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Relationship between Crystal Packing and Solid-State Fluorescence Quantum Yield in Pyrazine Monoboron Complexes

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Abstract

The relationship between crystal packing and solid-state fluorescence quantum yield (Φ_f) in pyrazine monoboron complexes **1**–**6** was investigated. The maximum fluorescence wavelength ($F_{\max}$) of the BPh₂ complexes **4**–**6** was blue-shifted (524–628 nm) and the Φ_f values were higher (0.13–0.29) than those of the corresponding BF₂ complexes **1**–**3** ($F_{\max}$: 531–672 nm, Φ_f : 0.04–0.13), probably due to inhibition of the intermolecular interactions. Despite weaker intermolecular interactions of the dimethylamino-substituted BPh₂ complex **6** compared to non-substituted BF₂ complex **1**, **6** ($\Phi_f = 0.13$, $F_{\max} = 628$ nm) had the same Φ_f value as **1** ($\Phi_f = 0.13$, $F_{\max} = 542$ nm) due to red-shifted $F_{\max}$, which promoted non-radiative processes.

Key-words: Boron complex, β -iminoenolate ligand, Pyrazine, Solid-state fluorescence, Crystal packing

1. Introduction

Despite the wide-ranging applications of solid-state fluorescent organic dyes in a variety of areas such as organic light-emitting diodes¹⁾, solid-state dye lasers²⁾, and organic light-emitting field-effect transistors³⁾, the development of these dyes is still challenging. Common organic dyes that fluoresce in dilute solution often quench or reduce the fluorescence intensity in the solid state; this phenomenon is called aggregation-caused quenching (ACQ) or concentration quenching⁴⁾. The solid-state fluorescence properties of organic dyes are known to be strongly dependent on the molecular packing⁵⁾. In many cases, the intermolecular π - π interactions in the solid state lead to ACQ⁶⁾. The introduction of bulky substituent group in organic dyes should prevent the formation of intermolecular π - π interactions and is often used for the expression of fluorescence and enhancement of the fluorescence quantum yield in the solid state⁷⁾.

Organoboron complexes are some of the most vital fluorescent dyes. Due to the rigid molecular skeleton, organoboron complexes often fluoresce in solution^{8,9)}. Additionally, the photophysical properties such as absorption and fluorescence wavelengths can be controlled by the type of ligand. However, similar to the common organic dyes, organoboron complexes exhibit the ACQ phenomenon in the solid state. In the course of our studies on the organoboron compounds^{10–14)}, we have found that the introduction of

bulky substituent groups, particularly on the boron atom, is a good strategy for enhancement of the fluorescence quantum yield of organoboron compounds. We have also reported pyrazine monoboron complexes featuring a β -iminoenolate ligand that show interesting fluorescence properties in solution such as fluorescence solvatochromism¹⁵⁾. In this paper, we reported the relationship between crystal packing and solid-state fluorescence quantum yield in the pyrazine monoboron complexes.

2. Experimental

The synthesis and fluorescence properties of pyrazine monoboron complexes **1**–**6** in solution were reported in our previous paper¹⁵⁾. Fluorescence spectra in the solid state were measured with a Jasco FP-8600 spectrofluorometer. Fluorescence quantum yields in the solid state were recorded with a Hamamatsu Quantaurus-QY instrument. The single crystals of **1**, **4**, and **6** were obtained by the slow diffusion of hexane into chloroform solutions of the corresponding compounds. Single-crystal X-ray diffraction measurements were performed on a Rigaku Mercury 375R/M CCD (XtaLAB-mini) diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71075$ Å). The crystal structures were solved using direct methods with SHELXS-97 or SHELXS2013 and refined by full-matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F^2 using SHELXL-97 or SHELXL2013. All hydrogen atoms were placed using AFIX instructions. The Cambridge Crystallographic Data Center (CCDC) numbers for **1**, **4**, and **6** are 1567751, 1567752, and

【Figures and illustrations】 Figures and illustrations published in black and white in the journal can be seen in color at our public website 「J-STAGE」. Please make use of it.

1567753, respectively.

