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White light emission from a single component system: remarkable concentration effects on the fluorescence of 1,3-diaroylmethanatoboron difluoride

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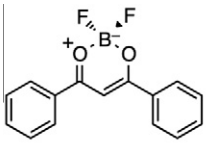
ABSTRACT

Concentration effects on the fluorescence (FL) emission of 1,3-dibenzoylmethanatoboron difluoride (**1aBF$_2$**) and its diisopropyl derivative (**1bBF$_2$**) in KBr and CH_2Cl_2 were investigated. Powder samples of **1aBF$_2$** and **1bBF$_2$** in KBr exhibit yellow and white FL emissions, respectively, whose intensities and wavelengths are not significantly affected by concentration. In contrast, remarkable concentration effects on FL properties of these compounds in CH_2Cl_2 solutions were observed. Increases in the concentrations of **1aBF$_2$** and **1bBF$_2$** from 1×10^{-7} to ca. 2×10^{-1} M lead to dramatic changes in the FL colors from blue (398 and 411 nm, respectively) to yellow (548 and 558 nm) via white. Careful analysis of the FL spectra, involving lifetime determinations and wave deconvolutions, reveals that emissions from **1BF$_2$** involve two FL domains, corresponding to an excited monomer and an excimer, and that concentration increases promote a continuous change from the former to the latter major FL domain. Thus, white FL of **1aBF$_2$** and **1bBF$_2$** is achieved by modulation of the dual FL of the excited monomer (blue) and excimer (yellow). These findings indicate that 1,3-diaroylmethanatoboron difluoride (**1BF$_2$**) represents a new white emitting material that has advantageous features which arise from the fact that it is an easily prepared, low molecular weight, single component system not containing a heavy metal atom.

Introduction

White fluorescent organic materials have attracted great attention in connection with their application to white organic light-emitting diodes (WOLEDs).[1] To obtain white emission, with the Commission Internationale de l'Eclairage (CIE) coordinate $(x, y) = (0.33, 0.33)$, mixing three primary colors (blue, green, and red) or two complementary colors (such as blue and yellow) is necessary. Thus, most of the materials employed for white emission consist of multiple light-emitting components.[2,3] However, some problems exist with systems of this type, such as the need for a complicated fabrication process of the emitting device and a change or degradation of the white color caused by the low stability of fluorescent compounds. Clearly, use of a single-component, white-emitting material would be an ideal solution to this problem.[4–6] However, examples of materials of this type are limited to complexes containing heavy metal atoms or organic compounds with highly π-conjugated skeletons.[6,7]

1,3-Dibenzoylmethanatoboron difluoride (**1aBF$_2$**, Chart 1) and its analogues exhibit intense fluorescence (FL) emissions in spite of their small molecular size and lack of heavy metal atoms.[8–13] The parent **1aBF$_2$** was synthesized for the first time by Morgan and Tunstall in 1924.[14] A report on FL property in $CHCl_3$ by Karasev and Korotkikh[15] opened up a field of various emission ability of **1aBF$_2$**, including FL in the crystalline states[16,17] and films,[18] FL induced by two-photon absorption,[19] etc. Motivated by these historical works, we have prepared a variety of 4,4′-disubstituted derivatives of **1aBF$_2$** and studied their FL properties in KBr and CH_2Cl_2. In the effort described below, we observed that CH_2Cl_2 solutions of the parent substance, **1aBF$_2$**, and its diisopropyl derivative, 1,3-bis(4-isopropylbenzoyl)methanatoboron difluoride (**1bBF$_2$**, Chart 1), display remarkable concentration effects on their


1aBF$_2$

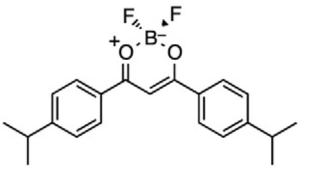

1bBF$_2$

Chart 1. Molecular structures of 1,3-dibenzoylmethanatoboron difluoride (**1aBF$_2$**) and its diisopropyl derivative (**1bBF$_2$**).

