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Mechanofluorochromism of 4-[bis(9,9-dimethylfluoren-2-yl)amino]benzaldehyde

Kei Mizuguchi, Hideyuki Nakano*

Department of Applied Chemistry, Muroran Institute of Technology, Mizumoto-cho, Muroran, Hokkaido 050-8585, Japan

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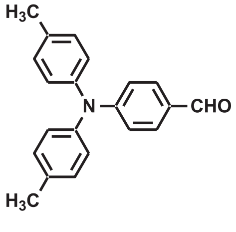
ABSTRACT

The titled compound exhibited mechanofluorochromism, the fluorescent color of the crystalline sample altering from light blue to greenish yellow by mechanical stress such as grinding. The state obtained by grinding the crystalline powder was more stable than that for the parent compound, 4-[bis(4-methylphenyl)amino]benzaldehyde, which we have previously reported. It was suggested that the change in emission color observed in the present study was due to morphological change from crystalline state to amorphous state by grinding and the state obtained by grinding was stabilized by increasing the glass-transition temperature of the material.

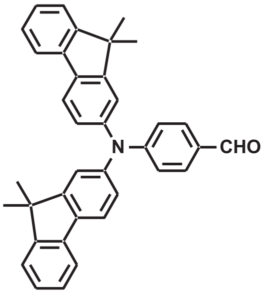
1. Introduction

Photoluminescent materials whose emitting properties are switchable by controlling the environments are of interest from both viewpoints of fundamental sciences and practical applications. Among them, materials that exhibit reversible change in fluorescent color induced by mechanical stress such as grinding, namely "mechanofluorochromism" or "piezofluorochromism", have recently been received attention. Several examples of both organometallic and pure organic materials have been reported to exhibit mechanofluorochromism [1–13] and the phenomena were generally believed to be due to change in intermolecular interactions caused by altering the molecular arrangements in the crystalline state by mechanical stress. However, only limited mechanofluorochromic materials have been reported and the precise details about the phenomena are not yet clear. Thus, it is of importance to find a variety of materials which exhibit such phenomenon and to investigate their fluorescent properties in various environments.

Very recently, we have reported that 4-[bis(4-methylphenyl)amino]benzaldehyde (BMABA) exhibited mechanofluorochromism caused by the formation of the amorphous state by grinding the crystalline sample [14]. However, the amorphous state of BMABA obtained by grinding the crystal sample was not so stable due to rapid re-crystallization and hence the fluorescent color returned to the original soon after grinding. It is expected that the increase in glass-transition temperature (*Tg*) of the material makes the amorphous state more stable to prevent crystallization at room temperature. Therefore, we focused to 4-[bis(9,9-dimethylfluoren-2-yl)amino]benzaldehyde (BFABA) whose *Tg* was expected to be higher than that of the parent compound, BMABA, in the present study.



BMABA



BFABA

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* Corresponding author. Tel.: +81 143 46 5753; fax: +81 6143 46 5701.
E-mail address: nakano@mmm.muroran-it.ac.jp (H. Nakano).

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2. Experimental

BFABA was prepared by the reported method [15]. Differential scanning calorimetry (DSC) was carried out by means of a Seiko DSC220C. Electronic absorption spectra of BFABA in solution and as the amorphous film obtained by spin-coating (3000 rpm) onto a transparent glass substrate from toluene solution were performed by means of a Hitachi U-3500 spectrophotometer. Fluorescent spectra in solutions and in solid states (crystalline sample obtained by re-crystallization from solution, amorphous glassy sample obtained by cooling the melt, and powder sample obtained by grinding the crystalline sample) sandwiched with two transparent glass substrates were measured with Hitachi F-4500 fluorescence spectrophotometer at 30 °C. Optical microscopy was performed with an Optiphot X2 (Nikon) microscope fitted with a TH-600PM hot stage (Linkam).

3. Results and discussion

3.1. Glass formation of BFABA

Before investigation of fluorescence properties, glass-forming property of BFABA was confirmed by differential scanning calorimetry (DSC). Fig. 1 shows DSC curves of BFABA. When the crystalline sample obtained by re-crystallization from solution was heated (Fig. 1a), an endothermic peak due to melting was observed at 188 °C. When the resulting melt sample was cooled on standing in air, the amorphous glass was readily formed. When the glass sample was again heated (Fig. 1b), well-defined glass transition phenomenon was observed around 86 °C. On further heating, no phase transition was observed upto the melting point. As intended, the *Tg* of BFABA was higher than that of BMABA (8 °C) [14].

