

Femtosecond Pump-Probe Microspectroscopy for Emissive Organic Solids

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Ultrafast time-resolved microspectroscopy is a fruitful technique to observe the dynamics of excited states and intermediates for photochemical processes in organic solids, which can help us gain rational designs of organic solids nanoaggregates having high emission yield and novel photo-functions. Usually, the signal detections in the time-resolved microspectroscopy are classified into two, emission and transient absorption. When emission of organic solids is detected, the detection sensitivity is high, and the temporal resolution is a few hundreds of picoseconds (ps). However, the target is limited to highly emissive materials. These indicate that the time-resolved fluorescence (e.g., time-correlated single-photon counting) technique makes it difficult to observe initial events of the photochemical processes in a few ps time scale. On the other hand, when transient absorption (transmitted light) of the solids is used for the detection, generally all the transient species are observed, and the temporal resolution becomes higher than that of the fluorescence by using a femtosecond laser pulse. Along with this, line, we have developed the novel femtosecond pump-probe microspectroscopic system and applied it to the elucidation the excited-state relaxation processes of single organic crystals having the size of a few micrometers.¹⁻³ Furthermore, when the size of the organic solids is smaller than the focusing beam diameter, the gain of the transient signal in the absorption-based mode becomes low because the photodetector detects the stray light which does not transmit a nanocrystal. To avoid detecting the stray light and increase the transient signal gain, we proposed the femtosecond pump and back-scattering-light probe technique to measure the nanometer-sized organic solids. As a result, we succeeded in the measurement of the excited-state relaxation dynamics of single nanocrystals.¹ In the presentation, we introduce two organic crystals results by using the developed femtosecond pump-probe spectroscopic system.

Figure 1 shows a schematic illustration of the developed experimental setup, where the output of a femtosecond Ti: Sapphire oscillator (790 nm, 1 W, 80 MHz) was used as a light source. The pump pulse was the second harmonics (395 nm) of the fundamental light of the oscillator, and the probe pulse was the super-continuum generated by focusing the fundamental light into the photonic crystal fiber. Pump and probe lights were co-linearly focused on a sample organic solid

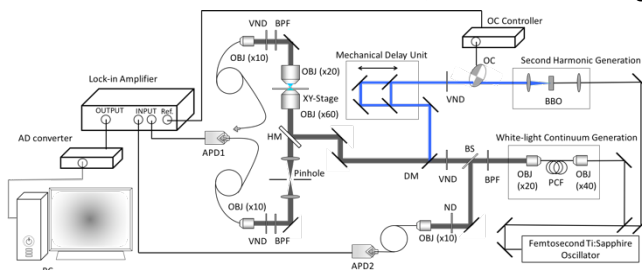


Figure 1. Schematic illustration of the developed pump-probe microspectroscopic system.

with an objective lens (60x, NA=0.70). The transmitted probe light was collected with another objective lens and detected with an avalanche photodiode (APD) combined with a lock-in amplifier as an absorption-based mode. The spatial and temporal resolutions of 700 nm and 350 fs, respectively. Here, we applied this absorption-based setup to single organic microcrystal of 6-Cyano-2-(2'-hydroxyphenyl)imidazo[1,2-a]pyridine (10 μm \times 15 μm) showing three crystalline polymorphs with different molecular packings (herringbone-like, antiparallel dimer stacking and two slip-stacked, parallel stacking modes) and polymorph-dependent excited-state intramolecular proton transfer (ESIPT) emission.³ In the case of the single microcrystal having the antiparallel dimer stacking, the transient signal due to the excited-state absorption of the enol decayed with the time constants of 0.8 ps and 25 ps and remained long-lived species in Figure 2. The 0.8-ps time constant was assigned to the ESIPT process, close to that in THF. After the ESIPT process, the heteroexcimer between excited keto and neighboring ground enol molecules was formed with a time constant of 25 ps and emitted in a few ns time scale. Comparing the results of three polymorphs, we demonstrated that the time constants of the ESIPT process and the heteroexcimer formation strongly depended on the molecular packings.

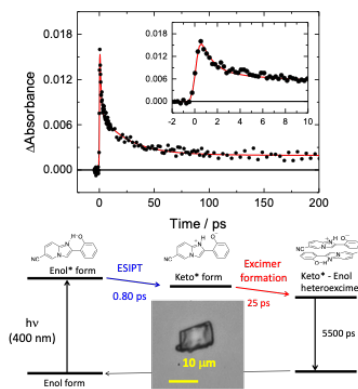


Figure 2. Time profile of the transient absorbance at 500 nm and schematic illustration of the ESIPT and the sequential processes.

The second result is the excimer formation dynamics of single α -form perylene nanocrystals having the size distribution of 100 to 500 nm.¹ In this measurement, we used a back-scattering light of the sample through the confocal optical setup as a probe one. Probe wavelength was set to 630 nm, where the rise curve due to the excimer formation was obtained. Considering that the peak wavelength of the excimer emission was blue-shifted as the perylene nanocrystal size became small,³ we also measured the emission spectrum of the identical nanocrystal. The representative results are shown in Fig. 3. The time constant of the excimer formation in each panel was different (0.3 ps for A, 1.2 ps for B, and 1.9 ps for C), which was shorter than that of the bulk crystal (3 ps). When the emission peak wavelength appeared in the shorter wavelength, the time constant became shorter. This result indicated the faster excimer formation in smaller perylene nanocrystal. We demonstrated the size-dependent excited-state dynamics of single organic nanocrystals.

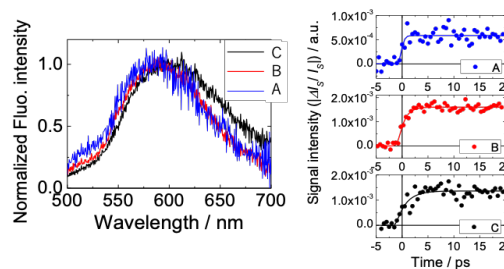


Figure 3. Representative emission spectra and time profiles of the transient signals of three single perylene nanocrystals.

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