Crystallographic details for **1**: $C_{12}H_8BClF_2N_2O$, $M = 280.46 \text{ g mol}^{-1}$; $T = 293(2) \text{ K}$; triclinic space group P-1; $a = 7.550(9)$, $b = 11.826(13)$, $c = 14.373(16) \text{ Å}$, $\alpha = 74.36(3)$, $\beta = 88.11(3)$, $\gamma = 75.57(2)^\circ$; $V = 1196(2) \text{ Å}^3$; $Z = 4$; $5.31 < 2\theta < 55.00^\circ$; $\rho_{\text{calcd}} = 1.558 \text{ g cm}^{-3}$; $\mu = 0.335 \text{ mm}^{-1}$; $R_{\text{int}} = 0.0363$; $R_1 = 0.0454$, $wR_2 = 0.1260$ for 5406 reflections with $I > 2\sigma(I)$ and 343 parameters; $S = 0.887$.

Crystallographic details for **4**: $C_{24}H_{18}BCl_3N_2O$, $M = 396.66 \text{ g mol}^{-1}$; $T = 293(2) \text{ K}$; triclinic space group P-1; $a = 7.211(8)$, $b = 16.616(16)$, $c = 17.872(19) \text{ Å}$, $\alpha = 76.23(2)$, $\beta = 89.04(3)$, $\gamma = 81.27(3)^\circ$; $V = 2055(4) \text{ Å}^3$; $Z = 4$; $5.09 < 2\theta < 55.05^\circ$; $\rho_{\text{calcd}} = 1.282 \text{ g cm}^{-3}$; $\mu = 0.203 \text{ mm}^{-1}$; $R_{\text{int}} = 0.0910$; $R_1 = 0.1106$, $wR_2 = 0.2978$ for 9317 reflections with $I > 2\sigma(I)$ and 523 parameters; $S = 1.164$.

Crystallographic details for **6**: $C_{26}H_{23}BClN_3O$, $M = 439.73 \text{ g mol}^{-1}$; $T = 293(2) \text{ K}$; monoclinic space group P21/c; $a = 13.768(7)$, $b = 9.731(4)$, $c = 18.160(7) \text{ Å}$, $\alpha = 90^\circ$, $\beta = 109.581(15)$, $\gamma = 90^\circ$; $V = 2292.3(18) \text{ Å}^3$; $Z = 4$; $5.23 < 2\theta < 55.04^\circ$; $\rho_{\text{calcd}} = 1.274 \text{ g cm}^{-3}$; $\mu = 0.190 \text{ mm}^{-1}$; $R_{\text{int}} = 0.1882$; $R_1 = 0.0900$, $wR_2 = 0.2225$ for 5202 reflections with $I > 2\sigma(I)$ and 289 parameters; $S = 1.013$.

3. Results and discussions

All pyrazine-boron complexes **1**~**6** demonstrated solid-state fluorescence (Fig. 1, Table 1). The F_{max} and Φ_f values of **1**~**6** in the solid state (F_{max} : 524~672 nm, Φ_f : 0.04~0.29) were red-shifted and decreased, respectively, compared to those in *n*-hexane (F_{max} : 464~529 nm, Φ_f : 0.13~0.80) due to the formation of aggregates. Similar to the results in *n*-hexane, the F_{max} values of dimethylamino-substituted derivatives **3** (672 nm) and **6** (628 nm) and trifluoromethyl-substituted derivatives **2** (531 nm) and **5** (524 nm) showed bathochromic and hypsochromic shifts compared to the non-substituted derivatives **1** (542 nm) and **4** (536 nm), respectively. However, distinct from the results of *n*-hexane, the BF₂ complexes **1**~**3** (F_{max} : 531~672 nm) demonstrated red-shifted F_{max} values compared to the corresponding BPh₂ complexes **4**~**6** (F_{max} : 524~628 nm) in the solid state. We attribute this result to the introduction of bulky phenyl groups on the boron atom, which decreased aggregate formation of the BPh₂ complexes. Interestingly, synthesized pyrazine monoboron complexes **1**~**6** (F_{max} : 524~672 nm) showed red-shifted F_{max} values compared to the previously reported corresponding pyrimidine monoboron complexes⁽¹¹⁾ (F_{max} : 474~629 nm) in the solid state. This indicates that introduction of pyrazine ring is more effective as compared to that of pyrimidine ring for the spectral red shift of F_{max} value in the boron complex containing a β -iminoenolate ligand.

X-ray crystallographic analyses were performed for

Fig. 1 Normalized fluorescence spectra of **1**~**6** in the solid state.

Table 1 Fluorescence properties of pyrazine boron complexes^a.

