Femtosecond microspectroscopic study on excited-state intramolecular proton transfer of crystalline cyano-substituted imidazo[1,2-*a*]pyridine

Yukihide Ishibashi[1], Mako Murakami[1], Koji Araki[2], Toshiki Mutai[2], and Tsuyoshi Asahi[1]

[1] *Graduate School of Science and Engineering, Ehime University, Matsuyama, Ehime Japan*
[2] *2Institute of Industrial Science, The University of Tokyo, Meguro, Tokyo Japan*

E-mail: ishibashi.yukihide.mk@ehime-u.ac.jp

Organic solid-state luminescent materials have been attracting considerable interest in various application fields. In recent years, tuning of solid-state luminescence by controlling the mode of molecular packing, instead of the commonly used synthetic modification of molecules, has attracted great interest. Mutai and co-workers reported that 6-cyano-2-(2'-hydroxyphenyl) imidazo[1,2-*a*]pyridine (6-CN, Figure 1) showed three solid-state luminescence colors, yellow, orange, and red, by controlling its crystalline polymorphs[1]. There are remarkable differences in the molecular packing (herringbone-like, antiparallel dimer stacking and two slip-stacked, parallel stacking modes, with similar coplanar molecular conformation) by X-ray crystallographic analyses as shown in Figure 1, and all luminescence was assigned to the IPT* form. In this study, in order to clarify the excited-state intramolecular proton transfer (ESIPT) process in crystalline phase, the femtosecond transient absorption measurement was carried out under a microscope.

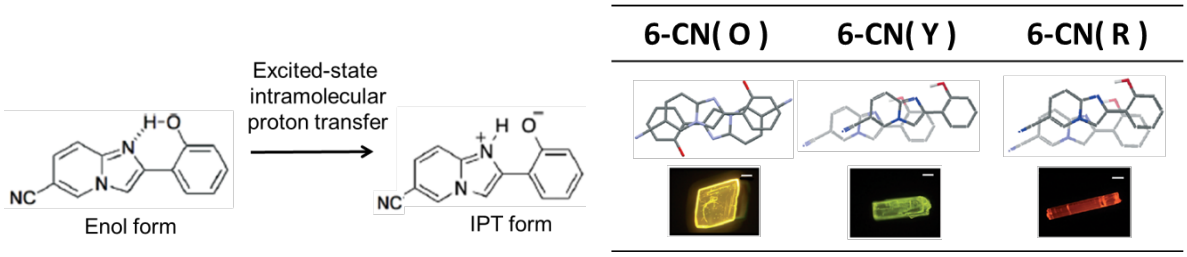

Figure 1. Molecular structures of the enol and intramolecular proton transferred (IPT) forms of 6-CN, and crystal structures and luminescent images of three crystals, 6-CN(Y), 6-CN(O) and 6-CN(R).

Sample preparation of three crystals (6-CN(O), 6-CN(Y) and 6-CN(R)) were described in ref. [1]. A home-built femtosecond transient absorption microspectrocopic system enabling measurement of transient absorption at sub-mirocmeter and femtosecomnd spatiotemporal resolutions was utilized[2]. Excitation wavelength was 400 nm, and probe wavelength was tuned from 450 to 850 nm. The diameter of the pump and probe pulse at the sample was 700 nm in fwhm, and the pulse duration was 350 fs in fwhm.

The conventional femtosecond transient absorption spectroscopy of 6-CN in THF solution reveals that the transient absorption around 500 nm, which was assigned to excited Enol (Enol*) form, appeared immediately after excitation, and its transient signal decayed with a time constant of 0.15 ps, and remained the positive one due to the IPT* form. We concluded that the ESIPT of 6-CN in THF took place with a time constant of 0.15 ps. On the other hand,

for crystalline 6-CN, because tightly focusing the white-light continuum into the sample crystal with 60x objective lens leads to the photo-damages, we selected the probe wavelength to be 500 nm, where the decay of Enol* form was observed. Figure 2 shows the time profile of the transient absorbance of crystalline 6-CN(O). The optical image of sample crystal is displayed in inset. The positive transient absorption appearing in the instrumental temporal response quickly decayed with a time constant of 1.0 ps, and remains long lifetime component. The 1.0-ps component was assigned to be ESIPT. The time constant of ESIPT for two crystals, 6-CN(Y) and 6-CN(R) were obtained to be 0.24, and 0.38 ps. The ESIPT in crystalline phase was slower than that in solution phase, and may depend on the crystal packing. At the presentation, we will discuss the correlation between ESIPT speed and different molecular packings of three crystals.

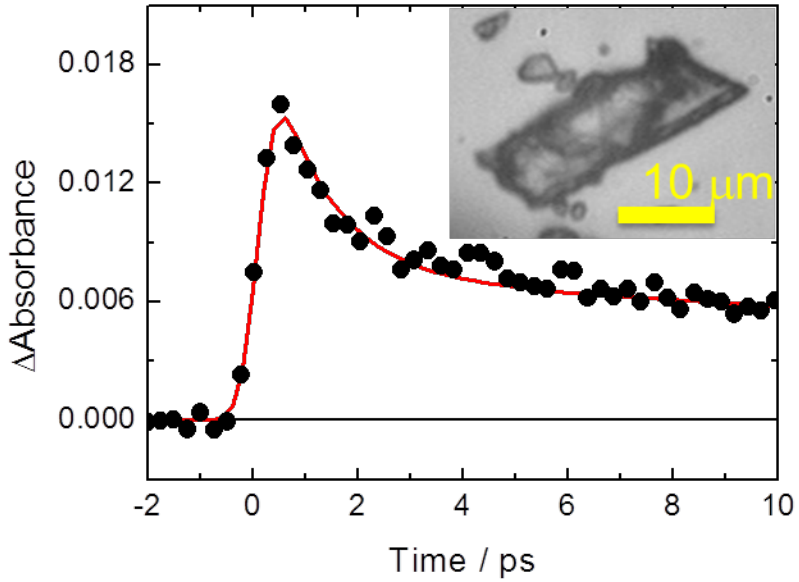

Figure 2. Time pro the time profile of the transient absorbance of 6-CN(O), monitored at 500 nm. Red solid line is the calculated curve with a triple exponential function taking the pulse duration of 350 fs fwhm into account. The optical image of sample crystalline 6-CN(O) is displayed in inset.

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References:

[1] T. Mutai, et al. *CrystEngComm.* **2014**, 16, 3890

[2] Y. Ishibashi, *Photochem. Photobiol. Sci.*, **2016**, 15, 1304.