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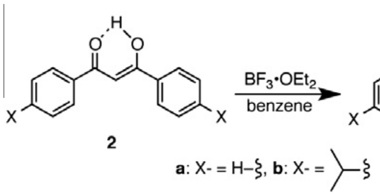

Scheme 1. Synthesis of **$1aBF_2$** and **$1bBF_2$**.

FL wavelengths. Although no significant difference in FL between **$1aBF_2$** and **$1bBF_2$** exists, the FL colors of these substances undergo dramatic changes from blue at low concentrations to yellow at high concentrations, as a consequence of changes from emitting excited monomers to excimers. Importantly, white emission from these substances can be achieved by adjusting their concentrations to bring about a suitable ratio of blue and yellow FL.

Synthesis of $1aBF_2$ and $1bBF_2$

The parent substance **$1aBF_2$** and the diisopropyl derivative **$1bBF_2$** were synthesized by treatment of the corresponding diaroylmethanes **2a** and **2b** with the boron trifluoride diethyl ether complex, (Scheme 1).[18–20] Preparation of **2b** was accomplished by use of a condensation reaction of methyl 4-isopropylbenzoate with 4′-isopropylacetophenone, while **2a** is commercially available.

Diffuse reflection and FL properties in KBr

The diffuse reflection and FL properties of the parent **$1aBF_2$** and the diisopropyl derivative **$1bBF_2$** in KBr are summarized in Table 1.[21] The diffuse reflection maxima of these substances in KBr powders ($\lambda_{DR,P}$) occur at ca. 400 nm, indicating that the isopropyl substituents do not alter this property.

In contrast, the FL properties of **$1aBF_2$** and **$1bBF_2$** are different. The sharp FL band of **$1aBF_2$** in KBr powder ($\lambda_{FL,P}$) appears at around 545 nm while that of **$1bBF_2$** is evidently broadened with some peaks at 439, 474, and 527 nm (Table 1 and Fig. 1). Moreover, the FL quantum yield ($\Phi_{FL,P}$) of **$1bBF_2$** was found to be 0.13, a value that is much higher than that of **$1aBF_2$** (0.03). Interestingly, the FL color of **$1bBF_2$** in KBr is almost white, with a CIE coordinate (x, y) = (0.29, 0.38), while that of **$1aBF_2$** is yellow with a coordinate (0.35, 0.44) (Fig. 2). Therefore, the incorporation of isopropyl groups at the 4-position of two phenyl groups in **$1aBF_2$** brings about a change of FL color of the powder from yellow to white and an improvement of $\Phi_{FL,P}$.

Table 1
Diffuse reflection, absorption, and FL properties of **$1aBF_2$** and **$1bBF_2$**

Sub.	Diffuse reflection and absorption				FL	
	KBr		CH_2Cl_2		KBr	CH_2Cl_2
	$\lambda_{DR,P}$[a] (nm)	K–M	$\lambda_{AB,S}$[b] (nm)	log ε	$\lambda_{FL,P}$[a] (nm)	$\lambda_{FL,S}$[b] (nm)
$1aBF_2$	400	0.05	365 380	4.37 4.43	545	398
$1bBF_2$	398	0.16	380	4.84	439 474 527	411

[a] $\lambda_{DR,P}$ and $\lambda_{FL,P}$ are wavelengths for the diffuse reflection maxima and the FL maxima, respectively, for the mixtures of **$1BF_2$** (0.2 μmol) and KBr (500 mg) powdered with ballmill at 50 Hz for 15 min.

[b] $\lambda_{AB,S}$ and $\lambda_{FL,S}$ are wavelengths for the absorption maxima and the FL maxima, respectively, for **$1BF_2$** in CH_2Cl_2 when their absorbance values are ca. 0.3 at the wavelength indicated (ca. 0.5×10^{-5} M).

