Journal of Photopolymer Science and Technology
Volume 29, Number 3 (2016) 369－372 ©2016SPST

Aggregation Induced Emission of 4-[Bis(4-methylphenyl)amino]acetophenone

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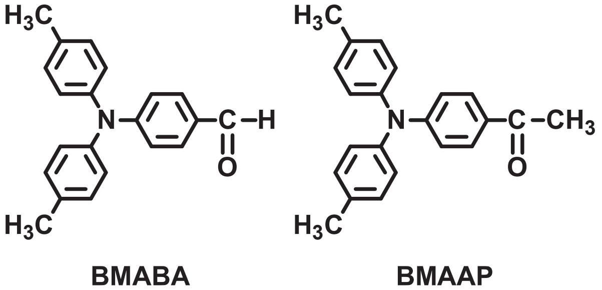
4-[Bis(4-methylphenyl)amino]acetophenone (BMAAP) exhibited solvatofluoro-chromism in solutions but the emission was quenched in ethanol. When a droplet of the ethanol solution of BMAAP was added into water, the resulting aqueous suspension was found to exhibit bright emission upon UV irradiation. It was found that the emission color of the resulting aqueous suspension was changed by vigorous stirring on heating. Morphological change of the aggregated particle of BMAAP plays a role for the emission color change.

Keywords: aggregation induced emission, emission color change, morphology, 4-[bis(4-methylphenyl)amino]acetophenone

1. Introduction

Fluorescence of organic materials is often quenched in their solid states, which is known as aggregation-caused quenching (ACQ). In contrast, organic fluorescent materials exhibiting high efficient luminescence in solid states have been investigated extensively for use in, e.g., emitting materials of organic electroluminescence devices and emitting field-effect transistors [1-6]. Recently, organic materials exhibiting aggregation induced emission (AIE) have attracted attentions, the phenomena being opposite to ACQ. That is, although such materials exhibit no or weak fluorescence in their solutions, the aggregated particles obtained by adding the solution into the poor solvent exhibit relatively intense fluorescence upon UV irradiation. A variety of AIE compounds have been created and their fluorescence properties have been investigated [7-13].

We have been studying the creation of photoactive functional organic low molecular-mass materials that readily form amorphous glasses, namely amorphous molecular materials [14-18], and in due course we have found that 4-[bis(4-methylphenyl)amin]benzaldehyde (BMABA) and 4-[bis(9,9-dimethylfluoren-2-yl)amino]benzaldehyde (BFABA) exhibit solvatofluorochromism, mechanofluorochromism, and AIE [19,20]. In addition, emission color of AIE particles of BMABA in the aqueous suspension was found to change by vigorous stirring on heating. In the present study, AIE property of 4-[bis(4-methylphenyl)amino]acetophenone (BMAAP) has been investigated.



BMABA **BMAAP**

2. Experimental

2.1. Material

BMAAP was prepared by the method

Received March 14, 2016
Accepted May 11, 2016

described in our previous paper [21].

2.2. Measurement and apparatus

Fluorescence spectra were measured by means of FP-8300 spectrofluorometer (JASCO Co). Fluorescence and polarizing microscopies were made with a OPTIPHOT X2 (Nikon) microscope.

3. Results and Discussion

As previously reported [21], BMAAP exhibit solvatofluorochromism as well as BMABA [19]. That is, the fluorescence spectra were depending upon the kind of solvent and the fluorescent maximum was shifted to longer wavelength with the increase in polarity of the solvent. We have also reported that the fluorescence spectrum of BMAAP in crystalline state was different from that in amorphous (supercooled liquid) state [21]. With regard to ethanol solution of BMAAP, no fluorescence was observed as shown in Fig. 1a, maybe due to high polarity of the solvent and/or intermolecular hydrogen bonding between BMAAP and solvent molecules. When a droplet of the ethanol solution of BMAAP was added into water, the resulting aqueous suspension was found to exhibit bright emission upon UV irradiation as shown in Fig. 1b.

