Fluorescence |Hot Paper|



New Fluorescence Domain "Excited Multimer" Formed upon Photoexcitation of Continuously Stacked Diaroylmethanatoboron Difluoride Molecules with Fused π-Orbitals in Crystals

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Abstract: The crystal-packing structures of seven derivatives of diaroylmethanatoboron difluoride (1 a-gBF_2) are characterized by no overlap of the π -conjugated main units of two adjacent molecules (type I), overlap of the benzene ring π orbitals of two adjacent molecules (type II), and overlap of the benzene and dihydrodioxaborinine rings π -orbitals of adjacent molecules (type III). The crystal-packing structures govern the fluorescence (FL) properties in the crystalline states. The FL domain that is present in type I crystals, in which intermolecular orbital interactions are absent, leads to excited monomer-like FL properties. In the case of the type II crystals, the presence of intermolecular overlap of the benzene rings π -orbitals generates new FL domains, referred to as "excited multimers", which possess allowed S₀–S₁ electronic transitions and, as a result, similar FL lifetimes at longer wavelengths than the FL of the type I crystals. Finally, intermolecular overlap of the benzene and dihydrodioxaborinine ring π -orbitals in the type III crystals leads to "excited multimer" domains with forbidden S₀–S₁ electronic transitions and longer FL lifetimes at similar wavelengths as that in type I crystals.

Introduction

In spite of many efforts,^[1-7] the relationships that exist between the modes of molecular aggregation and the fluorescence (FL) properties of organic compounds have remained unclear. Because crystals are a fundamental mode of molecular aggregation that can be unambiguously delineated by using X-ray crystallographic analysis, one of the best ways to investigate this relationship is through systematic and thorough studies of the FL properties and packing structures of crystalline substances.^[8–10] However, implementation of this approach is difficult because the preparation of single crystals of different crystalline forms of single organic substances or closely related derivatives is nontrivial.

Organoboron complexes^[11-22] have attracted growing attention as organic fluorescent materials owing to several advantages that include ease of preparation, large molar extinction coefficients, and high FL quantum yields ($\Phi_{\rm FL}$). Among the substances in this family, dibenzoylmethanatoboron difluoride

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[b] Dr. E. Ohta, Dr. Y. Matsui, Prof. Dr. K. Mizuno, Prof. Dr. H. Ikeda The Research Institute for Molecular Electronic Devices (RIMED) Osaka Prefecture University, Sakai, Osaka 599-8531 (Japan) (**P1BF**₂, Scheme 1) is an especially interesting compound from the viewpoint of probing relationships between aggregation mode and FL properties.^[23–35] Since the report by Mirochnik and co-workers showing that **P1BF**₂ FL involves emission from arrays of molecules in crystals in which intermolecular orbital interactions occur,^[30–35] many others have observed that **P1BF**₂ derivatives exhibit interesting molecular aggregation-based emission phenomena such as mechanofluorochromism,^[36–39] aggregation-induced emission (AIE),^[40] and room-temperature phosphorescence.^[41,42]

Guided by these earlier efforts, we carried out an investigation aimed at elucidating the FL properties and crystal-packing structures of **1 BF**₂ derivatives. The results of this effort showed that the crystals of parent compound **P1 BF**₂ exhibit FL with a longer lifetime (τ_{FL}) than that in CH₂Cl₂ solution, but that its *i*Pr derivative **1 eBF**₂ (Scheme 1) exhibits FL with almost identical τ_{FL} in CH₂Cl₂ as it does in the crystalline state.^[43,44] In a continuation of this investigation, we explored the FL properties



Scheme 1. Molecular structures of P1BF₂ and 1a-gBF₂.

Chem. Eur. J. 2015, 21, 18128-18137

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201503132.



of the alkyl- and trimethylsilyl-substituted dibenzoylmethanatoboron difluorides **1**a–gBF₂ (Scheme 1) in CH₂Cl₂ solutions and in crystalline states. As described below, the results of this comprehensive study show that **1**a–gBF₂ each have one of three types of crystal-packing structures that differ in the manner in which intermolecular π -orbital overlap takes place. Interestingly, the FL properties, especially the FL wavelength maxima (λ_{FL}) and τ_{FL} , are affected by the nature of the crystalpacking structures. This observation demonstrates that the differences in FL properties originate from differences in intermolecular orbital interactions taking place in the crystals.

Results

Crystal-packing structures

Crystals of $1 a - gBF_2$ all have packing structures in which molecules are stacked in a face-to-face manner (Figure 1). With the exception of $1 cBF_2$, the crystalline state of which contains molecules in a zigzag array along the molecular long-axis direction, the crystals of all other substances have continuously stacked molecular arrays at oblique angles to the long-axis molecular direction (Figure 1, Front View). Importantly, the crystals of $1 aBF_2$, $1 bBF_2$, $1 dBF_2$, $1 cBF_2$, $1 dBF_2$, and $1 gBF_2$ have the same space group of C2/c, whereas $1 cBF_2$ is in the space group of *Pnma*. Therefore, the major difference in crystal-packing structure among $1 a - gBF_2$, excepting $1 cBF_2$, could be simply considered to be a difference in the distances between neighboring molecules. The distances between centroids of adjacent molecules (D_c) in crystals of $1 a - gBF_2$ are listed in Table 1. Adja-



cent molecules in crystals of 1 aBF_2 and 1 bBF_2 , which possess linear alkyl groups, are aligned at longer distances from each other (D_c =12.69 Å for 1 aBF_2 and 11.34 Å for 1 bBF_2). As a result, molecules in these crystals are stacked in a manner that does not allow intermolecular overlap of the parent units corresponding to P1BF₂, but enables stacking of the *n*Bu or *n*Pr alkyl chain and benzene moiety (Figure 1, *No* overlap). The D_c values for 1 cBF_2 , 1 dBF_2 ,^[34] and 1 eBF_2 , which contain less bulky substituents, are smaller than those for 1 aBF_2 and 1 bBF_2 (Table 1, D_c =9.67 Å for 1 cBF_2 , 6.80 Å for 1 dBF_2 , and 8.63 Å for 1 eBF_2). As a result, adjacent molecules in crystals of



Figure 1. Crystal-packing structures of 1a-gBF₂ determined by using X-ray crystallographic analysis. The manners of overlap of adjacent molecules in continuously stacked molecular arrays are classified into three types.

