Ultrafast photocontrol of proton-mediated organic ferroelectric cocrystal

T Umanodan¹, T Ishikawa¹, S Koshihara¹,², S Horiuchi³ and Y Okimoto¹
¹Department of Chemistry, Tokyo Institute of Technology, Meguro, Tokyo 152-8551, Japan
²Institute of Innovative Research (IIR), Tokyo Institute of Technology, Meguro, Tokyo 152-8551, Japan
³National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8565, Japan

E-mail: umanodan.t.aa@m.titech.ac.jp

Abstract. Photoirradiation effect in a ferroelectric cocrystal Hdppz-Hca is investigated in terms of time-resolved second harmonic (SH) generation measurements. By the photoexcitation with a visible pulse (530 nm) causing the intramolecular transition of Hca molecule, the SH intensity was suddenly suppressed by ≈30% on the time scale of picosecond, while the reflectivity scarcely changed. This result is discussed based on reversal of the polarized domain by the photoexcitation.

1. Introduction
Ferroelectricity is one of the most important topics in condensed matter physics on account of several applications, e.g., mechanical actuator, capacitor, memory etc [1]. In addition to conventional oxide systems, some organic ferroelectrics have been developed. The organic system possesses several advantages in the light of various practical applications, such as mechanical flexibility, printability and cost-effectiveness. Among them, proton-mediated supramolecular cocrystals composed of proton-donor and -acceptor (DA) molecules have been developed as novel organic ferroelectric materials. Among them, the ionic cocrystal Hdppz-Hca (dppz = 2,3-di(2pyridinyl)pyrazine, Hca = chloranilate, as depicted in Figure 1(a)) shows excellent ferroelectricity with high Curie temperature ($T_c = 402$ K) and a large spontaneous polarization [2].

In Hdppz-Hca cocrystal, protons mediating hydrogen bonds exhibit ordering and disordering transition similar to that observed in KH$_2$PO$_4$ (KDP) [3]. Below $T_c$, the proton takes one of the stable positions in the double welled potential showing long range ordering, which realizes the ferroelectricity breaking the inversion symmetry. Above $T_c$, by contrast, protons can thermally cross the potential barrier, which restores the inversion symmetry of the crystal. Thus, proton dynamics plays an essential role in the ferroelectric nature of Hdppz-Hca cocrystal.

In addition to the chemical approach, there have been reported some studies on photo-control of ferroelectric materials using femtosecond pulsed laser system [4–6]. In the previous study, we reported the photoinduced dynamics in terms of the time-resolved second harmonic (SH) spectroscopy which can detect the temporal changes in macroscopic ferroelectricity [7,8]. The photoexcitation with a visible light (530 nm) causing intra-molecular transition ($\pi$-$\pi^*$) of Hca molecule [9] suppressed the SH intensity.
on the time scale of nanosecond, suggesting the macroscopic disordering of protons through the π electron-proton coupling by light [7]. However, the initial state of this observed photoexcited dynamics has not been studied. Here, we investigate the femtosecond dynamics of Hdppz-Hca cocrystal and discuss the origin of the ultrafast photonic change of the ferroelectricity.

2. Method
A rectangular single crystal of Hdppz-Hca was grown by the diffusion method in acetone solution as reported in [2]. The orientation of the crystallographic axes was determined by X-ray diffraction and polarized reflection spectroscopy.

The transient relative changes in SH intensity (ΔI_{SH}/I_{SH}) and in reflectivity (ΔR/R) were obtained by a conventional pump-probe technique using a regenerated mode-locked amplified Ti:sapphire laser system with about 120 fs pulse width, a 1 kHz repetition rate, and approximately 1.55 eV photon energy. The amplified light was separated into two beams and we used one beam for pumping the crystal and the other as a probe pulse to detect the reflectance and SH light. To photoexcite the π-π transition of Hca molecule, we converted the fundamental pulse into signal and idler pulses using an optical parametric amplifier and then obtained 530 nm pulse by sum-frequency generation from the signal and the fundamental pulse. After irradiation with the visible pulse, we monitored the change in reflectivity at around 1.55 eV and the SH light of the 1.55 eV (i.e., about 3.1 eV) generated from the sample.

