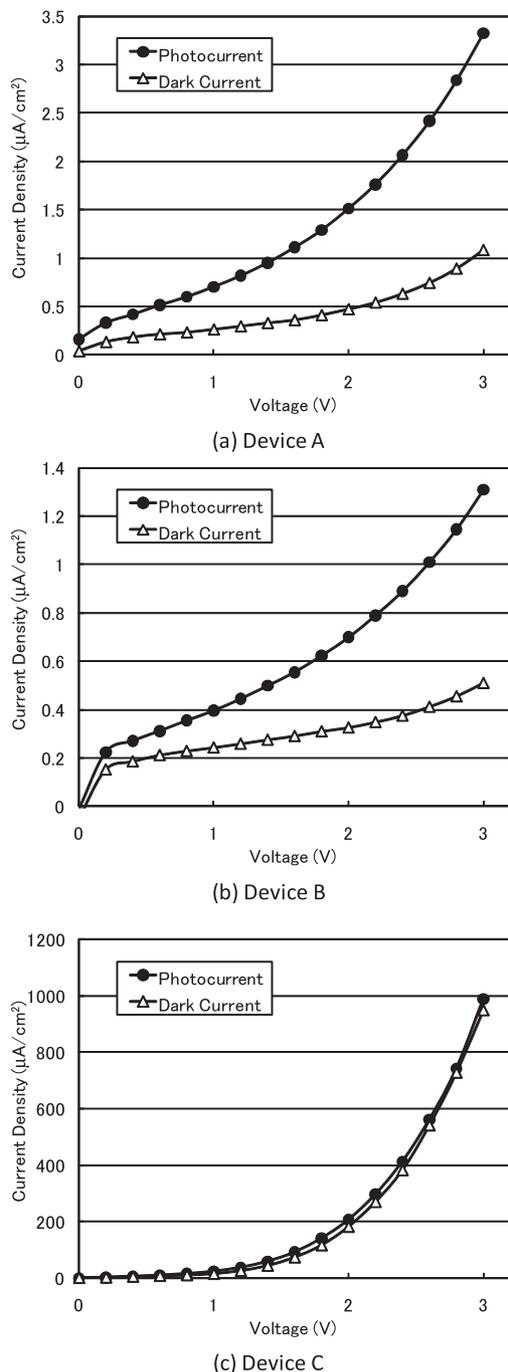
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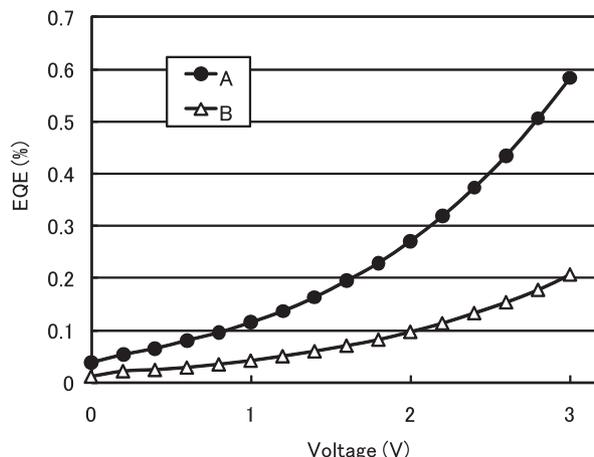
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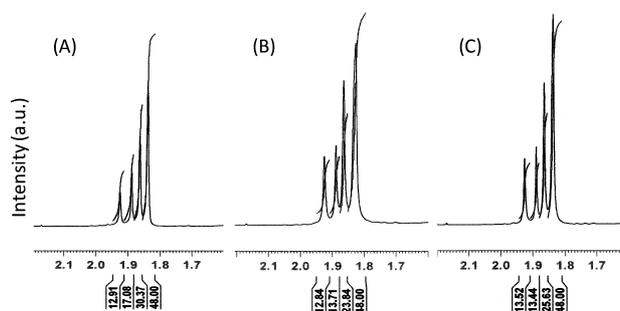
**Fig. 1** Influence of applied voltage on photocurrent and dark current density for devices A, B, and C. Optical intensity of red light was  $1 \text{ mW/cm}^2$ .

voltage owing to the high carrier mobility at a high voltage region [5]. As a result, most photo-excited carriers move to the electrode side with low recombination probability. A maximum EQE of device A was 0.58% at 3 V, implying approximately 2.8 times higher than that of device B. The EQE of device B was 0.21 at 3 V. The little photocurrent was observed for the device C, therefore, the EQE cannot be estimated for the device C.

To estimate the reason of the difference in the measured



**Fig. 2** External quantum efficiency of devices A and B with a different isomers ratio of  $\text{Ni}(t\text{-Bu})_4\text{Pc}$ .