Chem. Eur. J. 2015, 21, 18128-18137

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1 c-eBF₂ are stacked in a manner that allows overlap of the benzene ring π -orbitals (Figure 1, *B*-on-*B* overlap).^[44] Molecules of **1** fBF₂ and **1** gBF₂, with bulky substituents, are stacked more closely still (Table 1, D_c =5.41 Å for **1** fBF₂ and 5.62 Å for **1** gBF₂), which avoids intermolecular overlap of the parent unit and bulky substituents of adjacent molecules. Thus, molecules in the crystalline states of **1** fBF₂ and **1** gBF₂ are stacked in a manner that enables overlap of the benzene groups with the 1,2-dihydro-2,6-dioxaborinine moieties in the neighboring molecules (Figure 1, *B*-on-*D* overlap). The face-to-face distances (D_F) of molecules of **1** a-gBF₂ are all less than 4 Å (Table 1), indicating that π -orbital interactions exist when the parent units overlap with each other.

UV/Vis absorption and FL properties in CH₂Cl₂

Substances **1a–gBF**₂ in low concentration CH₂Cl₂ solutions have almost identical absorption wavelength maxima ($\lambda_{AB,5}$) of 381–392 nm (Figure 2a and Table 2). Upon photoexcitation using 365 nm light, **1a–gBF**₂ emit blue FL with almost the same $\lambda_{FL,S}$ of 409–414 nm (Figure 2b and Table 2) and $\tau_{FL,S}$ of



Figure 2. (a) UV/Vis absorption spectra and (b) FL spectra of $1\,a\text{-gBF}_2$ in CH_2Cl_2 (ca. $0.5\times10^{-5}\,\text{m},\,\lambda_{EX}\!=\!365$ nm).

1.3–1.6 ns. The $\Phi_{FL,S}$ of **1a–fBF**₂ were found to be high (0.81–0.91), whereas that of **1gBF**₂ is lower (0.66). Notably, $\lambda_{AB,S}$ and $\lambda_{FL,S}$ of **1a–fBF**₂ do not display a remarkable change when the solvent polarity is altered.^[45]

FL properties in the crystalline states

Crystals of **1 aBF**₂ and **1 bBF**₂ have $\lambda_{FL,C}$ at 450 and 456 nm, respectively (Figure 3 a and Table 2), which are approximately 40 nm higher than $\lambda_{FL,S}$ for the CH₂Cl₂ solutions of these substances. The crystals of **1 cBF**₂, **1 dBF**₂, and **1 eBF**₂ have $\lambda_{FL,C}$ at



Figure 3. (a) FL spectra (λ_{EX} =365 nm), (b) time-dependent changes in FL intensity (λ_{DET} =500 nm, λ_{EX} =371 nm), and (c) excitation spectra (λ_{DET} =560 nm) of **1 a-gBF**₂ crystals.

1BF ₂	In CH ₂ Cl ₂ ^[a]				In crystal			
	$\lambda_{\text{AB,S}}$ [nm]	$\lambda_{\text{FL,S}}^{[b]}$ [nm]	$ au_{FL,S}^{[c,d]}$ [ns]	$\Phi_{{\sf FL,S}}{}^{[b]}$	$\lambda_{\text{EX,C}}$ (band) ^[e] [nm]	$\lambda_{\text{FL,C}}^{[b]}$ [nm]	$ au_{\rm FL,C}^{\rm [c,f]}$ [ns]	$\varPhi_{\rm FL,C}{}^{\rm [g]}$
а	387	411	1.5	0.91	404 (386–448)	450	1.8	\approx 0.71
b	381	412	1.6	0.90	404 (386–453)	456	1.8	\approx 0.58
c	391	411	1.6	0.83	428 (386–481)	476	3.5	\approx 0.37
d	391	414	1.5	0.81	469 (388–517)	518	3.2	\approx 0.41
e	388	411	1.6	0.83	405 (386–498)	500	1.5	\approx 0.17
f	392	411	1.5	0.81	406 (386–443)	467	6.8	\approx 0.46
g	391	409	1.3	0.66	405 (385–441)	469	5.6	\approx 0.29

[a] The maximal absorbance of the solution was controlled to be 0.3 (ca. 0.5×10^{-3} M). [b] $\lambda_{EX} = 365$ nm. [c] $\lambda_{EX} = 371$ nm. [d] The detected wavelength, λ_{DEP} of the FL was controlled to be $\lambda_{FL,S}$. χ^2 values are in the range 1.0 ± 0.2 . [e] Analysis range: Int/Int_{max} > 0.3, $\lambda_{DET} = 560$ nm. [f] Average of values detected at $\lambda_{FL,C} = 460$, 480, 500, 520, 540, and 560 nm. χ^2 values are in the range 1.0 ± 0.2 . [g] Excitation was done at the peak top wavelength (± 5 nm) in the excitation spectrum ($\lambda_{EX,C}$).

