Emission Properties of Hybrid Films of Benzylideneaniline-based Amorphous Molecular Materials with Organic Acids

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A novel emitting amorphous molecular material, 4-[bis(9,9-dimethylfluoren-2-yl)-amino]benzylideneaniline (BFBZA), was designed and synthesized. BFBZA provided moisture-sensitive hybrid film combined with benzoic acid (BA) that exhibited reversible change in emission color in response to moisture like as hybrid films of 4-[bis(4-methylphenylamino)benzylideneaniline with pentafluorobenzoic acid (PFBA) and BA. On the other hand, another hybrid film of BFBZA combined with PFBA did not exhibit such reversible change in emission color. The balance of acidity level of organic acid and basicity level of the emitting amorphous molecular materials was suggested to play a role for exhibiting reversible change in emission color.

Keywords: Emitting amorphous molecular material, Organic acid, Fluorescence, Basicity, Excited-state intermolecular proton transfer

1. Introduction

Stimuli-responsive organic solid materials that exhibit reversible changes in object colors and/or emission colors triggered by external stimuli are the subjects of interest from both viewpoints of fundamental sciences including elucidation of the mechanism of the switching functions and practical applications such as displays, memories, and visible sensors. The phenomena of reversible changes in object color and emission color triggered by chemical vapors such as moisture, volatile organic molecules, and gaseous acids and bases in the surroundings of the materials are referred to as "vapochromism" and "vapochromic emission", respectively. A variety of materials exhibiting such phenomena have been created in recent years, including organic crystals, polymer films, organometallic and coordination complexes that exhibit change in their object colors and/or emitting colors due to change in, e.g., interactions to volatile molecules, conformation of the molecules, and/or crystal structures upon exposure to vapors [1–7].

We have been studying the creation of stimuli-responsive emitting amorphous molecular materials [8–12]. For example, we have reported that spin-coated films of diarylaminobenzaldehyde-based emitting amorphous molecular materials exhibited vapochromic emission [11]. In addition to such materials with single component systems, we have recently been studying the creation of hybrid systems of amorphous molecular materials with other materials exhibiting smart functions [13–23]. We have reported that the hybrid films of aminoazobenzene-based amorphous molecular materials with organic acids exhibited drastic and reversible color changes in response to moisture [20]. Novel moisture-sensitive hybrid films composed of diarylaminobenzaldehyde-based emitting amorphous molecular materials with p-toluenesulfonic acid were found to exhibit OFF–ON switching of fluorescent in response to moisture [22]. Very recently, we have investigated the response of emission properties to moisture for hybrid films composed of 4-[bis(4-methylphenylamino)benzylideneaniline (BMBZA) with a variety of organic acids, and finally found that hybrid films of BMBZA with organic acids with appropriate acidities, benzoic acid (BA) and pentafluorobenzoic
acid (PFBA), exhibited the emission color changes in response to moisture [23].

In the present study, a novel amorphous molecular material, 4-[bis(9,9-dimethylfluoren-2-yl)amino]benzylideneaniline (BFBZA), has been designed and synthesized. It was found that a hybrid film of BFBZA with BA exhibited reversible change in emission color in response to moisture. Chemical structures of BMBZA and BFBZA are shown in Scheme 1.

2. Experimental
BA and PFBA were purchased commercially and used without further purification. BFBZA was prepared as follows. A mixture of 4-[bis(9,9-dimethylfluoren-2-yl)amino]benzaldehyde (200 mg, 0.40 mmol) and aniline (5 cc) was stirred for more than 6 hours at 120 °C. Resulting mixture was poured into the mixed solution of water and ethanol (1:1 v/v) and the precipitate was collected. The crude product was recrystallized from ethanol to give yellow needles. Yield: 160 mg (70 %); m.p. 198 °C; ¹H NMR (500 MHz, CDCl₃): δ (ppm) = 8.38 (s, 1H), 7.77 (d, 2H, J = 8.6 Hz), 7.66 (d, 2H, J = 7.2 Hz), 7.63 (d, 2H, J = 8.0 Hz), 7.39 (d, 2H, J = 7.1 Hz), 7.36 (d, 2H, J = 8.0 Hz), 7.32 (t, 2H, J = 8.1 Hz), 7.28 (d, 2H, J = 8.6 Hz), 7.26 (s, 2H), 7.23-7.18 (m, 5H), 7.14 (d, 2H, J = 6.0 Hz), 1.42 (s, 12H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 159.75, 155.34, 153.70, 152.59, 151.05, 146.60, 138.90, 135.29, 130.07, 129.73, 129.23, 127.17, 126.88, 125.63, 124.18, 122.65, 122.11, 121.01, 120.87, 119.70, 119.66, 47.00, 27.14.

Hybrid films were prepared by spin coating onto transparent glass substrates (1500 rpm at room temperature) from THF solutions (0.5 ml) including BFBZA with BA or PFBA with a molar ratio of 1:1. Electronic absorption and fluorescence spectra upon excitation with 400 nm under the dry atmosphere were measured at ambient conditions (less than 50%RH at ca. 25 °C). In order to measure the spectra under wet atmosphere, the hybrid film was put into the sealed transparent quartz cell with ca. 0.3 ml of water and kept for more than one hour before measurements. Electronic absorption and fluorescence spectroscopies were made by means of U-3500 spectrophotometer (HITACHI Ltd.) and FP-8300 spectrofluorometer (JASCO Co), respectively.

