Photocarrier injection by two-photon excitation in rubrene single crystal

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Abstract. We performed photocarrier injection by two-photon excitation in rubrene crystal using laser pulses of nanosecond-duration at various wavelengths under an external electric field. Based on the excitation spectra, it is revealed that photocarriers are injected at excitation energies corresponding to the intrinsic absorption by two-photon process, in contrast to the midgap-states-mediated injection by one-photon process. This result means that the two-photon excitation method is useful to inject photocarriers free from the surface traps.

1. Introduction
Organic semiconductors are promising materials for the low cost and flexible electronics devices. A rubrene crystal, which exhibits an intrinsic mobility of 20 cm²/Vs [1] higher than that of amorphous silicon, attracts a lot of attentions as a high mobility organic semiconductor. Therefore, this material has been considered to be a good model to demonstrate the band transport mechanism in a molecular crystal. However, precise measurements of transport parameters, such as effective masses and scattering time, have been challenging so far, because of the difficulty in carrier injection at low temperature and unstable quality of specimen during the measurement period. Optical injection of free carriers will be a reliable method to further investigations, because carriers can be injected at a controlled density without doping or interface at the electrode. In our previous study [2], we found that photocarriers are injected by dissociation of neutral Frenkel excitons under an electric field higher than 1 kV/cm at room temperature. However, decrease of carriers by trapping was a severe problem for measuring transport parameters at lower temperatures.

In this study, we investigate the way to inject carriers free from traps. We perform the two-photon excitation method under an electric field with pulsed light at wavelengths of transparent under a linear response. It has been reported that the mid-gap states, which are generated on the surface by the oxidation of a rubrene crystal [3], are intermediate states for optical carrier generation [4] and trap carriers and excitons under one-photon excitation [2]. Such states potentially disturb carrier transport by trapping and scattering. Based on the excitation spectra of transient photocarrier generation, influence of such surface states for the carrier injection is examined in comparison between the two-photon excitation and one-photon excitation at room temperature.

2. Experiment
Rubrene single crystal was prepared by the physical vapor transport method in gas phase after sublimated purification of a commercial rubrene powder (Sigma-Aldrich, R2206). The typical size of the grown crystal was $1 \times 2 \times 0.2$ mm³, where the largest plane was the crystalline $ab$-plane. The
crystal was sandwiched with two transparent electrodes of indium-tin-oxide (ITO) glasses. An electric field was applied along the crystalline $c$-axis using a DC voltage source meter (Keithley, 6487J). The sample was mounted on a cold finger of a cryostat and irradiated through the ITO substrate by a nanosecond laser pulses from a tunable pulsed laser (Spectra-physics, MOPO, 5 ns, 10 Hz). One-photon excitation was performed in the wavelength ranges from 520 to 680 nm with typical incident pulse energy of 5 $\mu$J, and two-photon excitation was performed in the wavelength range from 800 to 1200 nm with typical incident pulse energy of 100 $\mu$J with loose focusing. Transient photocurrent was measured as a voltage drop across a 1 kΩ load resistance by an oscilloscope (Tektronix, TDS 3032) at room temperature as described elsewhere [2]. The detected voltage value was converted to that of current. Furthermore, we measured microwave response to the photogenerated carriers generated by the two-photon excitation inside a cylindrical microwave cavity at frequency of 9.6 GHz (Bruker, MD5W1).

3. Results and discussion

Figure 1 shows temporal profiles of transient photocurrent measured at various excitation wavelengths by (a) one-photon and (b) two-photon processes under an electric field of 71.4 kV/cm. The peak intensities of the transient response by one-photon excitation were approximately 20 times larger than those by two-photon excitation. However, we consider that the intensity of the displacement current is related to the generated carrier number but not proportional to it, because somewhat cancellation effect might appear in the displacement current for carriers generated deeply inside a crystal. The signal decayed three times faster by one-photon excitation than by two-photon excitation probably due to traps at the surface.

![Figure 1](image)

**Figure 1.** Time profiles of transient photocurrent at room temperature excited by excitation wavelengths (a) in the range from 520 nm to 680 nm for one-photon process and (b) in the range from 800 nm to 1200 nm for two-photon process.