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longer wavelengths (476, 518, and 500 nm, respectively) than those of **1aBF**₂ and **1bBF**₂. The $\lambda_{FL,C}$ values for crystalline **1fBF**₂ and **1gBF**₂ are 467 and 469 nm, respectively, which are higher than those of crystals of **1aBF**₂ and **1bBF**₂ and similar to those of **1cBF**₂, **1dBF**₂, and **1eBF**₂. However, the differences in the $\lambda_{FL,C}$ values between **1f-gBF**₂ and **1a-bBF**₂ are smaller than those between **1c-eBF**₂ and **1a-bBF**₂.

One FL transient arising from both crystalline **1 aBF**₂ and **1 bBF**₂ has $\tau_{FL,C}$ of 1.8 ns (Figure 3 b and Table 2),^[46] which is similar to the $\tau_{FL,S}$ (ca. 1.5 ns) observed in CH₂Cl₂ solutions of these substances. In addition, the $\tau_{FL,C}$ values of crystalline **1 cBF**₂ and **1 dBF**₂ are 3.5 and 3.2 ns, respectively, whereas those of crystalline **1 fBF**₂ and **1 gBF**₂ are 6.8 and 5.6 ns, respectively. Finally, only **1 eBF**₂ exhibits a short $\tau_{FL,C}$ of 1.5 ns in its crystalline state.

Excitation wavelength associated with FL from crystals

Inspection of the excitation spectra determined for FL emission of crystalline **1 aBF**₂ and **1 bBF**₂ show that the FL is associated with absorption between approximately 385–450 nm (Figure 3 c and Table 2). Moreover, although the FL bands of crystalline **1 cBF**₂, **1 dBF**₂, and **1 eBF**₂ are associated with excitation between approximately 385–520 nm, those of crystalline **1 fBF**₂ and **1 gBF**₂ are promoted by excitation in a shorter wavelength region of approximately 385–445 nm, which is almost identical to the peak top wavelength in the excitation spectrum ($\lambda_{EX,C}$) of **1 aBF**₂ and **1 bBF**₂ crystals.

Theoretical calculations

Calculations using density functional theory (DFT) methods gave optimum geometries for $1a-gBF_2$ in which the parent P1BF₂ unit in each adopts a nearly planar conformation. The calculated HOMO (E_H) and LUMO (E_L) energies of $1a-fBF_2$ (ca. -6.8 and -2.9 eV, respectively) are not significantly different, whereas the respective E_H and E_L values for $1gBF_2$ are -6.96 and -3.04 eV (Table 3). By using time-dependent (TD)-DFT calculations, the wavelengths associated with the S₀-S₁ electronic transitions ($\lambda_{ET,S0-S1}$) of $1a-gBF_2$ are approximately 350 nm. The results also show that the oscillator strengths of the S₀-S₁ electronic transition (f_{50-S1}) of $1a-gBF_2$ are approximately 1.

The results of single-point calculations for stacked molecules of **1**a–**gBF**₂, having X-ray-determined packing structures, were performed to elucidate the intermolecular π -orbital interactions operating in the crystal-packing structure. The results reveal that the E_L values for three stacked molecules are lower than those for the corresponding single molecule. On the other hand, the stacking-dependent trends of the E_H values are not uniform. For example, the E_H values for three stacked molecules of **1**a**BF**₂, **1**c**BF**₂, and **1**e**BF**₂ are lower than those for the respective single molecules, whereas the E_H values for three stacked molecules of **1**d**BF**₂ and **1**f**BF**₂ are higher than those for the corresponding single molecules. Furthermore, E_H of **1**b**BF**₂ and **1**g**BF**₂ are not dependent on the stacking manner.

1BF ₂	E _H [eV]	E _L [eV]	λ _{ετ,so-s1} [nm]	f _{so-s1}	E _H [eV]	E _L [eV]	λ _{ετ,so-s1} [nm]	f _{S0-S1}	
	single molecule with				single molecule with				
	optimized geometry ^[a]				geometry in crystals ^[b,c]				
а	-6.77	-2.88	352	1.01	-6.76	-2.75	340	1.03	
b	-6.79	-2.89	352	1.03	-6.80	-2.70	334	0.95	
с	-6.81	-2.90	351	0.98	-6.74	-2.82	347	1.00	
d	-6.85	-2.94	349	0.94	-6.80	-2.82	342	0.91	
e	-6.83	-2.93	352	1.03	-6.77	-2.74	340	1.02	
f	-6.80	-2.90	353	1.07	-6.72	-2.74	344	1.08	
g	-6.96	-3.04	354	1.09	-6.88	-2.94	348	1.11	
	two stacked molecules with				three stacked molecules with				
	geometry in crystals ^[b,c]			:]	geometry in crystals ^[b,c]				
а	-6.86	-2.87	346	2.18	-6.88	-2.98	349	3.15	
b	-6.87	-2.81	346	1.75	-6.83	-2.89	351	2.36	
с	-6.77	-2.93	359	1.39	-6.82	-3.01	364	2.26	
d	-6.66	-2.96	378	0.77	-6.63	-3.03	391	1.03	
e	-6.84	-2.91	352	1.32	-6.89	-3.03	359	1.29	
f	-6.62	-2.78	368	0.27	-6.59	-2.80	374	0.24	
g	-6.85	-3.05	378	0.00	-6.86	-3.01	381	0.00	
[a] Calculated by using the B3LYP method and a $6-311+G(d)$ basis set. [b] Calculated by using the B3LYP method and a $6-311G(d)$ basis set. [c] Molecular geometries were derived from X-ray-determined crystal- packing structures									

Table 3. Calculated $E_{\rm H}$, $E_{\rm L}$, $\lambda_{\rm ET, 50-S1}$, and $f_{\rm S0-S1}$ values for a single molecule

with optimized geometry and two and three stacked molecules of 1a-

gBF₂ with geometries in crystals.