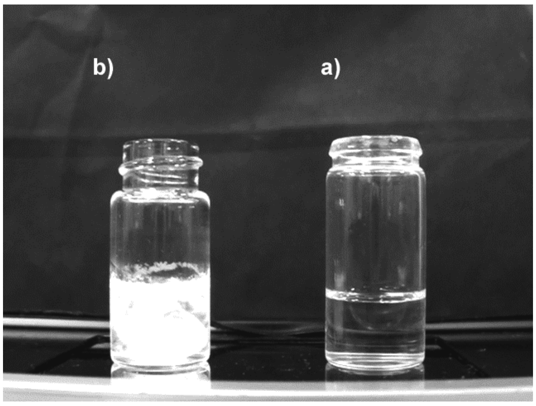


Fig. 1. Photograph of solutions upon irradiation with UV light (365 nm) from their bottoms. a) Ethanol solution of BMAAP. b) Aqueous suspension obtained by adding a droplet of ethanol solution of BMAAP into water.

When the ethanol solution of BMAAP was added to the mixed solvent of water and ethanol, the fluorescence intensity was found to depend upon the ratio of water and ethanol. As shown in Fig. 2, the fluorescence intensity increased with the increase in volume content of water like as other reported AIE materials including BMABA.

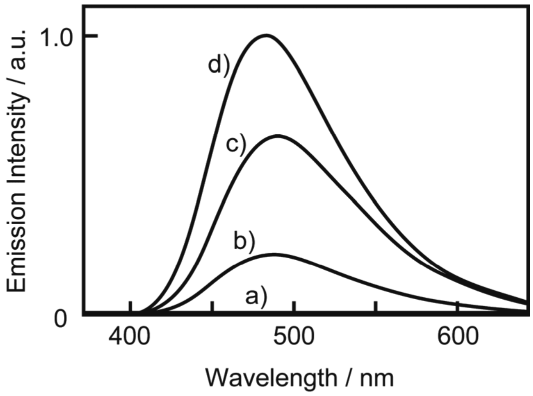


Fig. 2. Fluorescence spectra of BMAAP (1.1 x 10^{-4} mol dm^{-3}) in mixed solvents of water and ethanol. Volume ratios of water and ethanol were (a) 70:30, (b) 80:20, (c) 85:15 and (d) 90:10. Excitation wavelength: 350 nm.

Optical micrograph of the resulting aqueous suspensions showed that spherical particles with radii of several micrometers were produced. In addition, produced particles were found to exhibit light blue fluorescence upon UV irradiation without fluorescence at the periphery, confirmed by fluorescence microscopy as shown in Fig. 3. Thus, BMAAP was found to exhibit AIE. As well as BMABA, the present AIE was suggested to be due to exclusion of the intermolecular interaction between the BMAAP and solvent molecules by aggregation.

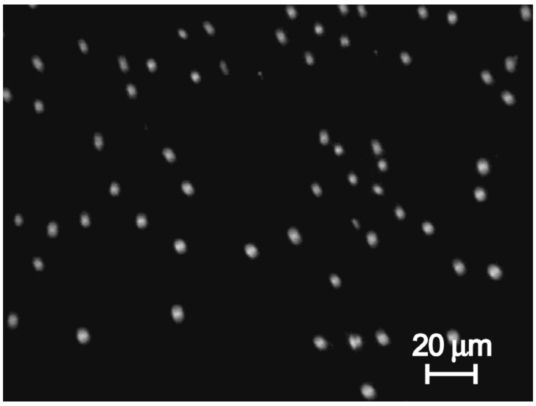


Fig. 3. Fluorescence microphotograph of the aqueous suspension of BMAAP upon irradiation with UV light (365 nm).