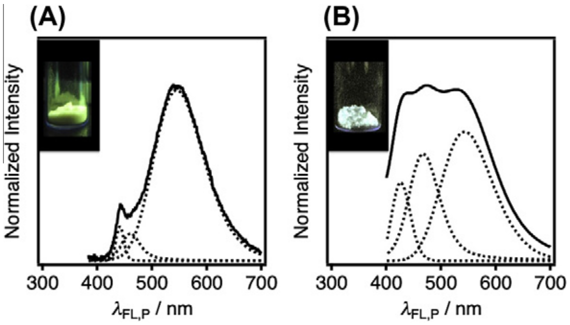

Figure 1. Observed FL spectra (solid curves) of **$1aBF_2$** (A) and **$1bBF_2$** (B) in KBr at 294 K with deconvoluted spectra (broken curves) and photographs of measuring samples (insets). λ_{EX} = 365 nm.

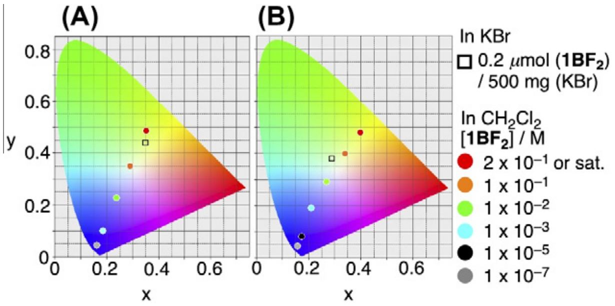

Figure 2. The CIE chromaticity diagrams for FL of **$1aBF_2$** (A) and **$1bBF_2$** (B) in KBr (squares) and CH_2Cl_2 (circles) at 294 K. λ_{EX} = 365 nm.

Wave deconvolutions of the FL spectra using a Gaussian function were carried out to determine the origin of differences between the FL properties of **$1aBF_2$** and **$1bBF_2$** in KBr. In both cases, the original FL spectra were deconvoluted to generate three component spectra (Fig. 1), suggesting that FL of **$1aBF_2$** and **$1bBF_2$** in KBr consists of three components involving multiple FL domains comprised minimally of excited monomers and excimers. It is likely that, the observed differences in the FL of **$1aBF_2$** and **$1bBF_2$**, caused by the presence of isopropyl groups in the latter substance, are a consequence of the difference in the degree of intermolecular interaction existing in the solid state.

These diffuse reflection and FL properties, obtained by using powder samples of **$1aBF_2$** or **$1bBF_2$** (0.2 μmol) grounded with KBr (500 mg), remain unchanged when different ratios of KBr and the substances are employed.[22]

Absorption and FL properties in CH_2Cl_2

The absorption and FL properties of **$1aBF_2$** and **$1bBF_2$** in CH_2Cl_2 solutions are summarized in Table 1.[21] The absorption maxima of both of these substances in CH_2Cl_2 solutions ($\lambda_{AB,S}$) are 380 nm, indicating that no significant effects of the isopropyl substituents exist.

The different FL properties of **$1aBF_2$** and **$1bBF_2$** are also observed in CH_2Cl_2. Specifically, at low concentration (e.g., 1×10^{-7} M), CH_2Cl_2 solutions of both **$1aBF_2$** and **$1bBF_2$** display blue emission at respective FL maxima ($\lambda_{FL,S}$) of 398 and 411 nm (Table 1 and Fig. 3). The 13-nm red shift observed for **$1bBF_2$** versus **$1aBF_2$** is consistent with the trend seen for FL of members of a series of **$1BF_2$**, in which a similar red shift of FL has been observed and rationalized by alterations of the electron-donating ability of diketonate ligands.[9,13] Moreover, the FL quantum yield in CH_2Cl_2 ($\Phi_{FL,S}$) of **$1bBF_2$** is nearly unity (0.99) while that of the parent **$1aBF_2$** is only 0.26 (Table 2).