The $\lambda_{\text{ET,S0-S1}}$ values for three stacked molecules of $1a-gBF_2$ calculated by using TD-DFT are longer than those for the respective single molecules (Figure 4 and Table 3). In particular, $\lambda_{\text{ET.SO-S1}}$ for **1 dBF**₂, **1 fBF**₂, and **1 gBF**₂ are significantly shifted to longer wavelength by more than 30 nm when the number of molecules in the stack is increased from one to three, whereas $\lambda_{\text{ET,S0-S1}}$ for three stacked molecules of 1 bBF_2 , 1 cBF_2 , and 1 eBF_2 are longer than those for the respective single molecules by less than 20 nm. In addition, $\lambda_{\rm ET, 50\text{-}S1}$ values for a single molecule and the three stacked molecules of **1 aBF**₂ are nearly the same. The respective f_{S0-S1} values calculated for the three stacked molecules of 1 aBF₂, 1 bBF₂, and 1 cBF₂ are 3.15, 2.36, and 2.26, which are larger than those for the corresponding single molecules. On the other hand, the respective f_{S0-S1} values for the three stacked molecules of 1 fBF2 and 1 gBF2 are reduced to 0.24 and 0.00 when the number of molecules is increased from one to three. Finally, the $f_{\rm S0-S1}$ values for three stacked molecules of 1dBF₂ and 1eBF₂ are 1.03 and 1.29, respectively, which are almost identical to those for the respective single molecules.

The transition dipole moments related to the S_0 - S_1 electronic transition (μ_{S0-S1}) calculated for three stacked molecules of **1 aBF₂**, **1 bBF₂**, and **1 cBF₂** are 15.3, 13.3, and 13.2 D, respectively (Figure 5). These values are larger than those determined for the respective single molecules. The μ_{S0-S1} for three stacked molecules of **1 dBF₂** and **1 eBF₂** are observed to be 9.27 and 9.92 D, respectively, which are larger than those for the respective single molecules but much smaller than those for three stacked molecules of **1 aBF₂**, **1 bBF₂**, and **1 cBF₂**. Moreover, the μ_{S0-S1} values for three stacked molecules of **1 fBF₂** and **1 gBF₂** are calculated to be 4.35 and 0.16 D, respectively.

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Figure 4. Electronic transitions estimated for (a) a single molecule, and (b) two and (c) three stacked molecules of $1a-gBF_2$ with geometries in crystals. Molecular geometries for TD-DFT calculations with B3LYP method and 6-311G(d) basis set were derived from X-ray-determined crystal-packing structures.

The results of the single-point calculations for a single molecule and two or three stacked molecules of $1 a - gBF_2$ show that molecules in some members of this group participate in intermolecular interactions involving the LUMO (Figure 6). The LUMOs of the two or three stacked molecules of $1 cBF_2$, $1 dBF_2$, $1 fBF_2$, and $1 gBF_2$ are comprised of a fusion of the LUMOs of the corresponding single molecules; however, this fusion phenomenon is not displayed by the LUMOs of two or three stacked molecules of $1 aBF_2$ and $1 eBF_2$. To a lesser degree, two stacked molecules of $1 bBF_2$ display similar fusion of the LUMOs at the edge of the parent unit, although the three stacked molecules of this substance do not.

Discussion

Electronic effects of substituents on the absorption and FL properties

Substances $1a-gBF_2$ have nearly identical $\lambda_{AB,Sr}$, $\lambda_{FL,Sr}$, and $\tau_{FL,Sr}$ values in CH_2Cl_2 solutions (Figure 2 and Table 2). Moreover, the optimized structures of $1a-gBF_2$ have almost the same $\lambda_{ET,SO-S1}$ values. These findings clearly show that the electronic effects of substituents on the absorption and FL properties of $1a-gBF_2$ in CH_2Cl_2 are negligible. It is reasonable to assume that substituent electronic effects do not operate significantly in

determining the FL properties of crystals of $1 a - gBF_2$. Thus, the differences observed in the FL properties of $1 a - gBF_2$ in their crystalline states likely originate from differences in the degree and/or manner of intermolecular stacking, which alter intermolecular orbital interactions.

Crystal-packing structures governed by substituents

Molecules in crystals of 1a-gBF₂ are aligned to form continuous stacks in a diagonal direction, except for those of 1 cBF₂, which stack in a lateral direction (Figure 1). Adjacent molecules in crystals of 1 a-gBF₂ are stacked in three types of molecular arrays, classified as type I for 1a-bBF₂, type II for 1c-eBF₂, and type III for 1 f-gBF₂. Because 1 a-bBF₂ possess long alkyl substituents, individual molecules in the crystals of these substances must be separated by relatively large distances. Consequently, molecules of 1 a-bBF₂, representing type I crystals, are stacked in a way that does not allow intermolecular π -orbital overlap of the parent units, but does allow overlap of the alkyl chains and benzene moieties of adjacent molecules. In type II packing structures, which are adopted by crystals of small alkyl substituent containing $1 c-eBF_{2}$, π -stacking exists between benzene moieties of adjacent molecules (B-on-B overlap). Although, similar packing structures with B-on-B overlap are possible for the molecules in crystals of $1 f - gBF_{2}$, in fact severe steric repulsion would exist between the bulky substituents and the dihydrodioxaborinine moieties of adjacent molecules in this type of structure. Therefore, molecules in crystals of 1 fgBF₂ align in a type III fashion, in which the parent units do not overlap with the bulky substituents of the adjacent molecules and continuous π -overlap of the benzene and dihydrodioxaborinine rings (B-on-D overlap) occurs.

