

Reversible transformation and fluorescence modulation in polymorphic crystals of *n*-butylammonium 2-naphthalenesulfonate

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ABSTRACT

An organic salt composed of 2-naphthalenesulfonic acid and *n*-butylamine yielded polymorphic crystals: the block-like *Form A* and the plate-like *Form B*. The former was obtained from 1-propanol by slow cooling, while the latter was dominantly done from 1,4-dioxane, *m*-xylene and so on. Interestingly, the former was transformed to the latter by mechanical grinding and the reverse occurred by heat treatment at 120 °C. X-ray crystallographic studies clarified that the former has π - π interactions among naphthalene rings and hydrogen bonding network involving two oxygen atoms of sulfonate group, while the latter has CH- π interactions and the network involving three oxygen atoms. Luminescent properties were different in these crystals and continuously switched with the transformation.

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1. Introduction

Organic luminescence materials have been extensively investigated because of their potential application to photonic and optoelectronic devices [1–4]. In particular, dynamic tuning or switching system of solid-state luminescence has attracted much attention in recent years. One conventional approach to modify the solid-state luminescence is alteration of molecular structures by chemical reactions [5–7]. The other fascinating approach consists of modulation of molecular arrangements which may lead to the development of the dynamic tuning system of solid-state luminescence without some difficult chemical reactions.

So far, there have been only a few reports of the solid-state luminescence system which deals with the modulation of molecular arrangements, because it is hard to control the molecular organization in the solid-state. For example, Araki and co-workers reported switching of solid-state luminescence by controlling molecular arrangements between polymorphs through heat-mode interconversion [8]. Recently, we have reported organic salts of anthracene-2,6-disulfonic acid with primary amines as a static tunable fluorescence system in the solid-state [9–11]. The amines control this crystalline system to change arrangements of anthracene moieties and concomitant solid-state fluorescence properties. In order to enhance universality of this system, we

further employed 2-naphthalenesulfonic acid (2-NS) as a fluorophore. When we measured fluorescence spectra and powder X-ray diffraction (PXRD) of salt crystals of 2-NS with various amines, we accidentally found that emission color and PXRD patterns of the crystal with *n*-butylamine were dynamically changed by grinding. Here, we focus on the change of the organic salt in solid-state by mechanical grinding. It is reported that an organic salt composed of 2-naphthalenesulfonic acid with *n*-butylamine (Scheme 1) yields polymorphic crystals: the block crystal and the plate crystal.

2. Experimental

2.1. General methods

All chemicals and solvents were commercially available and used without any purification. 2-NS and *n*-butylamine were dissolved in ethanol with a 1:1 molar ratio, and the resulting solution was evaporated to yield colorless precipitates as raw salts. The precipitates were recrystallized from various organic solvents such as *m*-xylene, 1,4-dioxane, THF, 1-propanol, and 2-butanol. Such recrystallization afforded well-refined crystals suitable for single X-ray crystallographic analyses and photophysical measurements.

2.2. Crystal structure determinations

X-ray diffraction data were collected on a Rigaku R-AXIS RAPID diffractometer with a 2D area detector using graphite-monochromatized Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$). Lattice param-

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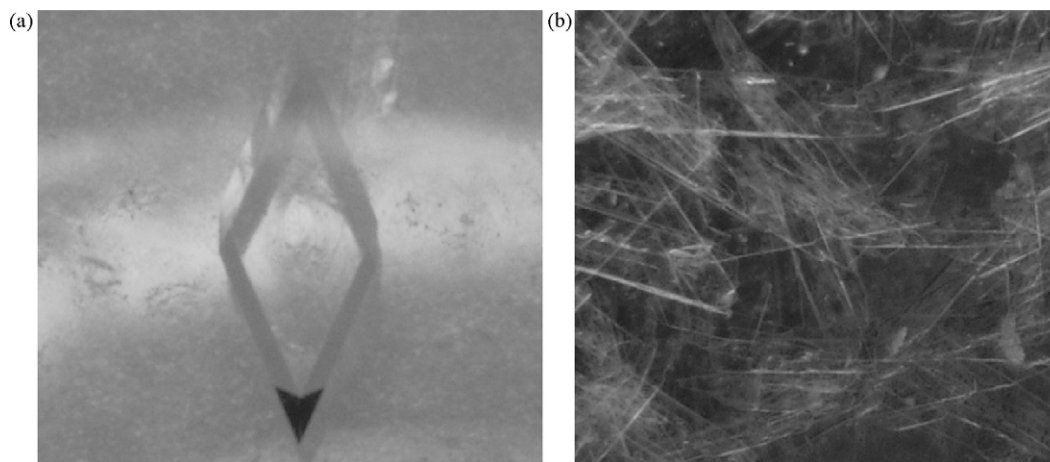
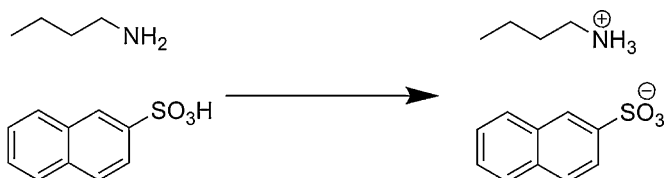


