

Synthesis and Mechanofluorochromism of 4-[Bis(4-methylphenyl)amino]acetophenone

Kenji Okoshi and Hideyuki Nakano*

Department of Applied Chemistry, Muroran Institute of Technology,
27-1, Mizumoto-cho, Muroran, Hokkaido 050-8585, Japan
nakano@mmm.muroran-it.ac.jp

In order to create a new mechanofluorochromic material, title compound (BMAAP) was designed and synthesized. BMAAP was found to readily form an amorphous glass with a glass transition temperature of 9 °C and exhibit solvatofluorochromism in solution. BMAAP was also found to exhibit fluorescence both in crystalline state and in amorphous one and the fluorescence color in amorphous state was different from that in crystalline state. Finally, we have found that BMAAP exhibited mechanofluorochromism and the phenomenon was suggested to be caused by morphological change from crystalline state to amorphous one by mechanical grinding.

Keywords : mechanofluorochromism, solvatofluorochromism, amorphous molecular material, morphorogy

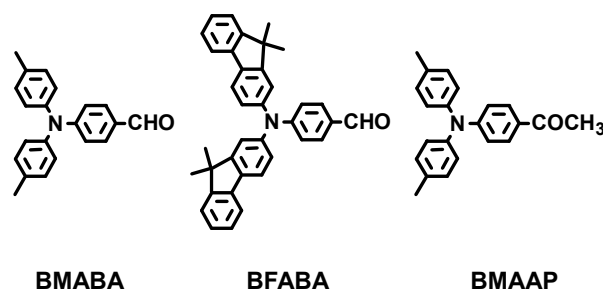
1. Introduction

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", have recently been received attention. Several examples of both organometallic and pure organic materials have been reported to exhibit mechanofluorochromism [1-13] and these 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.

We have been performing studies of the creation of amorphous molecular materials, namely low molecular-mass materials that readily form amorphous glasses above room temperature [14-18]. Recently, we have found that 4-di(4-methyl-

phenyl)amino]benzaldehyde (BMABA) and 4-[bis(9,9-dimethylfluoren-2-yl)amino]benzaldehyde (BFABA) exhibited fluorescence in both crystalline and amorphous states, and that their fluorescence spectra in amorphous states were different from those in crystalline states [19,20]. In addition, they exhibited mechanofluorochromism caused by morphological change from crystalline state to amorphous one by mechanical grinding. It was suggested that the materials with both abilities of glass formation and of large conformational change in excited state such as formation of twisted intramolecular charge transfer (TICT) structure become good candidates of new mechanofluorochromic materials.

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one (BMAAP) was designed synthesized and fluorescent properties including mechanofluorochromic property of BMAAP were investigated in the present study.

2. Experimental

2.1. Synthesis of BMAAP

A dichloromethane solution (50 mL) of aluminum chloride (4.0 g) and acetyl chloride (2.2 mL) was stirred for 30 min at 0 °C. 4,4'-Dimethyl-triphenylamine (6.8 g) was added to the solution and the solution was stirred for 20 h at room temperature. The resulting solution was washed with aqueous sodium hydroxide solution and then the solvent was removed under reduced pressure. The residue was chromatographed on silica-gel using chloroform followed by hexane as eluents. Crude yield of BMAAP: 6.5 g (82%). BMAAP was purified by recrystallization from hexane. MS (EI): m/z 315.1625 (M^+); 1H NMR (500 MHz, dioxane- d_8): δ (ppm) = 7.73 (d, 2H), 7.09 (d, 4H), 7.01 (d, 4H), 6.88 (d, 2H), 2.39 (s, 3H), 2.27 (s, 6H); ^{13}C NMR (500 MHz, dioxane- d_8): δ (ppm) = 20.77, 25.92, 119.60, 126.59, 130.36, 130.46, 130.84, 134.74, 145.08, 152.78, 195.33; EA: Found: H, 6.77; C, 83.82; N, 4.47 %.; Calcd for $C_{22}H_{21}NO$: H, 6.71; C, 83.78; N, 4.44 %.