Packing-structure-dependent FL properties of crystals

The observation that crystals of $1a-gBF_2$ have longer $\lambda_{FL,C}$ than $\lambda_{FL,S}$ observed for CH₂Cl₂ solutions of these substances is probably a consequence of J-aggregation.^(1,2,34) The $\lambda_{FL,C}$ of $1c-eBF_2$ are longer than those of $1a-bBF_2$ by approximately 20–70 nm (Figure 3 a and Table 2). Although the $\lambda_{FL,C}$ of $1f-gBF_2$ are also longer than those of $1a-bBF_2$, the differences between them are less than 20 nm, suggesting that the crystals of $1f-gBF_2$ resemble those of $1a-bBF_2$ in λ_{FL} . However, the $\tau_{FL,C}$ of $1f-gBF_2$ are more than three times as long as those of $1a-bBF_2$.

Importantly, the results show that the grouped FL properties of **1a–gBF**₂ are well correlated with their grouped crystal-packing structures. Namely, crystals of **1c–eBF**₂, which have the type II packing structure emit at long $\lambda_{FL,C}$ and **1f–gBF**₂, which have type III crystalline structures, have larger $\tau_{FL,C}$ values than those of **1a–bBF**₂, the crystalline structures of which fall into the type I family. Judging from the fact that λ_{EX} associated with the FL emission of **1c–gBF**₂ are longer than those of **1a–bBF**₂, the differences in $\lambda_{FL,C}$ observed between **1a–gBF**₂ are likely a consequence of the degree of J-aggregation, which occurs more effectively in crystals of **1c–gBF**₂ than in those of **1a– bBF**₂. However, further consideration needs to be given to the differences in $\tau_{FL,C}$ of **1a–gBF**₂.



Figure 5. Transition dipole moments related to the S_0 - S_1 electronic transitions estimated for (a) a single molecule and (b) two and (c) three stacked molecules of 1a-gBF₂ with geometries in crystals. Molecular geometries for TD-DFT calculations with B3LYP method and 6-311G(d) basis set were derived from X-ray-determined crystal-packing structures.

Orbital interactions operating in crystals and the corresponding excited species

The $\mu_{\text{S0-S1}}$ values, estimated for three stacked molecules of 1aBF₂ and 1bBF₂, which are in the type I crystal packing group, have directions that are nearly parallel to the long axis of the molecules, and magnitudes (10 D) that are larger than those for the respective single molecules (Figure 5). The results suggest that $\mu_{\text{S0-S1}}$ for continuously stacked molecular arrays of $1\,\mathrm{aBF_2}$ and $1\,\mathrm{bBF_2}$ are simply the sum of the $\mu_{\mathrm{S0-S1}}$ values for the individual molecules contained in the arrays.^[2] Moreover, the HOMOs and LUMOs for the two and three stacked molecules in the arrays of 1 aBF₂ and 1 bBF₂ are not fusions of the LUMOs of the corresponding single molecules. This finding indicates that π -orbital interactions between the parent units of molecules in each array is poor because of the packing features of type I crystals. Therefore, based on the results of calculations, we conclude that the emitting species formed in the type I crystals of 1 aBF₂ and 1 bBF₂ are of the type of excited monomers. This proposal is consistent with the fact that crystals of $\textbf{1} \textbf{aBF}_{2}$ and $\textbf{1} \textbf{bBF}_{2}$ exhibit FL with $\tau_{\text{FL,C}}$ values that are similar to those for FL in CH₂Cl₂ solutions.

In contrast, different FL domains exist in the type II and III crystals as a result of the presence of molecular alignments

that enable intermolecular π -orbital overlap of the parent units. The differences are reflected the distinct FL properties of **1 c–gBF**₂, especially $\lambda_{FL,C}$ and $\tau_{FL,C}$, which differ significantly from those of 1aBF₂ and 1bBF₂. Moreover, FL from 1cBF₂, 1 dBF₂, and 1 eBF₂, which are in the type II crystal group, occurs at long $\lambda_{\text{FL,C}}$, which is indicative of excimer emission. However, $\tau_{FL,C}$ of crystals of 1 cBF_2 , 1 dBF_2 , and 1 eBF_2 (3.5, 3.2, and 1.5 ns, respectively) are much shorter than τ_{FLS} (ca. 50 ns) from the corresponding excimers formed in CH₂Cl₂ at high concentrations. ^[43,45] Moreover, $\tau_{FL,C}$ of type III crystals of **1 fBF**₂ and 1gBF₂ are longer (6.8 and 5.6 ns, respectively) than those of crystalline **1 aBF**₂ and **1 bBF**₂ (both 1.8 ns), although λ_{FLC} of these crystals are nearly identical. Thus, it appears that the excited state species responsible for FL in type II and III crystals are neither excited monomers nor excimer-like, but rather a unique species created by unique intermolecular orbital interactions^[47] arising from the respective *B-on-B* and *B-on-D* overlap. We have termed the novel FL domains in these crystals "excited multimers" (Figure 7),[43,44] where "multimers" refer to ground-state species with "bonding" orbital interactions. A similar terminology "excited oligomer" has recently been proposed by Tohnai and co-workers,^[9] but the phenomenon to which it refers is completely different because "excited multimers" is utilized to designate excited species with "bonding"



stance cannot be categorized by employing the terminology presented above. However, the existence of intermolecular orbital interactions in the crystalline molecular array of 1cBF2 is strongly suggested by the LUMO fusion (Figure 6) seen for three stacked molecules in the array. The lack of LUMO fusion in two and three stacked molecules of 1 eBF₂ is likely a consequence of the uniquely large $D_{\rm F}$ of this substance. However, the existence of intermolecular orbital interactions in crystals of 1eBF₂ is strongly suggested by the experimentally determined $\lambda_{FL,C}$, which is larger than those of 1aBF₂ and 1 bBF₂, which do not exhibit intermolecular orbital interactions in their crystalline state. In the cases of 1 fBF₂ and 1 gBF₂ (type III), the magnitudes of μ_{so-s1} estimated for three stacked molecules in the arrays are much smaller than those for the respective single molecules (Figure 5). Furthermore, significant fusion takes place in the HOMOs and LUMOs for the two and three stacked molecules of 1 fBF₂ and 1 gBF₂. Consequently, continuously stacked molecular arrays in the type III crystals of 1 fBF₂ and 1 gBF₂ enable intermolecular orbital interactions that are responsible for the formation of "excited multimers".