1: R¹ = H, R² = F

2: R¹ = CF₃, R² = F

3: R¹ = NMe₂, R² = F

4: R¹ = H, R² = Ph

5: R¹ = CF₃, R² = Ph

6: R¹ = NMe₂, R² = Ph

Compd	In hexane		Solid state	
	F_{max}/nm	ϕ_f	F_{max}/nm	ϕ_f
1	446, 472	0.29	542	0.13
2	438, 464	0.13	531	0.12
3	506, 534	0.80	672	0.04
4	505, 531	0.62	536	0.29
5	502, 526	0.32	524	0.26
6	529, 549	0.71	628	0.13

^aMeasured at a concentration of $1.0 \times 10^{-5} \text{ M}$.

complexes **1** ($\Phi_f = 0.13$), **4** ($\Phi_f = 0.29$) and **6** ($\Phi_f = 0.13$) to explain differences in the Φ_f value. In the crystal of **1**, two crystallographically independent conformers, **1A** and **1B**, were observed (Fig. 2). The conformers **1A** (black molecules) and **1B** (gray molecules) formed independent stacking columns **1A'** and **1B'**, respectively, by π - π interactions (**1A'**: C-C: 3.45~3.69 Å, **1B'**: C-C: 3.50~3.69 Å). Furthermore, CH/F interactions were observed between **1A'** and **1B'** (C-F: 3.16~3.40 Å). Therefore, the relatively low Φ_f value of **1** was attributed to the strong and consecutive π - π interactions.

In the case of **4**, similar to the corresponding BF₂ complex **1**, two independent crystallographic conformers **4A** and **4B** were observed (Fig. 3). Each **4A** (black molecules) and **4B** (gray molecules) formed independent stacking columns by the π - π interactions (C-C: 3.53~3.68 Å in **4A**, 3.47~3.68 Å in **4B**). The stacking column of **4B** showed CH/ π interactions (C9-C8': 3.65 Å) with that of the neighboring stacking column of **4A**. The neighboring stacking column of **4A** also showed CH/ π interactions (C10-C16: 3.67 Å) with the neighboring stacking column of **4A**. The CH/ π interactions (C9-C8': 3.65 Å) also attached the stacking column of **4A** to the neighboring stacking column of **4B**. Consequently,

Fig. 2 (a) ORTEP view of **1**. Hydrogen atoms were omitted for clarity. (b) Molecular packing and list of intermolecular interactions of **1**.

Fig. 3 (a) ORTEP view of **4**. Hydrogen atoms were omitted for clarity. (b) Molecular packing and list of intermolecular interactions of **4**.

the stacking sequence **4S** was formed in the neighboring two stacking columns of **4B** and two stacking columns of **4A**. The molecular packing of **4** consisted of the repeated structure of **4S**. No interaction between the adjacent stacking sequences **4S** was observed. Compared to BF_2 complex **1**, BPh_2 complex **4** showed weaker intermolecular interactions: Complex **1** showed many strong π - π interactions in the stacking column; however, **4** showed less interaction than **1**. Because of the

weaker interactions, BPh_2 complex **4** ($\Phi_f = 0.29$) exhibited a higher Φ_f than BF_2 complex **1** ($\Phi_f = 0.13$).

In the crystal packing of dimethylamino-substituted BPh_2 complex **6**, the molecules depicted in black and gray formed dimers by the π - π interactions (C-C: 3.65 Å) (Fig. 4). Furthermore, the CH/ π interactions were observed for each dimer (C-C: 3.68 Å). Consequently, consecutive intermolecular interactions were formed throughout the

Fig. 4 (a) ORTEP view of **6**. Hydrogen atoms were omitted for clarity. (b) List of intermolecular interactions of **6**. (c) Molecular packing of **6**.

molecule. Similar to boron complex **4**, dimethylamino derivative **6** had weaker intermolecular interactions compared to boron complex **1**. Despite the weaker intermolecular interactions, the Φ_f value of **6** ($\Phi_f = 0.13$) was same as that of **1** ($\Phi_f = 0.13$). According to the energy gap law¹⁶, the nonradiative rate constant (k_{nr}) should increase with decreasing emission energy which is inversely proportional the F_{max} value. Since a red-shift of F_{max} was expected to promote the nonradiative processes, the red-shifted F_{max} values of **6** and **3** compared to the other complexes were considered to decrease the Φ_f values.