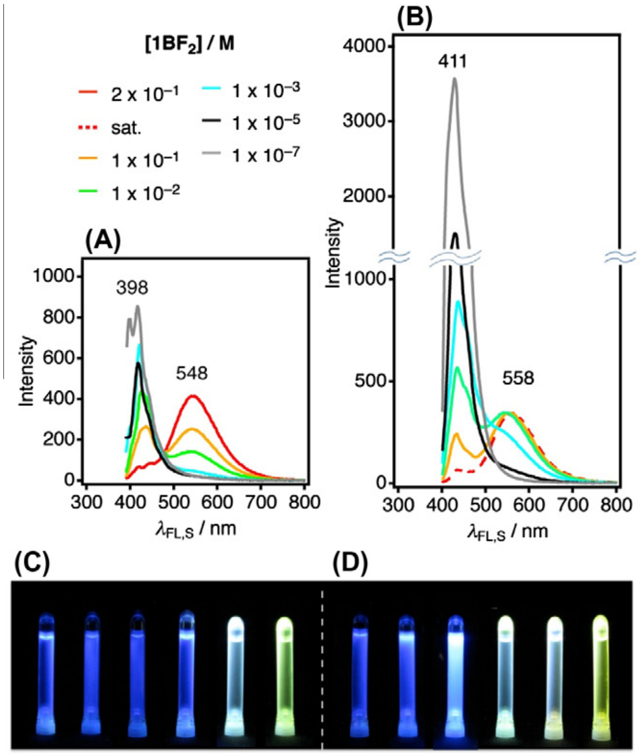

Figure 3. Concentration effects on the FL spectral profiles of $\mathbf{1aBF_2}$ (A) and $\mathbf{1bBF_2}$ (B) in CH_2Cl_2 at 294 K. λ_{EX} = 380 nm. Photographs of FL of $\mathbf{1aBF_2}$ (C) and $\mathbf{1bBF_2}$ (D) in CH_2Cl_2 at 294 K. λ_{EX} = 365 nm. The solutions of 1×10^{-7}, 1×10^{-5}, 1×10^{-3}, 1×10^{-2}, 1×10^{-1}, and 2×10^{-1} M for $\mathbf{1aBF_2}$ or the saturated concentration (ca. 1.5×10^{-1} M) for $\mathbf{1bBF_2}$ were serially put on from the left to the right.

Table 2
FL quantum yields and lifetimes of $\mathbf{1aBF_2}$ and $\mathbf{1bBF_2}$ in CH_2Cl_2

[$\mathbf{1BF_2}$] (M)	$\mathbf{1aBF_2}$			$\mathbf{1bBF_2}$		
	$\Phi_{FL,S}$	τ_{410}[a] (ns)	τ_{530}[a] (ns)	$\Phi_{FL,S}$	τ_{410}[a] (ns)	τ_{530}[a] (ns)
[b]	0.36	1.65 0.46	50.7 6.27 0.47	0.32	0.31 0.91	48.3 3.11 0.57
1×10^{-1}	0.28	0.41 0.74	51.5 2.60 0.44	0.37	0.80 1.20	57.8 11.5 2.03
1×10^{-2}	0.24	0.81	49.3 1.02	0.49	1.86	52.0 14.2 3.48
1×10^{-3}	0.22	0.51	39.5 0.51	0.53	1.80	23.9 1.95
1×10^{-5}	0.26	0.50	32.5 0.50	0.68	1.67	16.1 1.70
1×10^{-7}	0.26	0.50	0.69 0.44	0.99	1.56	13.2 1.58

[a] The τ values for the solution at a higher concentration (especially, [$\mathbf{1BF_2}$] > 1×10^{-2} M) may involve some systematic errors, because a probable intermolecular interaction is not accurately evaluated.

[b] 2×10^{-1} M for $\mathbf{1aBF_2}$ and the saturated concentration (ca. 1.5×10^{-1} M) for $\mathbf{1bBF_2}$.

To gain further insight into the observed substituent effects, concentration effects of $\mathbf{1aBF_2}$ and $\mathbf{1bBF_2}$ on FL properties, in the 1×10^{-7} to 2×10^{-1} M region, were explored. As is commonly observed for fluorescent organic compounds, self-quenching causes the $\Phi_{FL,S}$ of $\mathbf{1bBF_2}$ to significantly decrease (from 0.99 to 0.32) on increasing concentration (Table 2). Surprisingly, however, the parent $\mathbf{1aBF_2}$ at 2×10^{-1} M exhibits a relatively larger $\Phi_{FL,S}$ (0.36) as compared with that at 1×10^{-7} M (0.26). This observation suggests that radiationless relaxation of the excited monomer or related species, such as an excimer, of $\mathbf{1aBF_2}$ is effectively retarded at high concentration.