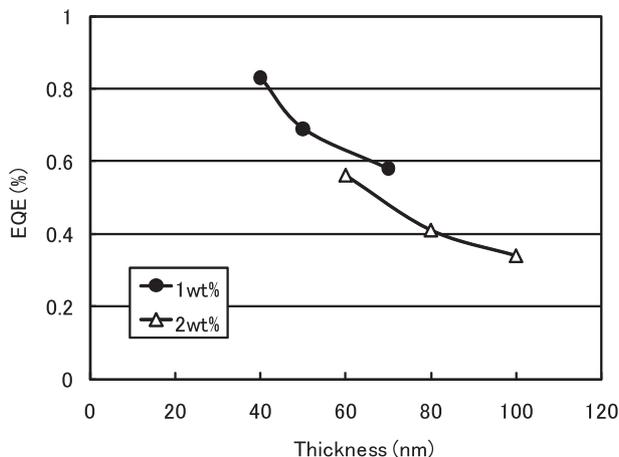


**Fig. 3** Aliphatic region of  $^1\text{H}$  NMR spectra of  $\text{Ni}(t\text{-Bu})_4\text{Pc}$ -A, B, and C.

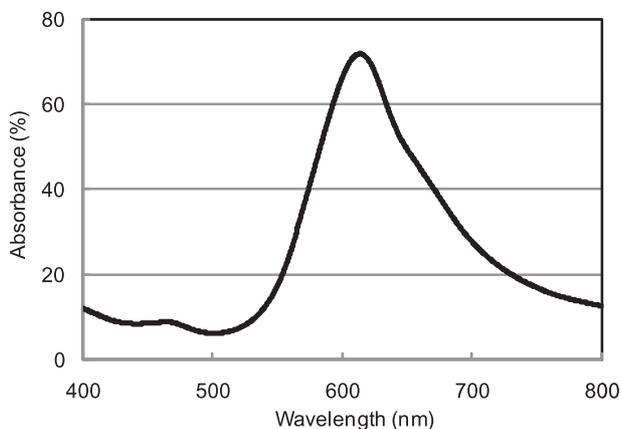
EQE, we determined a ratio of four  $[\text{Ni}(t\text{-Bu})_4\text{Pc}]$  regioisomers by  $^1\text{H}$  NMR spectra of the samples, as shown in Fig. 3. Each four signals assigned to *tert*-butyl substituents of four regioisomers were able to estimate the ratio by comparing with integration of each peak. The four regioisomers ratio of  $\text{Ni}(t\text{-Bu})_4\text{Pc}$ -A, B, and C were determined as 1:1:1.9:3.5, 1:1:1.9:3.7, and 1:1.3:2.4:3.7, respectively. Analysis by  $^1\text{H}$  NMR confirms that  $\text{Ni}(t\text{-Bu})_4\text{Pc}$ -A predominantly contains the  $[\text{Ni}(t\text{-Bu})_4\text{Pc}]$  isomer with  $C_{2v}$  symmetry [6].

These results indicate that the isomer ratio of  $\text{Ni}(t\text{-Bu})_4\text{Pc}$  is important factor to improve photoconductive characteristics. The carrier dynamics in the organic layer was not cleared in our experimental results.

Figure 4 shows the relationship between the thickness of  $\text{Ni}(t\text{-Bu})_4\text{Pc}$ -A layer (1:1:1.9:3.5 ratio) and the EQE at 3 V. The thickness was controlled by changing the concentration of  $\text{Ni}(t\text{-Bu})_4\text{Pc}$ -A into chloroform (1 and 2 wt%) and the rotation speed of the spin-coating process. The EQE increased with decreasing the thickness of  $\text{Ni}(t\text{-Bu})_4\text{Pc}$ -A layer. In generally the carrier transport path from the photo-absorbed region to the electrode relates with the thickness of organic layer. Therefore, the carrier transport efficiency increased with decreasing the thickness of the  $\text{Ni}(t\text{-Bu})_4\text{Pc}$ -A layer, resulting in the high EQE. A maximum EQE of 0.83% was achieved by the 40 nm thickness of  $\text{Ni}(t\text{-Bu})_4\text{Pc}$ -A layer.



**Fig. 4** External quantum efficiency of photoconductive device with Ni(*t*-Bu)<sub>4</sub>Pc-A as a function of the thickness. Concentration of Ni(*t*-Bu)<sub>4</sub>Pc-A into chloroform was changed as 1 and 2 wt%.



**Fig. 5** Absorption spectrum of Ni(*t*-Bu)<sub>4</sub>Pc-A neat film.

Figure 5 shows the photocurrent spectrum of the device A and the absorption spectrum of the Ni(*t*-Bu)<sub>4</sub>Pc-A neat

film. The center wavelength of the absorption spectrum was 618 nm, and the absorbance was decreased in both shorter and longer wavelengths. As a result, the incident light of the red wavelength region is only absorbed by the Ni(*t*-Bu)<sub>4</sub>Pc-A layer without sensitivities at blue and green wavelengths. This result indicate the red-sensitive organic photoconductive device can be realized by using the Ni(*t*-Bu)<sub>4</sub>Pc-A layer.

#### 4. Conclusion

We demonstrated the red-sensitive organic photoconductive device fabricated by the conventional spin-coating process. A ratio of [Ni(*t*-Bu)<sub>4</sub>Pc] regioisomers was confirmed by <sup>1</sup>H NMR analysis. The [Ni(*t*-Bu)<sub>4</sub>Pc] isomer with C<sub>2v</sub> symmetry was effective in the EQE of organic photoconductive devices.

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