4. Conclusions

Pyrazine monoboron complexes exhibited solid-state fluorescence. The maximum fluorescence wavelengths of dimethylamino (F_{max} : 628~672 nm) and trifluoromethyl (F_{max} : 524~531 nm) substituted derivatives were red-

shifted and blue-shifted, respectively, compared to the non-substituted derivatives (F_{max} : 536~542 nm). When considering the crystal packing, although the BF_2 complexes formed consecutive π - π interactions through CH/F interactions, no consecutive interactions were observed in BPh_2 complexes. Thus, the BPh_2 complexes exhibited higher fluorescence quantum yields (Φ_f : 0.13~0.29) compared to the corresponding BF_2 complexes (Φ_f : 0.04~0.13).

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References

- 1) Z. Chang, Y. Jiang, B. He, J. Chen, Z. Yang, P. Lu, H. S. Kwok, Z. Zhao, H. Qiu, B. Z. Tang: *Chem. Commun.*, **49**, 594 (2013).
- 2) A. Costela, I. Garcia-Moreno, R. Sastre: *Phys. Chem. Chem. Phys.*, **5**, 4745 (2003).
- 3) A. Dadvand, W.-H. Sun, A. G. Moiseev, F. Bélanger-Gariépy, F. Rosei, H. Meng, D. F. Perepichka: *J. Mater. Chem. C*, **1**, 2817 (2013).
- 4) J. Mei, N. L. C. Leung, R. T. K. Kwok, J. W. Y. Lam, B. Z. Tang: *Chem. Rev.*, **115**, 11718 (2015).
- 5) C. Kitamura, Y. Abe, T. Ohara, A. Yoneda, T. Kawase, T. Kobayashi, H. Naito, T. Komatsu: *Chem. Eur. J.*, **16**, 890 (2010).
- 6) K. Shirai, M. Matsuoka, K. Fukunishi: *Dyes Pigm.*, **42**, 95 (1999).
- 7) S.-Y. Park, M. Ebihara, Y. Kubota, K. Funabiki, M. Matsui: *Dyes Pigm.*, **82**, 258 (2009).
- 8) D. Frath, J. Massue, G. Ulrich, R. Ziessel: *Angew. Chem. Int. Ed.*, **53**, 2290 (2014).
- 9) A. Loudet, K. Burgess: *Chem. Rev.*, **107**, 4891 (2007).
- 10) Y. Kubota, K. Kasatani, T. Niwa, H. Sato, K. Funabiki, M. Matsui: *Chem. Eur. J.*, **22**, 1816 (2016).
- 11) Y. Kubota, H. Kasatani, K. Takai, K. Funabiki, M. Matsui: *Dalton Trans.*, **44**, 3326 (2015).
- 12) Y. Kubota, S. Tanaka, K. Funabiki, M. Matsui: *Org. Lett.*, **14**, 4682 (2012).
- 13) Y. Kubota, H. Hara, S. Tanaka, K. Funabiki, M. Matsui: *Org. Lett.*, **13**, 6544 (2011).
- 14) Y. Kubota, J. Uehara, K. Funabiki, M. Ebihara, M. Matsui: *Tetrahedron. Lett.*, **51**, 6195 (2010).
- 15) Y. Kubota, Y. Sakuma, K. Funabiki, M. Matsui: *J. Phys. Chem. A*, **118**, 8717 (2014).
- 16) W. Siebrand: *J. Chem. Phys.*, **46**, 440 (1967).

ピラジンホウ素錯体の結晶構造と量子収率との相関について

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要 旨

ピラジン単核ホウ素錯体**1**~**6**において結晶のパッキングと蛍光量子収率 Φ_f との相関について調べた。フェニル誘導体**4**~**6** (F_{max} : 524~628 nm, Φ_f : 0.13~0.29) は対応するフッ素誘導体**1**~**3** (F_{max} : 531~672 nm, Φ_f : 0.04~0.13) に比べて弱い分子間相互作用が観測された。このため最大蛍光波長 F_{max} は短波長化し、高い Φ_f 値を示した。ジメチルアミノ基を有するフェニル誘導体**6**は無置換体フッ素誘導体**1**よりも弱い分子間相互作用を示したにもかかわらず、**6**と**1**の Φ_f 値は同じであった。これは**6**の F_{max} が長波長化し無輻射失活が促進されたためだと考えられる。

キーワード: ホウ素錯体, β -イミノエノレート配因子, ピラジン, 個体蛍光, 結晶中でのパッキング