Vapochromic Fluorescence Observed for Emitting Amorphous Molecular Materials: Synthesis and Emitting Properties of 3-{4-[Bis(4-methylphenyl)amino]phenylcarbonyl}-6-{4-[bis(4-methylphenyl)amino]phenyl}-3,5-dimethyl-3,4-dihydro-2H-pyran

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In order to create novel vapochromic fluorescent amorphous molecular materials, title compound (BBMP) was synthesized and its emitting properties in solid states were investigated as well as in solution. It was found that BBMP exhibit solvatochromic fluorescence. BBMP was also found to exhibit fluorescence in solid states, the spectrum depending upon the morphology, and to exhibit mechanochromic fluorescence due to formation of glassy state by grinding the crystalline sample. And finally, BBMP film was found to exhibit vapochromic fluorescence. Two triphenylamine moieties with different structures in a BBMP molecule might play an important role for the difference between emitting properties in solution and in solid states.

Keywords: Emitting amorphous molecular material, Solvatochromic fluorescence, Mechanochromic fluorescence, Vapochromic fluorescence, Triphenylamine moiety

1. Introduction

Organic fluorescent materials exhibiting high efficient luminescence in solid states have been investigated extensively for use in, e.g., emitting materials of organic electroluminescent devices and emitting field-effect transistors [1-6]. In addition, organic materials that exhibit fluorescence switching triggered by external stimuli have also attracted attentions, including solvatochromic emitting materials [7], materials exhibiting aggregation induced emission (AIE) [8], mechanochromic luminescent materials [9], and so on. Fluorescence color change of the film upon exposure to different vapor molecules, namely vapochromic fluorescence, is also the subject of interest from both viewpoints of fundamental sciences and practical applications. Recently, polymers possessing riboflavin moieties [10] and coordination polymers with multinuclear copper cluster [11], for examples, have been reported to exhibit vapochromic luminescence.

We have been made a part of studies of the creation of organic low molecular-mass materials that readily form amorphous glasses, namely amorphous molecular materials [12-16], and in due course we have found that 4-[bis(4-methylphenyl)amino]benzaldehyde (BMABA) and 4-[bis(4-methylphenyl)amino]acetophenone (BMAAP) exhibited solvatochromic fluorescence, mechanochromic fluorescence [17,18], AIE [19,20], and vapochromic fluorescence [21].

In the present study, we have obtained a novel amorphous molecular materials with two triphenylamine moieties in a molecule, 3-{4-[bis(4-
methylphenyl)amino]phenylcarbonyl]-6-{4-[bis(4-
methylphenyl)amino]phenyl}-3,5-dimethyl-3,4-di-
hydro-2H-pyran (BBMP), and investigated its 
emitting properties in solution and in solid states in 
comparison with BMABA. As shown in Fig. 1, 
BBMP possesses two triphenylamine moieties A 
and B with slightly different \( \pi \)-conjugated systems 
from each other.

![Molecular structure of BBMP](image)

Fig. 1. Molecular structure of BBMP.

2. Experimental

2.1. Preparation of BBMP

4,4′-Dimethyltriphenylamine (10 g) and 
methacryloyl chloride (4.5 mL) were dissolved in 
dichloromethane (50 mL). The solution was 
stirred at room temperature and aluminum chloride 
(6.3 g) was gradually added into the solution. 
After the solution was refluxed for 3 h, further 
methacryloyl chloride (1.5 mL) and aluminum 
chloride (2.4 g) were added. The solution was 
refluxed for ca. 22 h and water (50 mL) was added 
to the solution at room temperature. The solution 
was washed with water and the solvent was 
removed under reduced pressure. The residue was 
chromatographed on silica gel using mixed solvent 
of toluene/hexane as eluent to obtain orange solid, 
which was purified by recrystallization from 
toluene/hexane. Yield: 730 mg (6%). \(^1\)H NMR 
(500 MHz, CDCl\(_3\)): \( \delta \) 7.24 (d, 2H), 7.06 (d, 4H), 7.04 
(d, 4H), 6.99 (d, 4H), 6.98 (d, 2H), 6.97 (d, 2H), 6.95 
(d, 4H), 6.93 (d, 2H), 2.97 (d, 1H), 2.80 (d, 1H), 2.31 
(s, 6H), 2.27 (d, 1H), 2.21 (d, 1H), 1.85 (s, 3H), 1.28 
(s, 3H) ppm; \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): 173.8, 
148.4, 147.1, 145.4, 145.0, 144.7, 133.1, 132.5, 
131.1, 130.1, 129.9, 129.3, 129.3, 125.7, 125.1, 
124.6, 122.3, 121.0, 108.3, 42.5, 41.3, 38.4, 23.2, 
20.9, 20.9, 18.6 ppm; HR-MS (EI) calcd. for 
C\(_{48}\)H\(_{46}\)O\(_2\)N\(_2\): 682.3548; found: 682.3564.