3. Results and discussion
BFBZA was synthesized by condensation reaction of 4-[bis(9,9-dimethylfluoren-2-yl)amino]-benzaldehyde and aniline. BFBZA was found to readily form amorphous glass by cooling the melt sample. A glass-transition temperature of BFBZA was 107 °C determined by differential scanning calorimetry.

Fig. 1 shows electronic absorption and fluorescence spectra of single BFBZA film. Electronic absorption band with a λₑₓ of 370 nm with a shoulder around 400 nm was observed, being in the similar wavelength region to the single BMBZA film [23]. With regard to fluorescence spectrum, the emission band of BFBZA film with a λₘₑₓ of ca. 500 nm was somewhat red-shifted relative to that of BMBZA film [23]. The result might be due to the fact that the π-conjugation system was more extended by introduction of fluorenyl groups.

As well as BMBZA–BA and BMBZA–PFBA films [23], a novel hybrid film of BFBZA–BA was found to exhibit reversible change in emission color in response to exhaled breath. The film emitted orange in color upon irradiation with UV lamp (365 nm) under ambient dry atmosphere. When we breathed onto the film, emission color changed immediately to yellowish green. When pausing the breath, the emission color of the film returned to

![Scheme 1. Chemical structures of BMBZA and BFBZA.](image-url)
the original. The phenomenon was due to moisture in the breath. Fig. 2 shows fluorescence spectra of the BFBZA–BA film. Under dry atmosphere, the emission band was observed around 630 nm (Fig. 2a), being considerably red-shifted from that observed for BFBZA (Fig. 1b). When the sample placed under wet atmosphere, the spectrum was drastically changed to be similar to that for the BFBZA film (Fig. 2b). These results were quite similar to those observed for BMBZA–BA film [23], and therefore, the emission bands in the shorter wavelength region around 500 nm and in the longer wavelength region around 600 nm were attributable to the emissions from excited states of BFBZA (BFBZA*) and its protonated iminium ion (BFBZA-H+*), respectively.

On the other hand, BFBZA–PFBA film did not show such change in fluorescent color. Orange emission was observed both under dry and wet atmospheres. As shown in Fig. 3, emission spectra of BFBZA–PFBA film under dry and wet atmospheres were almost similar to each other, the emission bands being in the longer wavelength region attributable to the fluorescence from BFBZA-H+*.

In order to gain further information, electronic absorption spectral changes of these films were investigated. With regard to BFBZA–BA film, the electronic absorption spectral change was quite similar to that observed for BMBZA–BA film [23]. As shown in Fig. 4, the spectrum under dry atmosphere was almost similar to that of the BFBZA (Fig. 1a) and did not change when the film placed under wet condition. The result suggested that BFBZA-H+ was scarcely produced in the hybrid film both under dry and wet atmospheres and the orange emission from BFBZA-H+* (Fig. 2a) took place through excited-state intermolecular proton transfer from BA to BFBZA* like as BMBZA–BA film [23].

With regard to BFBZA–PFBA film under dry atmosphere, two absorption bands were observed (Fig. 5a). The band in shorter wavelength region around 350 nm was attributable to the absorption of BFBZA since the band was almost similar to that of BFBZA (Fig. 1a). On the other hand, the broad band in longer wavelength region around 485 nm was suggested to be the protonated iminium ion, BFBZA-H+. The result was similar to that observed for BMBZA–PFBA film and suggested that protonation to BFBZA by PFBA took place in the film to produce BFBZA-H+. When the film was placed under wet atmosphere, the absorption band in the longer wavelength region relatively reduced due to moisture as shown in Fig. 5b. However, the band in the longer wavelength region remained whereas the corresponding band for BMBZA–PFBA film was completely disappeared under wet condition [23]. The facts suggested the incomplete deprotonation of BFBZA-H+ took place.
under wet atmosphere, resulting in no change in emission color of BFBZA–PFBA film. Since the emission band attributable to BFBZA* was well overlapped with the absorption band of BFBZA–H+, effective FRET from BFBZA* to BFBZA–H+ might take place to exhibit orange emission for BFBZA–PFBA film both under dry and wet atmospheres. Incomplete deprotonation in the present film might be due to larger basicity of BFBZA than BMBZA.

4. Conclusion
We have designed and synthesized of a novel molecule, BFBZA, and found that the hybrid amorphous film of BFBZA with BA exhibited reversible change in emission color in response to exhaled breath whereas BFBZA–PFBA film did not change the emission color. In our previous paper [21,23], acidity levels of organic acids were the important factor for providing hybrid films that exhibit reversible changes in object colors and emission colors in response to moisture. The present study suggested that the basicity level of emitting material was also the important factors, that is, the balance of acidity level of organic acid and basicity level of emitting amorphous molecular materials plays a role for exhibiting reversible change in emission color. Further studies are in progress.

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