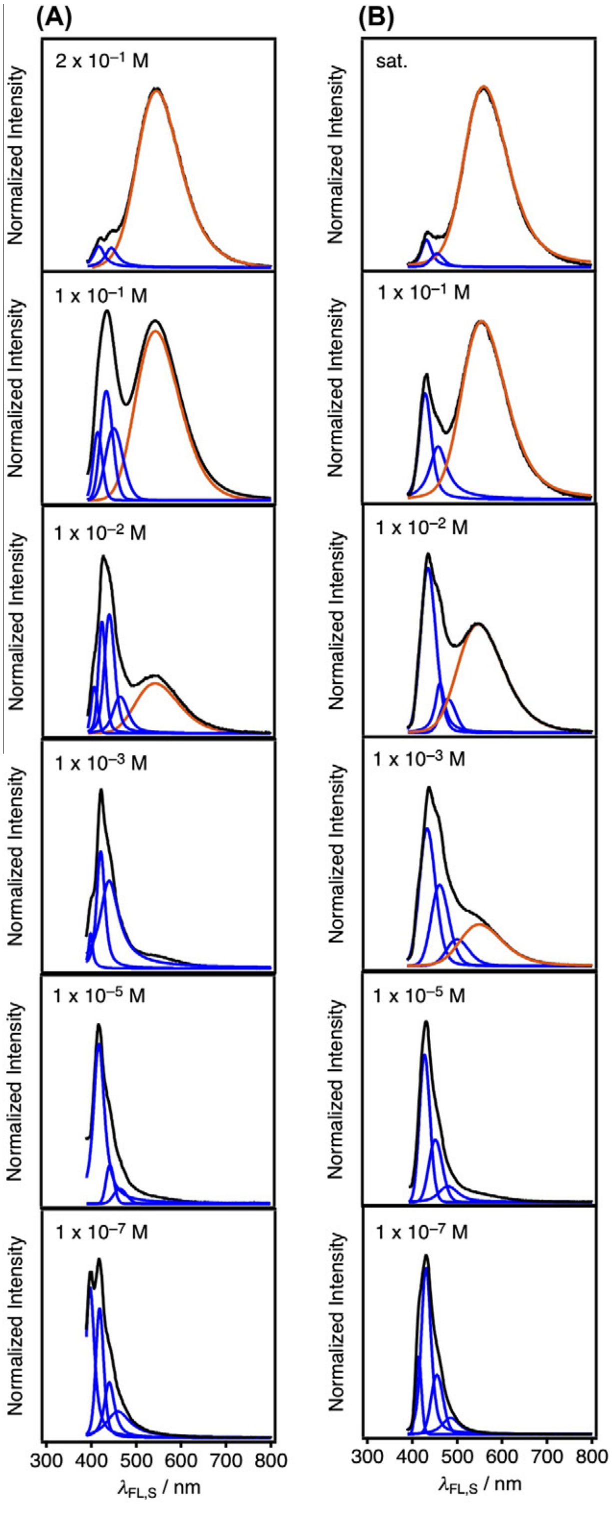

Figure 4. Observed FL spectra (black) of $\mathbf{1aBF_2}$ (A) and $\mathbf{1bBF_2}$ (B) with deconvoluted curves (blue: FL domain attributable to the excited monomer, orange: FL domain attributable to the excimer).

Importantly, as the concentrations of $\mathbf{1aBF_2}$ and $\mathbf{1bBF_2}$ become higher, an FL band appears at 548 and 558 nm, respectively, in concert with a drastic FL color change from blue to yellow (Fig. 3).[23] It is significant that at certain concentrations, solutions of the $\mathbf{1BF_2}$

emit white FL. The CIE chromaticity diagrams for FL of **1aBF$_2$** and **1bBF$_2$** in CH_2Cl_2 show successive transitions (Fig. 2).[24] The CIE coordinates for 1×10^{-1} M solutions are (*x*, *y*) = (0.29, 0.35) and (0.34, 0.40) for **1aBF$_2$** and **1bBF$_2$**, respectively, values that are close to the coordinate for ideal white emission, (*x*, *y*) = (0.33, 0.33).