2.2. Measurement and apparatus

Differential scanning calorimetry (DSC) was 
made by means of DSC6220 (Seiko Instruments 
Inc). Electronic absorption and fluorescence 
spectra were measured by means of U-3200 
spectrophotometer (Hitachi) and FP-8300 
spectrofluorometer (JASCO), respectively. The 
sample amorphous film was prepared by spin-
coating method onto a transparent glass substrate 
dichloromethane solution. Vapochromic 
fluorescence were measured with the sealed cell in 
which the sample film and gauze impregnated with 
appropriate solvent existed together.

3. Results and discussion

3.1. Synthesis and glass formation of BBMP

We have found that the reaction of 4,4′-
dimethyltriphenylamine with methacryloyl chloride 
under Friedel-Crafts acylation condition to give 
BBMP by chance. Plausible mechanism to 
produce BBMP was shown in Scheme 1. After the 
production of the acylated compound, dimerization 
was thought to take place to give BBMP under 
acidic condition. Unfortunately, the 
reproducibility of the production of BBMP was 
quite poor maybe due to extreme reaction condition 
and/or trace impurities.

![Plausible reaction mechanism of BBMP](image)

Scheme 1. Plausible reaction mechanism of BBMP. Ar: 
4-[bis(4-methylphenyl)amino]phenyl.

BBMP was found to readily form an amorphous 
glass. Figure 2 shows DSC curves of BBMP. When the 
crystalline sample obtained by 
recrystallization from toluene/hexane was heated, 
the sample melted at 180 °C (Fig. 2a). When the 
melt sample was cooled on standing, an amorphous
glass formed readily. When the glassy sample was again heated, a glass transition phenomenon was clearly observed at 78 °C (Fig. 2b). The formation of amorphous glass was also confirmed by X-ray diffraction. We could easily obtain the amorphous film of BBMP by spin-coating method onto a transparent glass substrate.

3.2. Fluorescence of BBMP in solutions

As we have previously reported [17,18], BMABA and BMAAP exhibited solvatochromic fluorescence, their fluorescence spectra depending upon the type of solvent. Figure 3 shows fluorescence spectra of BBMP in various solutions. BBMP was also found to exhibit solvatochromic fluorescence. The fluorescence band seemed to shift to longer wavelength with increasing solvent polarity as well as BMABA and BMAAP.

Figure 4 shows the plots of wavelengths of electronic absorption and fluorescence maxima in solution vs. ET(30) values as a parameter of solvent polarity [7] for BMABA and BBMP. As previously reported [17], fluorescence maxima for BMABA solutions shifted to longer wavelength with increasing polarity of the solvent (Fig. 4c) while the absorption maxima seemed to be almost constant irrespective of the type of solvent (Fig. 4a). The electronic absorption and fluorescence spectra for BBMP solutions were found to shift to shorter wavelength region relative to the corresponding spectra for BMABA. For example, the fluorescence maximum for BBMP was ca. 60 nm shorted than that for BMABA in cyclohexane. As well as BMABA, fluorescence maxima for BBMP solutions shifted to longer wavelength with increasing polarity of the solvent (Fig. 4d) while the absorption maxima seemed to be almost constant irrespective of the type of solvent (Fig. 4b). However, the slope of the plots for fluorescence maxima depending upon solvent polarity for BBMP (Fig. 4d) was smaller than that for BMABA (Fig. 4c). Thus, the emitting properties of BMABA and BBMP were different from each other although π-conjugated system of the triphenylamine moiety B in the BBMP molecule shown in Fig. 1 is quite similar to that of BMAMA. The results suggested that the absorption and fluorescence properties of BBMP in solution were mainly affected from the moiety A.
3.3. Fluorescence of BBMP in solid states

