Exciton fission and interfacial charge transfer in rubrene/fullerene mixed film revealed by femtosecond and nanosecond transient absorption spectroscopy

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Previously we have reported that the singlet exciton in rubrene single crystal underwent exciton-fission to produce two triplet excitons [1]. This process is though to be beneficial for the application of the exciton-fission solar cell, where the photocurrent generation quantum efficiency more than 100% (200% in the ideal situation) can be expected due to production of two triplet excitons from one singlet exciton. In this study, charge transfer process from the triplet exciton was revealed in the mixed film of rubrene and fullerene by means of femtosecond and sub-nanosecond transient absorption spectroscopic techniques.

Rubrene single crystal was made by the train sublimation technique. The rubrene/fullerene mixed film was made by the melting-cooling method using PCBM as the fullerene derivative, and the X-ray diffraction pattern indicated that rubrene formed the crystal phase in the film. It is considered that PCBM molecules were dispersed in and/or around the rubrene crystal domains.

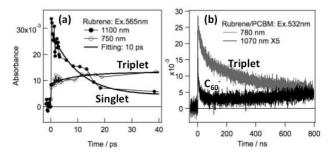
In the femtosecond transient absorption measurement, the excitation wavelength was 565 nm and the white-light continuum was used as the probe light. In the subnanosecond transient absorption spectroscopy, 532 nm was the excitation wavelength, and a flash lamp was used as the probe light. All measurements were performed at the room temperature (295 K).

We have already shown that just after excitation of the rubrene single crystal singlet exciton absorption was observed at around 1100 nm. As this band completely disappeared with the time constant of ~10 ps, the triplet absorption appeared with three peaks at ~790 nm, 880 nm, 990 nm, indicating that exciton-fission process occurred efficiently. In Fig. 1a, the kinetics is shown. Note that this assignment to exciton fission was further confirmed by observed magnetic field effects of the fluorescence yield and the decay kinetics of the singlet exciton absorption.

For the mixed rubrene/PCBM film, we observed decay processes of the triplet absorption in the sub-100 ns time scale and ~300 ns. The former seemed to be due to triplet-triplet annihilation, while the latter was due to charge separation with PCBM from the triplet state because we observed corresponding rise of the PCBM anion band at around 1070 nm as shown in Fig. 1b.

Judging from the observed small amplitude of the PCBM anion band, the charge separation yield seems very low. This reason may be the small free energy change between rubrene triplet and the charge-separated state (rubrene cation and PCBM anion) or the large

domain size of rubrene single crystal. We will present and discuss more details regarding the primary process of the rubrene/fullerene singlet-fission solar cell.



**Fig. 1.** Transient absorption kinetics of rubrene single crystal (a) and rubrene/PCBM mix film (b).

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## Reference

[1] A. Furube, R. Katoh, H. Mitsuta, T. Miyadera and Y. Yoshida, ECS Meeting Abstracts, 2011, 1101, 1831–1831.