The SH signal was detected by a photomultiplier after the SH light went through high-pass filters and a grating-type monochromator to cut out the fundamental pulses, while the reflectance light was directly detected by a Si photodiode. The polarizations of the pump and probe pulse were along the c-axis (the polarization axis). All the measurements were done at room temperature.

![Figure 1](image_url)

**Figure 1.** (a) Structural formula of Hca and dpdz molecule. (b) Power dependence of SH intensity (I_{SH}) of Hdppz-Hca. The inset shows the polar plot of the observed I_{SH}.

3. Results and discussion

3.1. Bulk SH signal generated from Hdppz-Hca cocrystal
We first investigated the bulk SH signal generated from Hdppz-Hca cocrystal to evaluate the degree of χ(2) of the sample. In Figure 1(b), we show the incident pulse intensity dependence of the SH signal (I_{SH}) in Hdppz-Hca by filled circles. The polarization of the incident light is along the polarization axis (c-axis) and the SH measurements were done in the geometry of S-in and S-out configuration. The value of I_{SH} nonlinearly increases as the incident intensity increases, and is well fitted by the parabolic curve as shown by the solid line, directly indicating SH generation from the cocrystal.
For reference, in the inset of Figure 1(b), we show the polar plot of the intensity of the c-axis polarized SH pulse as a function of the incident angle. The angles of 90° and 270° in the inset denote that the polarization of the incident pulse corresponds to the c-axis (i.e., S-in configuration). The SH intensity is plotted along the radial direction and its relative scale is written in the inset. The SH shows remarkable angle dependence and the pattern is a four-leaf shape in the directions of the parallel and perpendicular to the c-axis. To estimate $\chi^{(2)}$ of the sample, we analyze the obtained angle dependence considering the crystal symmetry of Hdppz-Hca (monoclinic, space group $Cc$, point group $m$ [2]). Under these circumstances, the observed angle dependence can be described as

$$I_{SH} \propto (d_{31} \cos^2 \theta + d_{33} \sin^2 \theta + 2d_{35} \cos \theta \sin \theta)^2,$$

(1)

where $d_{31}, d_{33}$ and $d_{35}$ are components of the nonlinear optical coefficient tensor [10]. We performed a fitting analysis based on the equation (1) and the result is shown by the solid line in the inset of Figure 1(b). The values of the obtained components are $d_{31}/d_{33} \approx -0.99$, and $d_{35} \approx 0$.

3.2. Time resolved SHG spectroscopy

Next, we discuss the photoexcited state in Hdppz-Hca cocrystal with irradiation of the visible pulse. Figure 2 shows the delay time ($t_d$) dependence of the relative change in SH intensity ($\Delta I_{SH}/I_{SH}$). As depicted by the filled circles, the SH intensity suddenly decreases by $\approx 30\%$ just after photoexcitation and shows a fast recovery. To evaluate the relaxation dynamics of $\Delta I_{SH}/I_{SH}$, we fitted the profile by the following function:

$$f(t) = I_1 \exp \left( -\frac{t}{\tau_1} \right) + I_2 \exp \left( -\frac{t}{\tau_2} \right) + I_3,$$

(2)

The first and second terms denote exponential decays of the photoexcited state, and $I_1, I_2, \tau_1$ and $\tau_2$ amplitude of the change and the decay time of the first and second terms, respectively. The third term is a constant component which is constant when $t_d$ is positive ($t_d > 0$). We performed the fitting analysis considering the convolution between $f(t)$ and the response function of the present fs laser system. We plotted the fitting result based on equation (2) by the red line, which well fit the observed time profile. The obtained relaxation times are $\tau_1 \approx 0.15$ ps and $\tau_2 \approx 3.0$ ps.

For comparison, we display the time dependence of the relative change in reflectivity ($\Delta R/R$) by the solid line in Figure 2. Like the time profiles of $\Delta I_{SH}/I_{SH}$, $\Delta R/R$ also shows decaying by the relaxation of the $\pi^*$ electrons after the photoexcitation. However, the amplitude of the reduction was even smaller.
than that of $\Delta I_{SH}/I_{SH}$, which is quite similar to the case of the inorganic polar material, BiCoO$_3$ [6]. This suggests that the $\pi-\pi^*$ excitation causes some photoirradiation effects that largely change SH intensity but hardly modulates reflectivity in this system.