The results of TD-DFT calculations reveal that $\lambda_{\text{ET,SO-S1}}$ for single **1a–gBF**₂ molecules are nearly identical (Figures 4 and 5 and Table 3). Although $\lambda_{\text{ET,SO-S1}}$



Figure 6. Distributions of the HOMOs and LUMOs estimated for (a) a single molecule, and (b) two and (c) three stacked molecules of $1 a-gBF_2$ with geometries in crystals. Molecular geometries for single-point calculations with B3LYP method and 6-311G(d) basis set were derived from X-ray-determined crystal-packing structures. Iso value = 0.01.

orbital interactions, whereas the "excited oligomers" relates to excited species with "nonbonding" π -orbital interactions.

The magnitudes of the μ_{S0-S1} values estimated for the three stacked molecules of $1 \, dBF_2$ and $1 \, eBF_2$ (type II) are nearly equal to those for the respective single molecules (Figure 5). Moreover, the directions of μ_{S0-S1} for three stacked molecules of $1 \, dBF_2$ and $1 \, eBF_2$ are at oblique angles with respect to the long-axis direction of the molecule. These findings strongly suggest that μ_{S0-S1} for the continuously stacked molecular arrays of $1 \, dBF_2$ and $1 \, eBF_2$ are indicative of intermolecular orbital interactions that enable formation of "excited multimers". Owing to the unique way in which molecules of $1 \, eBF_2$ pack in the crystalline state (type II), the μ_{S0-S1} estimated for this subvalues for **1**aBF₂ and **1**bBF₂ (type I) do not show marked changes when the number of molecules in the arrays increase, the values for **1**cBF₂, **1**dBF₂, and **1**eBF₂ (type II) become larger upon increasing in the number of molecules in the arrays. On the other hand, f_{50-51} values for these crystals become smaller with increasing the number of molecules, whereas $\lambda_{ET,50-51}$ for **1**fBF₂ and **1**gBF₂ (type III) get longer.

The results indicate that S_0-S_1 electronic transitions, arising from intermolecular π -orbital interactions caused by *B-on-B* overlap in type II crystals, are "allowed" whereas those resulting from *B-on-D* overlap in type III crystals are "forbidden" (Figure 7), which is probably due to symmetry reasons. This explanation is consistent with the fact that the type II crystals ex-

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Figure 7. Summarized illustration for emissive species of $1a-gBF_2$ in CH_2Cl_2 and in crystals, in which the strengths of orbital interactions and the S_0-S_1 electronic transitions were governed by the geometry of substituents.

hibit FL at longer $\lambda_{FL,C}$ compared with those of type I crystals, and that type III crystals do not exhibit FL at long $\lambda_{FL,C}$. As S_0-S_1 electronic transitions are forbidden in the type III crystals, S_0-S_n ($n \ge 2$) transitions should be dominant and may lead to FL emission with long $\tau_{FL,C}$ compared with that observed in types I and II crystals.

Further evidence supporting the proposal that intermolecular π -orbital interactions govern the FL properties in the crystalline state comes from the observation of a linear relationship between melting points and the energies associated with S_0-S_1 electronic transitions ($E_{ET,S0-S1}$), which were calculated from $\lambda_{ET,S0-S1}$, estimated for three stacked **1a-gBF**₂ molecules



Figure 8. (a) The relationship between melting point (mp) and $E_{EPS0-S1}$ estimated for three stacked molecules of $1 a-gBF_2$ with geometries in crystals. (b) The relationship between melting point (mp) and E_{FLC} of $1 a-gBF_2$ in crystals. $1 aBF_2$ (black), $1 bBF_2$ (gray), $1 cBF_2$ (orange), $1 dBF_2$ (red), $1 eBF_2$ (green), $1 fBF_2$ (blue), and $1 gBF_2$ (purple).

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with X-ray-determined geometries (Figure 8a). This relationship is in accord with the general tendency that melting points of organic compounds become higher when intermolecular attractive forces, such as those arising from bonding orbital interactions, become larger in crystals.^[51-54] Thus, the relationship suggests that intermolecular orbital interactions elongate $\lambda_{FL,C}$ of $1a-gBF_2$. Note that the S_0-S_1 electronic transitions in the molecular arrays of 1 fBF₂ and 1 gBF₂ do not contribute to the FL emission because they are forbidden. Thus, other allowed S_0-S_n transitions are involved in FL emission of 1 fBF₂ and 1 gBF₂. In fact, melting points and experimentally determined ener-

gies for fluorescence emission of $1a-gBF_2$ in crystals ($E_{FL,C}$), which were calculated from $\lambda_{FL,C}$, also show linear relationships, except in the cases of $1 fBF_2$ and $1 gBF_2$ (Figure 8 b).