The fluorescence spectra of BMAAP as shown in Fig. 2 were found to be almost similar to that in the amorphous (supercooled liquid) state of BMAAP [21], suggesting that the resulting AIE particles of BMAAP were in amorphous state. It is conceivable that BMAAP molecules aggregated too rapid to allow molecular arrangement to crystallize when the ethanol solution was added into water due to nature of these materials to readily form amorphous glasses.

When the aqueous suspension was heated with vigorous stirring at ca. 80 °C for 30 min, the light blue fluorescence turned to bluish violet, the fluorescence spectrum being shifted to shorter wavelength as shown in Fig. 4. Since BMAAP in the crystalline state exhibited fluorescence with shorter wavelength than that in the amorphous state [21], the present result of fluorescence color change of BMAAP was suggested to be due to crystallization of the particles taking place in the aqueous suspension.

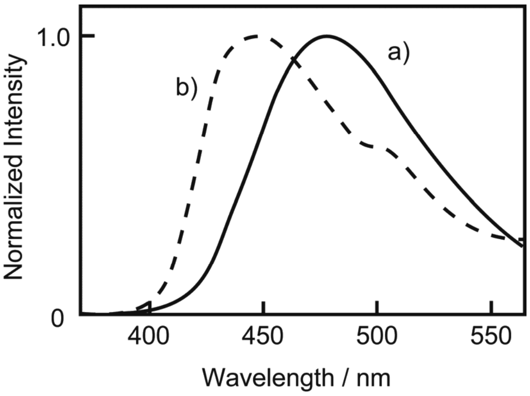


Fig. 4. Fluorescence spectra of the BMAAP particles in the aqueous suspension. a) as prepared. b) after the treatment with vigorous stirring on heating. Excitation wavelength: 350 nm.

Crystallization of BMAAP in the particles after such treatment could be confirmed by polarizing microscopy. As shown in Fig. 5, particles were observed to be bright through cross polarizers, indicating that the particles were optically anisotropic, whereas particles before the treatment were observed to be dark indicating the particles were in isotropic amorphous state.

We have already reported that BMABA also exhibited not only AIE but also emission color change of AIE particles after vigorous stirring on heating [20]. On the other hand, BFABA exhibited AIE but no emission color change by the treatment due to relatively high glass transition temperature (Tg) of BFABA (86 °C). Since the Tg of BMAAP (9 °C) is almost similar to that of BMABA (8 °C), morphological change of the BMAAP particles could be induced by the treatment as well as BMABA.

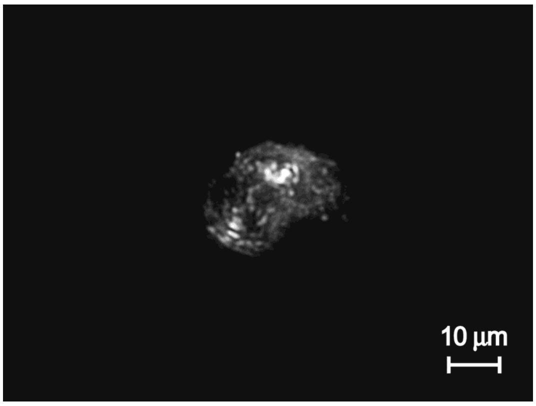


Fig. 5. Polarizing microphotograph of BMAAP particle in the aqueous suspension observed through cross polarizers after the treatment with vigorous stirring on heating.

4. Conclusion

As well as BMABA and BFABA, BMAAP was found to exhibit AIE when a droplet of the ethanol solution of BMAAP was added into water due to exclusion of the intermolecular interaction between the emitter and solvent molecules by aggregation. In addition, the emission color of the aggregated particles changed after the treatment of vigorous stirring on heating. The morphological change from amorphous to crystalline states was suggested to cause the emission color change. Emitting amorphous molecular materials that exhibit different emission color depending upon the morphology and that have relatively low Tg might exhibit emission color changeable AIE.

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