2.2. Measurements and Apparatus

Differential scanning calorimetry (DSC) was carried out by means of a Seiko DSC220C. Electronic absorption spectra in solution were measured with Hitachi U-3500 spectrophotometer at 30 °C. Fluorescent spectra in solution and in solid states were measured with Hitachi F-4500 fluorescence spectrophotometer at 30 °C.

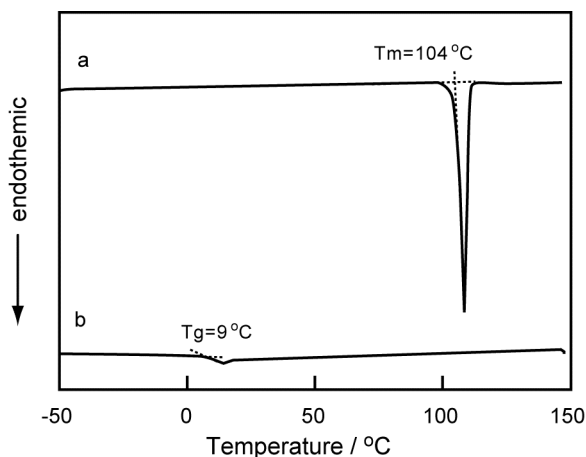


Fig. 1. DSC curves of BMAAP. a: recrystallized sample. b: amorphous glassy sample.

3. Results and discussion

3.1. Glass Formation of BMAAP

Before investigation of fluorescence properties, glass-forming property of BMAAP was confirmed by differential scanning calorimetry (DSC). Fig. 1 shows DSC curves of BMAAP. When the crystalline sample obtained by recrystallization from solution was heated (Fig. 1a), an endothermic peak due to melting was observed at 104 °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, well-defined glass transition phenomenon was observed around 9 °C (Fig. 1b). On further heating, no phase transition was observed upto the melting point. The glass transition temperature of BMAAP was similar to that of the parent compound BMABA (8 °C) [19].

3.2. Electronic Absorption and Fluorescence Spectra of BMAAP in Solutions

As shown in Fig. 2, BFABA was found to exhibit solvatofluorochromism, i.e., the fluores-

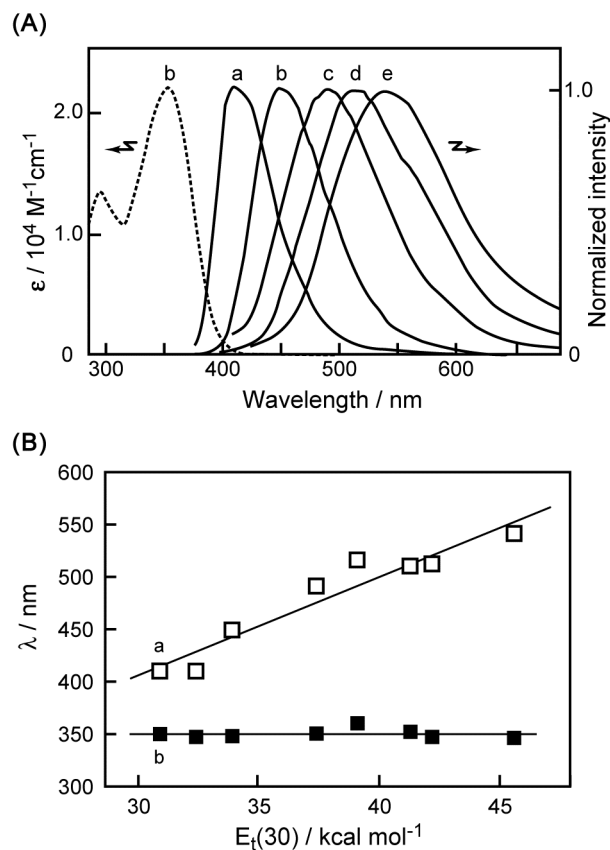


Fig. 2. (A) Electronic absorption and fluorescence spectra of BMAAP in various solvent. a: hexane. b: toluene. c: THF. d: acetone. e: acetonitrile. (B) Electronic absorption (b) and fluorescence (a) maxima of BMAAP vs. $E_T(30)$ value of the solvent.

cence spectra were depending upon the kind of solvent. The fluorescent maximum was shifted to longer wavelength with the increase in polarity of the solvent ($E_T(30)$ value [21] was used as the parameter of solvent polarity here). On the other hand, the absorption maxima were almost constant irrespective of the kinds of solvent. These results were quite similar to those of BMABA, and therefore, the excited state of BMAAP was suggested to take a structure with twisted intramolecular charge transfer (TICT) as well as BMABA reported in our previous paper [19].