Conclusion

In the investigation described above, a relationship was observed between the crystal-packing structures and FL properties of crystals of various alkyl- and silyl-substituted dibenzoylmethanatoboron difluoride derivatives, 1 a-gBF₂. The results of this comprehensive study reveal that the crystal-packing structures of these substances can be classified into three groups, referred to as type I, II, and III, and that the structures are governed by the geometry of the substituents. No intermolecular orbital overlap of the parent unit exists in type I crystals. In contrast, type II and type III crystals are comprised of continuously stacked molecular arrays, with the former having "B-on-B overlap" and the latter "B-on-D overlap". The FL properties of 1 a-gBF₂ crystals are affected by the nature of their packing structures. The FL domain of type I crystals (1 a-bBF₂) is excited-monomer-like, owing to the absence of intermolecular orbital interactions. As a result, type I crystals emit FL with λ_{FLC} of 450–456 nm and τ_{FLC} of approximately 1.8 ns. The τ_{FLC} values are similar to those at low concentrations in CH₂Cl₂ solutions. In the case of type II crystals (1 c-eBF₂), B-on-B overlap results in the formation of novel electronically excited molecular arrays that we term "excited multimers", which have allowed S₀-S₁ electronic transitions as a result of intermolecular orbital interactions in the ground state. As a result, type II crystals show FL with λ_{FLC} of 476–518 nm and τ_{FL} of 1.5–3.5 ns, which are larger values than those for the type I crystals. Finally, excited species of type III crystals (1 f-gBF₂) have B-on-D overlap and are longer lived "excited multimers", which are associated with $S_0 - S_n$ (n > 2) electronic transitions as the $S_0 - S_1$ transition is forbidden. As the S_0-S_1 electronic transition is not involved in



the FL emission, the $\lambda_{FL,C}$ of type III crystals are 467–469 nm, which are smaller values than those for the type II crystals. Moreover, the participation of S₀–S_n transitions may lead to the FL with long τ_{FL} of 5.6–6.8 ns. The insight gained in this effort concerning the novel "excited multimer" FL domain could shed light on ways to manipulate FL properties through changes in the nature of molecular aggregation.

Experimental Section

General

Melting points were measured by using a Rigaku Thermo plus EVO II/DSC8230 differential scanning calorimeter. The X-ray diffraction data for the crystals were collected by using a Rigaku RAXIS-RAPID diffractometer and were refined by using SHELX^[48] and Yadokari-XG 2009^[49] programs. UV/Vis absorption spectra were recorded by using a JASCO V-570 spectrophotometer. FL spectra were recorded by using a JASCO FP-8500 spectrophotometer. The $\tau_{\rm FL}$ values were determined by using a HORIBA Jobin Yvon FluoroCube lifetime spectrofluorometer and analyzed by DAS6 FL decay analysis software. The absolute $\Phi_{\rm FL}$ values were determined by utilizing the integrating sphere method with a Hamamatsu Photonics C9920–02 absolute photoluminescence quantum yields measurement system.

Preparation of organic substances

Diaroylmethanes **1**a–gH, possessing two alkyl or trimethylsilyl groups, were prepared by using Claisen condensation reactions between the corresponding 4-substituted methyl benzoate and 4'-substituted acetophenone. Treatment of **1**a–gH with BF₃·OEt₂ gave the corresponding BF₂ complexes **1**a–gBF₂.^[43,45]

X-ray crystallographic analysis

X-ray crystallographic analyses were performed on single crystals of **1a–gBF**₂, which were obtained by recrystallization from benzene or toluene. CCDC1412042–1412048 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Crystal data for C₂₃H₂₇O₂BF₂ (1 aBF₂): Pale yellow needles, 1.0× 0.5×0.2 mm³, monoclinic, C2/c, *a*=17.257(4), *b*=6.9753(14), *c*= 17.605(4) Å, β=93.218(5)°, V=2115.8(8) Å³, Z=4, ρ_{calcd}= 1.206 g cm⁻³, μ=0.086 mm⁻¹, Mo_{Kα} radiation, λ =0.71070 Å, *T*= 298 K, 2θ_{max}=55.0°, 9801 reflections measured, 2408 unique reflections, *R*_{int}=0.103, 129 parameters, *R*₁=0.081 (*l*>2σ*l*), *wR*₂=0.234 (all data), CCDC-1412048.

Crystal data for $C_{21}H_{23}O_2BF_2$ (1bBF₂): Pale yellow needles, 0.8× 0.3×0.2 mm³, monoclinic, C2/*c*, *a* = 16.8514(15), *b* = 6.8712(5), *c* = 15.9835(17) Å, β = 93.412(4)°, *V* = 2115.8(8) Å³, *Z* = 4, ρ_{calcd} = 1.281 g cm⁻³, μ = 0.093 mm⁻¹, Mo_{Kα} radiation, λ = 0.71070 Å, *T* = 298 K, 2 θ_{max} = 55.0°, 8690 reflections measured, 2103 unique reflections, R_{int} = 0.068, 120 parameters, R_1 = 0.054 (*l* > 2 σl), wR_2 = 0.186 (all data), CCDC-1412045.

Crystal data for $C_{19}H_{19}O_2BF_2$ (1 cBF₂): Pale yellow platelets, 0.8× 0.5×0.3 mm³, orthorhombic, *Pnma*, *a* = 12.5719(12), *b* = 17.2908(19), *c* = 7.9430(7) Å, *V* = 1726.6(3) Å³, *Z* = 4, $\rho_{calcd} = 1.262 \text{ g cm}^{-3}$, $\mu = 0.094 \text{ mm}^{-1}$, MO_{Ka} radiation, $\lambda = 0.71070 \text{ Å}$, *T* = 298 K, $2\theta_{max} = 55.0^{\circ}$, 15820 reflections measured, 2014 unique reflections, $R_{int} = 0.083$, 118 parameters, $R_1 = 0.086$ (*I* > 2 σ *I*), $wR_2 = 0.297$ (all data), CCDC-1412047.