3.2. Fluorescence of BFABA in solution

BFABA has already been synthesized as a starting material for preparing the sensitizers for use in dye-sensitized solar cell [15]. However, fluorescence of BFABA has not been well investigated so far. First of all, we examined fluorescent property of BFABA in solution. As shown in Fig. 2, BFABA was found to exhibit solvatofluorochromism, i.e., the fluorescence spectra were depending upon the kind of the solvent. The fluorescent maximum was shifted to longer wavelength with increasing polarity of the solvent ($E_T(30)$ value [16] was used as the parameter of solvent polarity here) while the absorption maxima was almost constant irrespective of the kinds of solvent. These results were quite similar to those of BMABA, and therefore, the excited state of BFABA was suggested to take a structure with twisted intramolecular charge transfer (TICT) as well as BMABA reported in our previous paper [14].

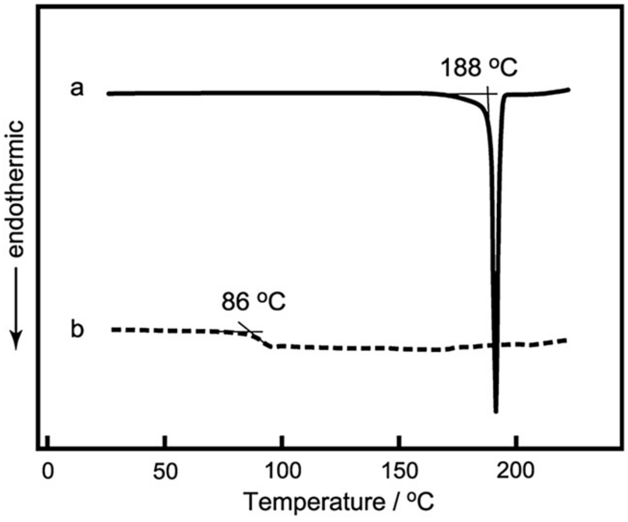

Fig. 1. DSC curves of BFABA. a: Crystalline sample. b: Glass sample obtained by cooling the melt.

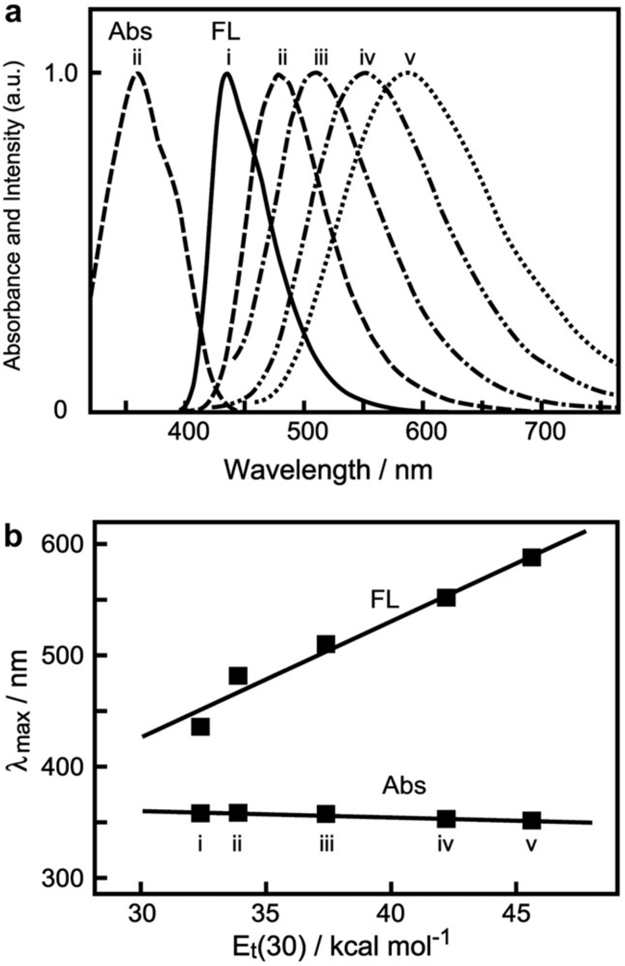

Fig. 2. a) Electronic absorption (Abs) and emission (FL) spectra of BFABA in various solvent. b) Plots of wavelengths of absorption (Abs) and emission (FL) maxima vs. $E_T(30)$ values. i: hexane, ii: toluene, iii: THF, iv: acetone, v: acetonitrile.

3.3. Mechanofluorochromism of BFABA

As well as BMABA, BFABA was found to exhibit mechanofluorochromism. The crystalline powder sample emitted in light blue color upon UV irradiation (Fig. 3a). By grinding the crystalline sample, the emission color was changed to greenish yellow, and therefore we could write the letters which could be recognized upon UV irradiation as shown in Fig. 3b. Whereas the amorphous sample obtained by grinding the crystal of BMABA re-crystallized soon, the state obtained by grinding the BFABA crystal was found to be quite stable at room temperature as intended. The letters were recognizable under UV irradiation for more than three weeks at room temperature. It was suggested that the change in emission color by grinding the crystalline sample was due to morphological change from crystalline state to amorphous state by grinding and the amorphous state was stabilized by increasing the *Tg* of the material. When the sample was heated above the *Tg*, the letters disappeared due to re-crystallization of the sample.