As in the case of KBr powder samples, a study of wave deconvolution analyses is the key to elucidate the effects of substituents on the FL properties of CH_2Cl_2 solutions of **1aBF$_2$** and **1bBF$_2$**. As displayed in Figure 4, the original FL spectra at the lowest concentrations were deconvoluted to generate several spectra with $\lambda_{FL,S}$ at ca. 400–500 nm (Fig. 4, blue), which can be reasonably assigned to the excited monomers of **1BF$_2$**. In contrast, the original FL spectra at higher concentrations were deconvoluted to generate several spectra at ca. 400–500 nm and spectra with $\lambda_{FL,S}$ at ca. 550–560 nm (orange). The latter FL band is usually assigned to the excimer in the case of **1aBF$_2$**.[17] Additionally, a stationarity of FL wavelength against changes in the concentration also implies that the FL domain is likely associated with the excimers of **1BF$_2$**. Thus, the results of wave deconvolution analyses reveal that the FL of **1BF$_2$** in CH_2Cl_2 consists of two types of the FL domains corresponding to the excited monomers and excimers.

These conclusions gain support from the results of FL lifetime (τ) measurements. The τ values at 410 nm for the FL shorter wavelength domains of **1aBF$_2$** and **1bBF$_2$** ($<1 \times 10^{-2}$ M) are τ_{410} = ca. 0.5 and ca. 1.7 ns, respectively. In contrast, the τ values at 530 nm for the longer wavelength FL domains of these substances are τ_{530} = ca. 50 ns, much longer than the τ_{410} values. The observed τ values are typical for emission from excited monomers and excimers of common organic substances.[25,26]

The results presented above clearly indicate that increasing concentrations of **1BF$_2$** cause continuous changes of the major FL domain from the excited monomers to excimers that are accompanied by changes of FL colors from blue to yellow. Mixing blue and yellow emissions from the excited monomers and excimers, respectively, in suitable ratios results in white emission.

Conclusion

The results of the effort described above show that single component, organoboron complexes **1BF$_2$** exhibit white FL not only in KBr but also in CH_2Cl_2. The white FL consists of blue and yellow FLs (complementary colors), corresponding to the FL domains of excited monomers and excimers, respectively.[27] As compared to conventional systems used for white FL, **1BF$_2$** are single-component, low molecular weight materials that are readily synthesized and do not contain heavy metal atoms.

It is interesting that $\lambda_{FL,P}$ of **1bBF$_2$** in KBr experiences a blue shift, but $\lambda_{FL,S}$ of **1bBF$_2$** in CH_2Cl_2 undergoes a red shift as compared to the parent **1aBF$_2$** (Table 1). Although, no clear explanation exists for these phenomena at this stage, the observation may be a consequence of the existence of another FL domain in the KBr powder, which probably depends on the molecular arrangement in the solid state. From this point of view, the relationship between FL properties and the crystal structures of **1BF$_2$** is an intriguing subject now being probed in our laboratory.

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2012.05.122.

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21. For the detail, see Figure S1 in the Supplementary data.
22. The FL properties of **1BF$_2$** in KBr seem to depend on rather the degree of mixing or grinding the sample. A study on this phenomenon is now in progress and results will be published elsewhere.
23. For the detail, see Table S1 in the Supplementary data.
24. Similar concentration effects on FL were also observed in not only less polar toluene but also polar solvent such as CH_3CN. The detail of the solvent effects on the absorption and FL properties will be given elsewhere.
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27. We observed some excitation spectra of **1BF$_2$** at higher concentration that might be explainable by assuming an aggregation of **1BF$_2$** in the ground state. However, this hypothesis has not proved yet by absorption spectroscopy or ^{1}H NMR at this stage. Further study is now in progress and the detail will be given elsewhere.