Crystal data for $C_{17}H_{15}O_2BF_2$ (1 dBF₂): Yellow blocks, $0.8 \times 0.6 \times 0.2 \text{ mm}^3$, monoclinic, *C2/c*, *a* = 15.3182(13), *b* = 7.0036(5), *c* = 13.5957(10) Å, β = 95.440(2)°, *V* = 1452.01(19) Å³, *Z* = 4, ρ_{calcd} = 1.386 g cm⁻³, μ = 0.105 mm⁻¹, Mo_{Ka} radiation, λ = 0.71070 Å, *T* = 93.1 K, $2\theta_{max}$ = 55.0°, 6790 reflections measured, 1645 unique reflections, R_{int} = 0.026, 102 parameters, R_1 = 0.047 (*I* > 2 σ *I*), *wR*₂ = 0.149 (all data), CCDC-1412043.

Crystal data for C₂₁**H**₂₃**O**₂**BF**₂ (1e**BF**₂): Yellow needles, $1.0 \times 0.5 \times 0.1 \text{ mm}^3$, monoclinic, C2/*c*, *a*=21.794(3), *b*=7.0013(13), *c*= 16.034(3) Å, *β*=129.094(6)°, *V*=1898.9(5) Å³, *Z*=4, *ρ*_{calcd}= 1.246 g cm⁻³, μ =0.091 mm⁻¹, Mo_{Kα} radiation, λ =0.71070 Å, *T*= 298 K, 2θ_{max}=55.0°, 8709 reflections measured, 2150 unique reflections, *R*_{int}=0.092, 121 parameters, *R*₁=0.070 (*I*>2σ*I*), *wR*₂=0.234 (all data), CCDC-412046.

Crystal data for C₂₃H₂₇O₂BF₂ (1 fBF₂): Pale yellow platelets, $1.0 \times 0.5 \times 0.4 \text{ mm}^3$, monoclinic, C2/c, a = 29.455(3), b = 7.0775(6), c = 10.4286(8) Å, $\beta = 104.082(3)^\circ$, V = 2108.7(3) Å³, Z = 4, $\rho_{calcd} = 1.210 \text{ g cm}^{-3}$, $\mu = 0.086 \text{ mm}^{-1}$, MO_{Kα} radiation, $\lambda = 0.71070$ Å, T = 298 K, $2\theta_{max} = 55.0^\circ$, 9679 reflections measured, 2387 unique reflections, $R_{int} = 0.074$, 131 parameters, $R_1 = 0.061$ ($I > 2\sigma I$), $wR_2 = 0.194$ (all data), CCDC-1412042.

Crystal data for C₂₁H₂₇O₂BF₂Si₂ (1 gBF₂): Pale yellow platelets, 0.6× 0.3×0.1 mm³, monoclinic, C2/*c*, *a*=29.625(5), *b*=7.2557(15), *c*= 10.8706(18) Å, β =103.918(4)°, *V*=2268.0(7) Å³, *Z*=4, ρ_{calcd} = 1.220 g cm⁻³, μ =0.186 mm⁻¹, Mo_{Ka} radiation, λ =0.71070 Å, *T*= 298 K, 2 θ_{max} =55.0°, 10636 reflections measured, 2546 unique reflections, *R*_{int}=0.194, 131 parameters, *R*₁=0.085 (*l*>2 σ *l*), *wR*₂= 0.248 (all data), CCDC-1412044.

Measurement of UV/Vis absorption and FL spectra

UV/Vis absorption spectra were recorded for approximately 0.5×10^{-5} M CH₂Cl₂ solutions of 1 a-gBF_2 . FL spectra were recorded by using the same solutions and crystals of these substances with a λ_{EX} of 365 nm. Analyses of time-dependent changes of FL intensities in CH₂Cl₂ solutions and in crystals were carried out by using first- and multi-order fittings to give τ_{FLS} and τ_{FLC} respectively.

Computational methods

Theoretical studies were carried out by using the Gaussian 09 program.^[47] Geometry optimizations for **1a–gBF**₂ were carried out by DFT calculations with the B3LYP method and a 6–311+G(d) basis set. Single-point calculations for a single molecule or two or three stacked molecules in geometries derived from the X-ray-determined packing structures were performed with a 6–311G(d) basis set to determine $E_{\rm H}$ and $E_{\rm L}$. Electronic transitions associated with a single molecule or two or three stacked molecules were estimated by using TD-DFT calculations with a 6–311G(d) basis set.

Acknowledgments

A.S. and M.T. are grateful for financial support in the form of a Grant-in-Aid for JSPS Fellows from the Japan Society for the Promotion of Science (Nos. 25·10489 and 26·11802, respectively). E.O. acknowledges financial support from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan, in the form of a Grant-in-Aid for Young Scientists (B) (No. 24750044) and the Challenging Exploratory Research (No. 26620034). K.M. is grateful for financial support from MEXT, Japan in the form of a Grant-in-Aid for Scientific Research (C)

Chem. Eur. J. 2015, 21, 18128 – 18137



(No. 23550058). H.I. acknowledges financial support from MEXT, Japan in the form of a Grant-in-Aid for Scientific Research on Priority Areas 'New Frontiers in Photochromism' (Nos. 20044027 and 21021025 in the Area No. 471), Innovative Areas ' π -Space' (Nos. 21108520 and 23108718 in the Area No. 2007), and Stimuli-Responsive Chemical Species (No. 24109009), the Scientific Research (B) (Nos. 20044027 and 23350023), and the Challenging Exploratory Research (Nos. 21655016 and 24655037).

Keywords: aggregation • electronic structure • fluorescence spectroscopy • organoboron complexes • solid-state structures

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Received: August 8, 2015 Published online on November 9, 2015

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