In the next stage, fluorescence properties of BBMP were investigated in its solid states.

Figure 5 shows fluorescence spectra of BBMP in different solid states. Both crystalline sample obtained by recrystallization and glassy one obtained by cooling the melt exhibited fluorescence emission (Fig. 5a and Fig. 5b, respectively) but their fluorescence spectra were different from each other, the spectrum for the glassy sample being observed in longer wavelength region relative to that for the crystalline sample. The result was quite similar to those for BMABA and BMAAP [17,18], being suggested to be because the relaxation of excited molecule by conformational change was permitted in the free volume in the amorphous state whereas such relaxation by conformational change was restricted in the crystalline state. It is noted that the fluorescence maximum for BBMP glass was observed at 470 nm, being similar to those for BMABA and BMAAP (490 and 470 nm, respectively) whereas the fluorescence spectrum of BBMP solution was observed in considerably shorter wavelength region relative to those of BMABA and BMAAP described above. The triphenylamine moiety B in BBMP might contribute the emitting property in the amorphous state.

Fig. 5. Fluorescence spectra of the BBMP in solid states.

a) Recrystallized sample.  b) Amorphous glassy sample obtained by cooling the melt.  c) Powder obtained by grinding the crystalline sample.  d) Powder obtained by immersing the ground sample to acetone. Excitation wavelength: 340 nm.

It was found that the fluorescence spectrum for the crystalline state shifted to longer wavelength region by grinding the crystal (Fig. 5c). After immersing the ground sample to acetone, the spectrum recovered to the original (Fig. 5d). Thus, the BBMP crystal exhibited mechanochromic luminescence as well as BMABA and BMAAP [17,18]. Since the X-ray diffraction peaks of the crystalline sample disappeared after grinding, the shift of the fluorescence spectrum by grinding was suggested to be due to formation of amorphous state by grinding although the spectrum for ground sample did not shift enough to reach the spectrum for glassy sample obtained by cooling the melt (Fig. 5b).

3.4. Vapochromic fluorescence of BBMP film

BBMP film prepared onto a glass substrate by spin-coating was finally found to exhibit vapochromic fluorescence. As shown in Fig. 6a, the fluorescence spectrum at ambient atmosphere was almost similar to that for glassy sample of BBMP obtained by cooling the melt, suggesting that the film was in amorphous state. When the film was exposure to cyclohexane, THF, and acetonitrile vapors, the fluorescence spectrum shifted depending upon the type of vapors (Figs. 6b-d). After the film was moved to ambient atmosphere without solvent vapors, the spectrum recovered to original immediately.

Fig. 6. Fluorescence spectra of BBMP film.  (a) At ambient atmosphere.  (b-d) Upon exposure to (b) cyclohexane, (c) THF, and (d) acetonitrile vapors. Excitation wavelength: 340 nm.

Figure 7 shows the plots of wavelengths of fluorescence maxima vs. $E_{r}(30)$ values of the exposed solvents. For both BMABA and BBMP films, the fluorescence maxima shifted to longer wavelength with increasing polarity of the exposed solvent vapor. As reported in our previous paper [21], the spectrum of the BMABA film upon exposure to the vapor of the organic solvent was almost similar to that in the corresponding solution,
that is the slope of the plots shown in Fig. 4c was similar to that shown in Fig. 7a, suggesting that the solvent molecules penetrated in the film and interacted with fluorescent molecules when the film was exposed to the solvent vapor. Interestingly, the slope of the plots for BBMP film shown in Fig. 7b was found to be larger than that for BBMP solution shown in Fig. 4d. As well as the emitting property of amorphous glass described above, the vapochromic fluorescence of BBMP might be affected by the triphenylamine moiety B with similar structure of BMABA molecule.