Fig. 1. Polymorphs: the block crystal (a); the plate crystal (b).



Scheme 1. Organic salt composed of naphthalenesulfonate and *n*-butylammonium.

eters were obtained by a least-squares analysis from reflections for thirty oscillation images. A direct method, SIR92, was used for structure solution. The structures were refined by a full matrix least-squares procedure with all the observed reflections based on F^2 . All non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were placed in idealized positions with isotropic displacement parameters relative to the connected non-hydrogen atoms, and not refined. All calculations were performed using the TEXSAN [14] crystallographic software package.

Powder X-ray diffraction (PXRD) patterns were measured by a Rigaku RINT-1100 using graphite-monochromatized Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$).

2.3. Solid-state fluorescence measurements

Fluorescence spectra measurements were performed by using a FP-6500 spectrofluorometer (JASCO) with an attachment for solid-state fluorescence measurement. The samples for the measurements in the solid-state were encapsulated in a cylindrical cell (JASCO). The excitation wavelength was 300 nm.

3. Results and discussion

3.1. Crystal structures: the block crystal and the plate crystal

The polymorphic crystals of the salt of 2-NS with *n*-butylamine were acquired by accident. Methanol and ethanol did not afford any crystals, but 1-propanol did only block crystals. Meanwhile, 2-butanol provided both block and plate crystals, whose photographs are shown in Fig. 1a and b, respectively. Further recrystallization from *m*-xylene, 1,4-dioxane and THF dominantly gave the plate crystals. These results indicate that the block crystals tend to be precipitated from polar solvents, while the plate ones from non-polar solvents. This polymorphism also depended on recrystallization conditions. For example, in the case of 2-butanol, slow crystallization under low concentration or slow cooling preferred the block crystals, while rapid crystallization under high concentration or quick cooling did the plate crystals.

X-ray crystallographic studies revealed that the block and plate crystals have different structures, *Form A* and *Form B*, with space groups, $P2_1/n$ and $P-1$, respectively [12]. Fig. 2a and b shows the corresponding unit cell structures with eight pairs of the binary components. It can be seen that *Form A* and *Form B* have different assembly and hydrogen bonding modes. Although sulfonate anions and ammonium cations seem to be held together by similar charge-assisted hydrogen bonds, their resultant two-dimensional networks are different as follows. One is that the network for the block crystal involves two oxygen atoms of the anions participated and one oxygen atom separated. The other is that the network for the plate crystal involves three oxygen atoms participated. Therefore, it is considered that the two-dimensional hydrogen bond network for the block is weaker than that for the plate.

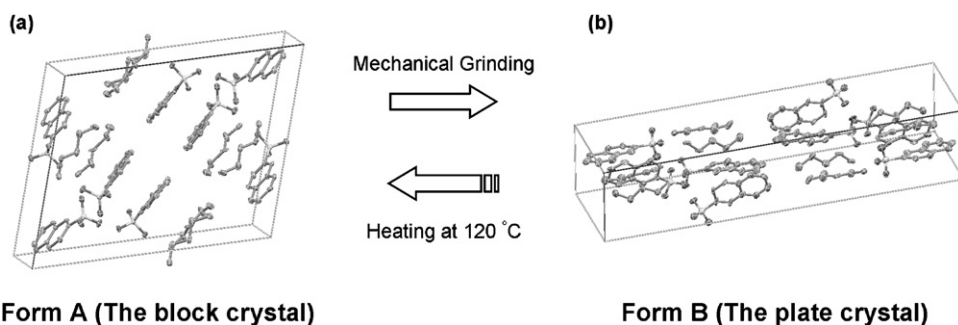


Fig. 2. The unit cell structure: *Form A* (the block crystal) (a); *Form B* (the plate crystal) (b).

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