

Crystal structures and fluorescence behaviors of 2-(2'-Hydroxyphenyl)benzothiazole derivatives

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Fluorescent chromic materials can show drastic change in the fluorescent property by the outer stimuli such as temperature, mechanical force, vapor adsorption, and light-irradiation etc., which have been attracted much attentions due to its great potentials for the application to memory and sensor devices.^{[1], [2]} As a unique fluorescent property, Excited State Intramolecular Proton Transfer (ESIPT) fluorescence has been examined from the viewpoint of remarkably large Stokes shift (10000 cm⁻¹) through the intramolecular hydrogen-bonding.^[3] Although a large number of ESIPT fluorophore has been synthesized, there are still no reports about fluorescent chromic behavior of ESIPT fluorophore by the outer stimuli in the solid state.

In this work, we focused on 2-(2'-hydroxyphenyl)benzothiazole (HBT), which has been known as a ESIPT fluorophore, and synthesized new sulfonic acid substituted HBT derivative (HSBT). The crystal structures and fluorescent properties of HSBT derivative were examined. Especially, the fluorescent chromic behavior of HSBT by the adsorption of pyridine vapor in the solid state was also evaluated.

From the crystal structural analysis, molecular structure of HSBT showed the zwitterionic structure, in which proton of sulfonic acid was transferred to nitrogen site of benzothiazole (Figure 1a). Since HSBT lacked the intramolecular hydrogen-bonding conformation, HSBT itself showed small magnitude of Stokes shift (6000 cm⁻¹) with fluorescence maximum at 445 nm in the absence of ESIPT (blue spectrum in Figure 2). Interestingly, after the adsorption of base molecules such as pyridine, HSBT showed the large Stokes shift (10000 cm⁻¹) with fluorescence maximum at 515 nm, which can be assigned to ESIPT fluorescence (green spectrum in Figure 2). From the crystal structural analysis, molecular structure of HSBT•(pyridine) showed the intramolecular hydrogen-bonding structure (Figure 1b). Therefore, dynamic conformational change from the zwitterionic to the intramolecular hydrogen-bonding structure should be critical for appearing ESIPT fluorescence after the pyridine adsorption. Detail of the molecular structures and fluorescent chromic behaviors of HSBT will be discussed.

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[2] Wenger, O. S Chem. Rev. (2013) 113, 3686-3733.

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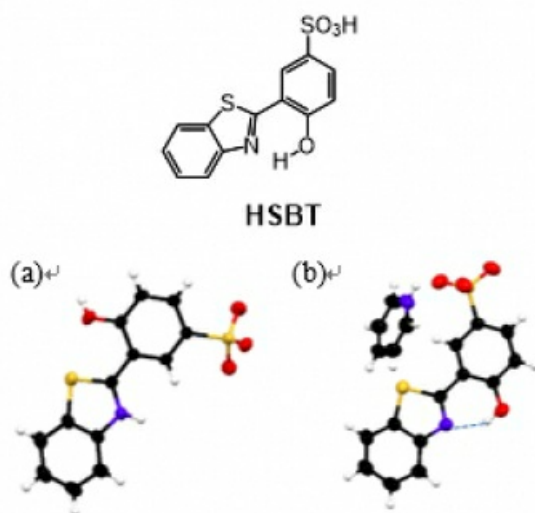


Figure 1. Molecular structure of (a) HSBT and (b) HSBT•(pyridine).

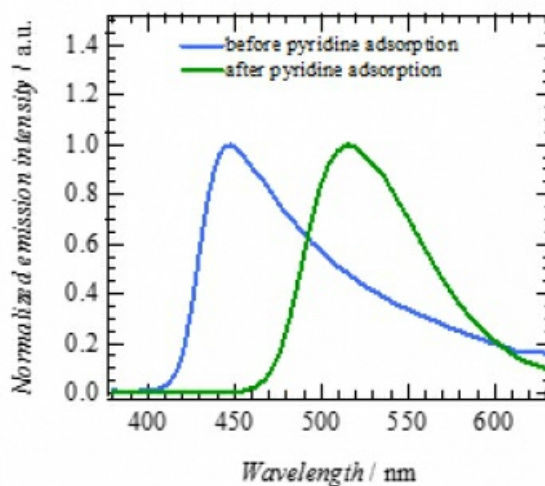


Figure 2. Solid state fluorescent spectra of HSBT and HSBT•(pyridine).

Keywords: [ESIPT](#), [Fluorescence](#), [Hydrogen-bonding](#)