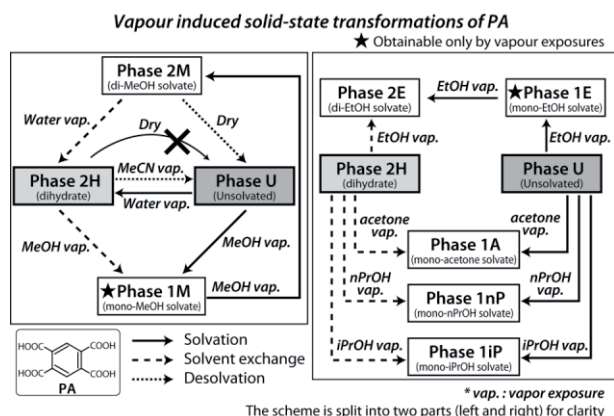


the difficulty to obtain the structural information of the resulted phase, which is mainly caused by the disintegration of the single crystalline form of the parent phase during the transformations. In such cases, the crystal structure determination from the powder X-ray diffraction data is clearly most powerful technique. Herein, we report several examples of the vapour induced crystalline transformations of organic materials investigated using *ab initio* powder diffraction analysis [1]- [3].

One of the examples is the vapour induced transformations of pyromellitic acid (PA : benzene-1,2,4,5-tetracarboxylic acid). As shown in the scheme (see below), PA exhibits a wide variety of the vapour induced transformations. Eight solvates and one unsolvated phase were found by vapour induced transformations. Single crystals of some solvates could be obtained by alternative crystallise pathway, however, some of the solvates (phase U, 1M, 1E and 1iP) could only be obtained by the vapour induced transformations. Thus, the crystal structures of these phases were determined from the powder X-ray diffraction data. The structural analyses revealed that phase 1M and 1E are the mono-methanol and mono-ethanol phases, respectively. Further vapour exposures on the mono-solvate phases gave di-solvate phases (2M and 2E) and these di-solvate phases were also obtained by recrystallisation from the solutions or from the slurry of PA in these solvents. Therefore, phase 1M and 1E are the metastable phases under the existence of the solvent vapour. These mono-solvate phases are obtainable only by the vapour exposure and it clearly shows that solvent vapour exposures are very useful technique to control pseudo-polymorphs.



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Keywords: *ab-initio* powder structure determination, solid-state transformation, pseudo-polymorphism

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Time-resolved structure analysis of photo-induced molecular dynamics in TTF-CA

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Recent progress of the time-resolved X-ray diffraction technique

enables to elucidate photo-induced dynamics in some crystals [1,2]. But diffraction intensities' change was mainly discussed and three-dimensional geometrical change have not been clarified in detail. In this study, we reveal the photo-induced molecular dynamics in a crystal with subnanosecond time resolution by single crystal X-ray structure analysis.

Time-resolved X-ray diffraction experiment was performed at PF-AR NW14A in KEK [3]. The co-crystal of tetrathiafulvalene and *p*-chloranil (TTF-CA; Figure), which shows neutral to ionic phase transition by laser irradiation at 90 K, [4] was selected as a target sample. Diffraction data sets were collected at 150, 500, 800, 1000 ps after laser excitation.

In photo-induced phase transition of TTF-CA, intensity reconstruction of symmetrically forbidden Bragg spots should be observed [2]. But in this study, significant intensity of these spots were not observed in all data sets. This indicated that phase transition was not fully progressed and recovered to the initial phase within the time-resolution of X-ray (pulse width = 150 ps) due to a weak excitation condition to minimize the damage by laser irradiation for prolonged data collection time. However, gradual movement of Cl and O in CA was observed by crystal structure and precise electron density analyses. These movements are assigned as thermal relaxation from the photo-induced ionic phase. Moreover, shortening of C=O in CA, which corresponds to enhancement of the neutral character of CA, was observed. These molecular dynamics indicates thermal relaxation from photo-induced ionic phase to initial phase go through the novel phase which has more strong neutral character than the initial phase. That novel phase was not generated by heating, so to speak, 'hidden' in the thermal process [1,5].

In sum, we succeeded to clarify the photo-induced dynamics of TTF-CA by time-resolved crystal structure analysis. In our excitation condition, the photo-induced 'hidden' phase was generated in subnanosecond time scale. This result will lead the progress of study about non-equilibrium dynamics in condensed matters.

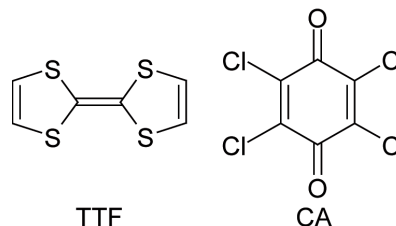


Figure. TTF and CA

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Keywords: time-resolved crystallography, photocystallography, non-equilibrium dynamics

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Reorientation of hydrogen bonds in clathrates of Dianin's compound and hydroquinone

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