Here, let us discuss microscopic origins of the observed $\Delta I_{SH}/I_{SH}$. Very lately, Iwano et al. [11] noticed a croconic acid crystal that also shows the proton mediated ferroelectricity and theoretically revealed that the photoexcited $\pi^*$ electrons adiabatically act on the protons and cause resultant reversal of polarized domain. This domain reversal driven by the cooperative proton movement is an origin of the observed photonic suppression of the SH signal. It is worth noting that this is consistent with the observed small reflectance change by light, because reflectivity itself is not affected by polarized domain orientation of a crystal. Under the scenario, the two relaxation times can be assigned as time for the domain reversal ($\tau_1$) and relaxation from the depolarized domain ($\tau_2$).

The inset of Figure 2 shows excitation power dependence of $\Delta I_{SH}/I_{SH}$ just after the photoexcitation ($t_e \approx 0$ ps). The horizontal axis ($N_e$) denotes number of photons for the excitation per DA pair. (The data of $\Delta I_{SH}/I_{SH}$ displayed in Figure 2(a) has been obtained with $N_e \approx 0.15$). $\Delta I_{SH}/I_{SH}$ linearly increases with the photons, indicating that $\Delta I_{SH}/I_{SH}$ is almost proportional to the number of the injected photons. The maximum value of $|\Delta I_{SH}/I_{SH}|$ is about $\approx 30\%$ just after the photoexcitation and, in that case, the efficiency of the photonic change is estimated as $\approx 3.5$ DA pairs per one photon show the polarization reversals.

4. Summary
We investigated ultrafast nonlinear optical properties and the photoexcited state in a proton-mediated organic ferroelectric cocrystal, Hdppz-Hca. We irradiated the sample with 530 nm fs laser pulse to excite the intramolecular $\pi-\pi^*$ transition of Hca molecule. After the irradiation, the SH intensity abruptly decreased by $\approx 30\%$, implying reversal of the ferroelectric domains driven by the photoinduced proton transfer. This observed results can be viewed as a novel technique of controlling the ferroelectricity by light at room temperature.

Acknowledgments
The authors thank S. Naruse and Y. Iita for their technical assistance. This research was supported by JSPS KAKENHI Grant No. JP16K05397.

References
[1] Lines M E and Glass A M 2001 Principles and Applications of Ferroelectrics and Related Materials (New York: Oxford University Press)
[2] Horiuchi S, Kumai R and Tokura Y 2013 J. Am. Chem. Soc. 135 4492
[3] Blinc R 1960 J. Phys. Chem. Solids. 13 204
[4] Yamamoto K, Iwai S, Boyko S, Kashiwazaki A, Hiramatsu F, Okabe C, Nishi N and Yakushi K 2008 J. Phys. Soc. Jpn. 77 074709
[5] Miyamoto T, Yada H, Yamakawa H and Okamoto H 2013 Nat. Commun. 4 2586
[6] Okimoto Y, Naruse S, Fukaya R, Ishikawa T, Koshihara S, Oka K, Azuma M, Tanaka K and Hori H 2017 Phys. Rev. Applied 7 064016
[7] Umanodan T, Tanaka S, Naruse S, Ishikawa T, Onda K, Koshihara S, Horiuchi S and Okimoto Y 2015 J. Phys. Soc. Jpn. 84 073707
[8] Umanodan T, Kaneshima K, Takeuchi K, Ishii N, Itatani J, Hori H, Sanari Y, Tanaka K, Kanemitsu Y, Ishikawa T, Koshihara S, Horiuchi S and Okimoto Y 2019 J. Phys. Soc. Jpn. 88, 013705
[9] Kumai R, Horiuchi S, Okimoto Y and Tokura Y 2006 J. Chem. Phys. 125 084715
[10] Authier A 2013 International Tables for Crystallography vol D 2nd online ed, ed A Authier (Chester: International Union of Crystallography) part 1 pp 18
[11] Iwano K, Shimoi Y, Miyamoto T, Hata D, Sotome M, Kida N, Horiuchi S and Okamoto H 2017 Phys. Rev. Lett. 118 107404