4. Conclusion
We have created a new emitting amorphous molecular material, BBMP, with two different triphenylamine moieties in a molecule. As well as BMABA and BMAAP, BBMP was found to exhibit solvatochromic, mechanochromatic, and vapochromic fluorescence. With regard to fluorescence property in solution, the triphenylamine moiety A was suggested to play a main role. On the other hand, the triphenylamine moiety B was also suggested to contribute to the emitting properties in amorphous states.

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References
1. Y. Shirota, *J. Mater. Chem.*, 10 (2000) 1.
2. U. Mitschke and P. Baueerle, *J. Mater. Chem.*, 10 (2000) 1471.
3. Y. Guo, G. Yu, and Y. Liu, *Adv. Mater.*, 22, (2010) 4427.
4. J. H. Kim, A. Watanabe, J. W. Chung, Y. Jung, B.-K. An, H. Tada, and S. Y. Park, *J. Mater. Chem.*, 20 (2010) 1062.
5. L. Xiao, Z. Chen, B. Qu, J. Luo, S. Kong, Q. Gong, and J. Kido, *Adv. Mater.*, 23 (2011) 926.
6. S. Z. Bisri, T. Takenobu, K. Sawabe, S. Tsuda, Y. Yomogida, T. Yamao, S. Hotta, C. Adachi, and Y. Iwasa, *Adv. Mater.*, 23 (2011) 2753.
7. C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, Weinheim: Wiley-VCH; 2003.
8. Y. Hong, J. W. Y. Lam, and B. Z. Tang, *Chem. Soc. Rev.*, 40 (2011) 5361.
9. Z. Chi, X. Zhang, B. Xu, X. Zhou, C. Ma, Y. Zhang, S. Liu, and J. Xu, *Chem. Soc. Rev.*, 41 (2012) 3878.
10. H. Iida, S. Iwahana, T. Mizoguchi, and E. Yashima, *J. Am. Chem. Soc.*, 134 (2012) 15103.
11. T. Hayashi, A. Kobayashi, H. Ohara, M. Yoshida, T. Matsumoto, H.-C. Chang, and M. Kato, *Inorg. Chem.*, 54 (2015) 8905.
12. W. Ishikawa, H. Inada, H. Nakano, and Y. Shirota, *Chem. Lett.*, 20 (1991) 1731.
13. H. Inada, K. Ohnishi, S. Nomura, A. Higuchi, H. Nakano, and Y. Shirota, *J. Mater. Chem.*, 4 (1994) 171.
14. E. Ueta, H. Nakano, and Y. Shirota, *Chem. Lett.*, 23 (1994) 2397.
15. H. Utsumi, D. Nagahama, H. Nakano, and Y. Shirota, *J. Mater. Chem.*, 12 (2002) 2612.
16. T. Tanino, S. Yoshikawa, T. Ujike, D. Nagahama, K. Moriwaki, T. Takahashi, Y. Kotani, H. Nakano, and Y. Shirota, *J. Mater. Chem.*, 17 (2007) 4953.
17. K. Mizuguchi, H. Kageyama, and H. Nakano, *Mater. Lett.*, 65 (2011) 2658.
18. K. Okoshi and H. Nakano, *J. Photopolym. Sci. Technol.*, 27 (2014) 535.
19. M. Kurita, M. Momma, K. Mizuguchi, and H. Nakano, *ChemPhysChem*, 14 (2013) 3898.
20. K. Shishido and H. Nakano, *J. Photopolym. Sci. Technol.*, 29 (2016) 369.
21. K. Ogura and H. Nakano, *Kobunshi Ronbunshu*, in press.