Characterization of optical and photoelectric properties of a new boron-based organic semiconductor in the near-infrared regions

Ryota Fujioka, Tatsuya Fukushima, Yasuko Koshiba, and Kenji Ishida Department of Chemical Science and Engineering, Graduate School of Engineering, Kobe University. 1-1, Rokkodai-cho, Nada-ku, Kobe, 657-8501, Japan Phone:+81-78-803-6150 E-mail:kishida@crystal.kobe-u.ac.jp

Abstract

Optical and photoelectric properties, especially in near infrared ray (NIR) region, of dibenzopyrromethane boron chelate derivatives (BODIPY-Ph) were investigated. The BODIPY-Ph vacuum-evaporated thin films showed broad-band absorption in the wavelength rang of 600-1000 nm with the peak at 770 nm. The NIR organic photodetector (OPD) fabricated with BODIPY-Ph exhibited photocurrent of 2.18×10^{-3} mA/cm² at 1.5 V under 800 nm irradiation. This value was about 700 times higher than dark current at the same voltage. These results suggest that BODIPY-Ph is one of the promising candidates for use in NIR-OPDs.

1. Introduction

NIR-OPD is one of the fundamental device for the modern vital sensors and monitoring system of blood conditions. To effectively measure the biological information, it is demanded that the NIR-OPD deform and directly attached along the shape of the human body. Several groups have reported NIR-OPDs so far, however, a sensitivity of NIR region for the device has been still low due to a mismatch between a transparent wavelength through the body and absorption wavelength of the materials.¹⁻³⁾ To improve the performance of NIR-OPDs, developments of NIR materials are required.

Recently, dibenzopyrromethane boron chelate (BODIPY) derivatives were reported by researchers.⁴⁻⁶⁾ The BODIPYs give us material interests, because their photoabsorption spectra significantly change by substituent introductions and some of the derivatives show photoelectric conversion characteristics. In this study, we report the optical and photoelectric properties of a new BODIPY-Ph, shown in Fig.1, as a boron based organic semiconductor, and propose NIR sensor application.



Fig.1 Chemical structure of BODIPY-Ph.

2. Experiments

Synthesized BODIPY-Ph was purified by a tempera-

ture-gradient sublimation. The BODIPY-Ph thin films of 50nm thickness were prepared on various substrates appropriate for experiments by vacuum deposition. The optical property of the BODIPY-Ph film was measured by ultraviolet-visible-near infrared absorption (UV-Vis-NIR) spectroscopy. The surface morphology was observed by a tapping mode of scanning probe microscopy (SPM). Electrical properties of OPD (glass / indium-tin-oxide (ITO) / BOD-IPY-Ph / Al) were measured with a source measure unit and an infrared irradiation apparatus.

3. Results and discussion

The sublimation and decomposition temperatures of BODIPY-Ph was 379°C and ~550°C, respectively. For Fourier Transform Infrared (FTIR) spectroscopy measurements, significant difference between BODIPY-Ph powder and its deposited film was not observed. These results indicate that BODIPY-Ph have high thermal stability.

Figure 2 shows the surface morphology of BODIPY-Ph thin film, observed by the atomic force microscopy(AFM). The film had a very smooth surface. A root mean square roughness and a maximum pitch difference were approximately 0.4 nm and less than 10 nm, respectively. We considered that its morphology suppress and limit leakage current, resulting in improvements of production yield of the NIR-OPDs and a signal to noise (S/N) ratio.



Fig.2 AFM image of the BODIPY-Ph thin film.

Figure 3 shows the UV-Vis-NIR spectra of BODIPY-Ph in chloroform solution and the deposited film. The solution sample exhibited an absorption in 650-750 nm with the peak (λ_{max}) of 725 nm. Also, the thin film exhibited an absorption in the visible and near-infrared region, from 650-950 nm with the λ_{max} of 767 nm. From the results, BODIPY-Ph is expected to have photoconductivity under NIR irradiation and be applicable to NIR-OPDs for use as biosensing,

because transmitted wavelength through the living body is mainly 700-800 nm. Optical band gap was estimated to be 1.3 eV using the absorption edge of the film.



Fig. 3 UV-Vis-NIR spectra of the BODIPY-Ph in chloroform solution and deposited thin-film.

Figure 4 (a) shows an energy diagram of the OPD in this study. An ionization potential (IP) of BODIPY-Ph film was determined to be 5.1 eV with an atmospheric photoelectron spectroscopy (AC-3). An electron affinity of the film was also estimated to be 3.8 eV by the optical band gap and the IP. Figure 4 (b) shows the result of current density-voltage (J-V) curves of the NIR-OPD in the dark and under light illumination at 800 nm. The J-V curve exhibited a clear diode characteristic with the threshold voltage of 0.45 V in the dark condition. This value is considered to originate from the Schottky barrier at the semiconductor/metal interface, namely at the BODIPY-Ph/Al interface. When NIR light irradiate the NIR-OPD, photocurrent density (J_{ph}) was observed. The $J_{\rm ph}$ was 2.18×10^{-3} mA/cm² at the reverse bias of 1.5 V. This current density was about 700 times higher than the current density in the dark at the same reverse voltage. Figure 4 (c) shows the UV-Vis-NIR spectrum of BODIPY-Ph deposited film and a photocurrent spectrum of the NIR-OPD at the reverse bias of 1.5 V. The photocurrent spectrum was similar to absorption spectrum of the BODIPY-Ph film. The NIR-OPD consisting of **BODIPY-Ph** demonstrates photoelectric conversion characteristics and clear on/off response in the NIR region. This results suggest that BODIPY-Ph is one of the appropriate NIR organic materials.

3. Conclusion

BODIPY-Ph thin films prepared by vacuum deposition had absorption in the visible and near-infrared region, corresponding to the transparent wavelength through the living body. The film showed smooth surface morphology, which was advantageous in device fabrications. The NIR-OPD based on BODIPY-Ph exhibited clear diode characteristics and the photocurrent of 2.18×10^{-3} mA/cm² under illumination of 800 nm at -1.5 V. This value was 700 times higher than the current in the dark at the same driving voltage. BODIPY-Ph have a potential application to the biosensing device. (a)

(b)

(c)





Fig.4 (a) Energy diagram of the NIR-OPD in this study. (b) *J-V* curves of ITO/BODIPY-Ph/Al device in the dark and under NIR illumination. (c) UV-Vis-NIR spectrum of BODIPY-Ph deposited thin-film (left axis) and a photocurrent spectrum of the NIR-OPD at the reverse bias of 1.5 V (right axis).

Acknowledgements

This work was partially supported by JPS KAKENHI.

References

- [1] X. Gong, M. Tong, Y. Xia, W. Cai, J. S. Moon, Y. Cao, G. Yu, C.L. Shieh, B.Nilsson, and A.J. Heeger, Science **365** (2009) 1665.
- [2] X. Wanga, H. Li, Z. Su, F. Fang, G. Zhang, J. Wang, B. Chu, X. Fang, Z. Wei, B. Li, and W. Li, Org. 15 (2014) 2367.
- [3] L. Zhang and T. L. Andrew, Org. **33** (2016) 135.
- [4] A. Loudet and K. Burgess, Chem. Rev. **107** (2007) 4891.
- [5] A. Loudet, R. Bandichhor, K. Burgess, A. Palma, S. O. McDonnell, M. J. Hall, and D. F. O'Shea, Org Lett. 10 (2008) 4771.
- [6] Y. Kubo, K. Watanabe, R. Nishiyabu, R. Hata, A. Murakami, T. Shoda, and H. Ota, Org Lett. 13 (2011) 4574.