3.3. Fluorescence Spectra of BMAAP in Condensed States

In the next stage, we have investigated the fluorescence spectra of BMAAP in condensed states. As shown in Fig. 3 and Table 1, the spectrum in amorphous state was found to be shifted to longer wavelength relative to that in crystalline one. The phenomenon was also quite similar to those observed for BMABA and BFABA. It was suggested that the difference in fluorescence spectra between in the crystalline state and in amorphous one was attributable to the difference in the ease of conformational change in these condensed states. That is, the excited molecule in the crystalline state cannot relax to the TICT structure so that the fluorescence emission occurred in shorter wavelength than that for the molecules in the amorphous state where the excited molecules can relax to the TICT structure.

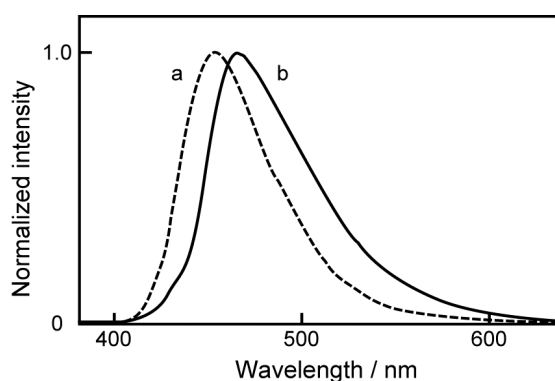


Fig. 3. Fluorescence spectra of BMAAP in solid states. a: crystalline sample. b: amorphous glassy sample.

Table 1. Fluorescence maxima in solid states

Material	crystalline state	amorphous state
BMAAP	453 nm	465 nm
BMABA	469 nm	491 nm

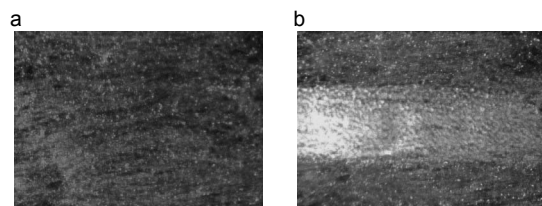


Fig. 4. Photographs of the sample powder of BMAAP upon UV irradiation. a: before grinding. b: just after grinding.

The difference of the fluorescence maxima between in crystalline state and in amorphous one was found to be 12 nm for BMAAP, being smaller than that for the parent material BMABA (23 nm). Steric hindrance of methyl group substituted at carbonyl carbon of the molecule might affect the ease of conformational change in the amorphous state.

3.4. Mechanofluorochromism of BMAAP

As well as BMABA and BFABA, BMAAP was found to exhibit mechanofluorochromism. The crystalline sample emitted in bluish violet upon UV irradiation (Fig. 4a) and the emission color was changed to light blue by grinding with a spatula (Fig. 4b). Furthermore, the resulting emission color was found to gradually recover to the original. These results were also quite similar to those for the parent material BMABA. Although the fluorescence spectrum just after grinding could not be measured because of too rapid recovery of the emission color, the mechanofluorochromism observed here could be understood by the formation of the amorphous state by grinding and following recrystallization.

4. Conclusion

A novel fluorescent material, BMAAP with both abilities of glass formation and of large conformational change in excited state was designed and synthesized. Like as the parent material BMABA, BMAAP exhibited mechanofluorochromism due to morphological change from crystalline state to amorphous one by grinding. Thus, the present study verified the concept of molecular design, that is, the materials that have both abilities of glass formation and of large conformational change in excited state become good candidates of new mechanofluorochromic materials.

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