Observation of anhydried and hydrated DAST crystals using multiplex fourth order Raman microscope

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1. Introduction
Fourth order Raman effect is one of the even order nonlinear optical effects, which is the phenomenon to observe even-order nonlinear susceptibility $\chi^{(2)}$ when polarization of molecular is distorted nonlinearly with a strong laser light. This effect has a selectivity of non-centrosymmetric structure because $\chi^{(2)}$ become zero with centrosymmetric structure. Fourth order Raman effect has been used for an interferential study because molecular in interface is non centrosymmetric.

We pay attention that solution is considered as centrosymmetry due to the isotropic nature, and apply to the monitoring of the crystallization process in solution using microscope without influence of solution. The purpose of this research is to prove the selectivity of the non-centrosymmetric structure in the fourth order Raman scattering microscopy. DAST is used as a sample, which is known to be changed non-centrosymmetric structure into centrosymmetric structure when this crystal is hydrated. The anhydried and hydrated DAST crystals are observed by CARS and fourth order Raman scattering microscope because CARS microscope is not dependent on symmetry of the crystal.

2. Preparation of anhydried and hydrated DAST crystal
Anhydried DAST crystal was recrystallized in desiccator using only dewatered ethanol solution, and hydrated DAST crystal using ethanol solution including 5% of water. The color and shape of anhydried DAST crystal were red and square, and that of hydrated DAST crystal were orange and needle. These shape and color were coincide with the those reported by Jazbinsek et al.[1].

3. Result
We observed both anhydrate and hydrated DAST crystals using multiplex fourth order Raman and CARS microscope we developed. Figure 1 shows bright field images of (a) anhydried DAST and (b) hydrated DAST, and Figure (c-f) shows fourth order Raman and CARS spectra of each DAST crystals. From both CARS spectra in Fig. (c) (d), we succeeded in observing three vibrational modes of DAST crystal at 1170, 1347, and 1577 cm$^{-1}$, which are in plane aromatic ring deformations, CH$_3$ umbrella deformation and C-C=C-C in plane stretching of stilbazolium, respectively. This is because CARS signal is not dependent on symmetry of crystal. Meanwhile, we observed fourth order Raman signal from only anhydried DAST crystal because fourth order Raman signal has selectivity in non-centrosymmetric structure.

Figure1. Bright field images of (a) anhydried DAST crystal and (b) hydrated DAST crystal. The blue point is shown as laser spot. (c - d) CARS spectrum and fourth order Raman spectrum of anhydried DAST crystal. The total laser power at sample and exposure time were 2.7 mW and 0.1 s, respectively. (e - f) CARS spectrum and Fourth order Raman spectrum of hydrated DAST. The total laser power at sample and exposure time were 2.9 mW and 0.1 s, respectively.

4. Conclusins
We succeeded in observing three Raman bands from CARS spectra of both DAST crystals, because CARS microscope do not depend on crystal symmetry. On the other hand, fourth order Raman signal is observed from only anhydried DAST crystal. From these results, it is revealed that we distinguished between non-centrosymmetry crystal and centrosymmetry crystal by using multiplex fourth order Raman scattering microscope. This will enable us to discriminate easily where non-centrosymmetry of is collapsed during nonlinear optical crystal growth in solution.

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References