Figure 2 shows the excitation pulse energy dependence of the transient photocurrent peak intensity excited at wavelengths of 530 nm and 830 nm for one- and two-photon excitations, respectively. Photocurrent injected at 530 nm increased linearly to the excitation pulse energy ensuring a one-photon process, whereas photocurrent injected at 830 nm increased as square of the excitation pulse energy ensuring a two-photon process. Therefore, we confirmed that the photocurrents can be injected by both one- and two-photon excitation processes under an external electric field. Note that the crystal was damaged by the excitation pulse energy over 285 $\mu$J with a loose focus into a few hundred $\mu$m.
Figure 2. Excitation pulse energy dependence of the transient photocurrent peak intensity excited at 530 nm (black squares) and 830 nm (red circles). The broken lines guide the linear (left) and square (right) dependence of excitation pulse energy.

Figure 3 shows the excitation spectra of the time-integrated photocurrent, which was converted to the value in the unit of charge, measured by one- and two- photon excitations. By the one-photon excitation, a maximum was apparent around the photon energy of 2.2 eV (open circles) below the intrinsic absorption edge of rubrene crystal. This broad peak coincides with the mid-gap level which is attributed to the oxidized state on the crystal surface [3] and an intermediate state of the photocarrier generation [4]. On the other hand, by the two-photon excitation, the photocurrent appeared above the photon energy of 2.4 eV (solid squares) which is corresponding to the absorption edge for polarized light in the crystalline ab-plane. The spectral shape roughly traced the absorption spectrum [5] up to 3.1 eV. From these results, we emphasize that the two-photon excitation process is appropriate to generate carriers deeply inside a crystal where carriers are not affected by the surface conditions.

Figure 3. Excitation spectra of photocurrent injected by one- (open circles) and two- (solid squares) photon excitations. Excitation spectrum of microwave response to photocurrent injected by the two-photon excitation (pale triangles) was also shown. Data points obtained by the two-photon excitation were plotted at twice the photon energy.
In a rubrene crystal, the lowest energy edge of absorption is attributed to an electric dipolar transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The symmetries of HOMO and LUMO are belonging to the irreducible representations of $A_g$ and $A_u$, respectively, in the point group $C_{2v}$ of a rubrene molecule. The electric dipole transition between HOMO and LUMO for one-photon excitation polarized in the crystalline $ab$-plane is allowed only by the assistance of molecular vibration of $b_g$-mode, so-called vibronic transition [6]. Observed absorption and photoluminescence spectra polarized in the $ab$-plane is explained by the vibronic transitions with a Raman-active $b_g$ mode of 1520 cm$^{-1}$ (188 meV) [7] under the Franck-Condon model. For the two-photon excitation polarized in the crystalline $ab$-plane, the HOMO-LUMO transition is allowed only by the assistance of molecular vibration of $b_u$-mode. Referring to an infrared absorption spectrum of rubrene [8], IR-active mode at 1494 cm$^{-1}$ (185 meV) may allow the transition by two-photon excitation. Then, the excitation spectrum by two-photon process is roughly similar to the absorption spectrum for the polarized light in the crystalline $ab$-plane.

Finally, we add an experimental fact that a part of microwave response to the photocarriers injected by the two-photon excitation exhibited the similar excitation spectrum to that of photocarriers by the two-photon excitation (pale triangles in Fig.3). This fact indicated that the two-photon excitation method matches to the spectroscopy monitoring by microwave, because carriers injected deeply inside a crystal can be probed. It is a hint to future study by the cyclotron resonance of the free carriers in an organic crystal in order to measure the transport parameters precisely.

4. Conclusion
We measured photocurrent in a rubrene crystal with polarized light in $ab$-crystal plane by one- and two-photon excitations under an electric field. We found that photocarriers are injected by two-photon excitation free from the mid-gap levels which strongly affect the carrier injection under one-photon excitation. The excitation spectrum of photocurrent injected by two-photon excitation roughly coincided with the intrinsic absorption of rubrene crystal, which was achieved by HOMO-LUMO transition with the assistance of molecular vibrations. Therefore, Frenkel excitons generated deeply inside a crystal dissociate into charge carriers under an external electric field. The two-photon excitation method is effective to inject carriers which can move free from the surface traps for future investigation of carrier transport.

References
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