Photogeneration and relaxation dynamics of excitons and charge carriers in an organic molecular semiconductor rubrene

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Organic semiconductors are attracting much attention because of their promising applications to cost-effective and flexible devices. Rubrene is considered to be a potential candidate for the applications to the organic field-effect transistors and organic light-emitting devices. In fact, a number of field-effect studies on rubrene single crystals have been performed, revealing their large mobilities. Although carrier generation and relaxation dynamics is essential for understanding of charge transport and photoconductive properties, few studies of carrier dynamics using ultrafast optical spectroscopy have been carried out in rubrene single crystals. Thus, the overall picture of the photocarrier generation and relaxation mechanisms has not been obtained.

In this study, we measured transient absorption spectra of rubrene single crystals using the fs pump-probe (PP) method from visible to far-infrared region. The single crystals were grown by physical vapor transport in a stream of argon gas. Pump and probe pulses were polarized along the b axis, along which rubrene shows the highest mobility. Photomodulated absorption spectra for the 2.23 eV excitation (the lower energy side of the lowest exciton peak) show several peaks with different relaxation dynamics. A sharp peak at ~0.4 eV for the delay time t_d=0 ps is attributable to the induced absorption of the exciton states. A broad peak at around 1.5 eV observed for t_d ~100 ps is quite similar to the absorption of the ionic molecules, so that it can be attributed to charge carriers. The decay time of the 0.4 eV-peak and the rise time of the 1.5 eV-peak are equal to each other, indicating that photogenerated excitons are dissociated into charge carriers within 100 ps. The decay time of charge carriers is as long as a few microseconds and much longer than that of excitons.

By comparing the results of the PP spectroscopy and the transient photoluminescence measurements, the photocarrier generation and relaxation mechanisms will be discussed in detail. In addition, primary photoexcited states and photocarrier generation mechanism in rubrene single crystals will be discussed by measuring excitation energy dependence of photomodulated absorption spectra and their dynamics.