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# Solid-emissive boron-fluorine derivatives with large Stokes shift

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## ABSTRACT

Novel BOPIM (boron 2-(2'-pyridyl)imidazole complex) derivatives with large Stokes shift were efficiently synthesized through two-step reactions, starting from commercially available 2-pyridinecarboxaldehyde and  $\alpha$ -diketone. The dyes exhibit high fluorescent intensity in solution and also in solid state due to the intermolecular non-planar interactions. According to X-ray single crystal measurements, the non-covalent interactions (such as C–H···F–B, etc.) play important role in inhibiting planar  $\pi$ – $\pi$  stacking, and the existence of terminal phenyl rings increases the electronic density of  $\pi$  system, which facilitates the charge transfer from the electron-donating  $\pi$  system to the electron-accepting boron moiety. DFT calculation based on X-ray crystallographic analysis was carried out for compound **2**, giving consistent results with photophysical measurements.

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## 1. Introduction

Fluorescent dyes continue to be developed because of their utilities in various research fields, and the many important applications in advanced science and technology.<sup>1</sup> In recent years there has been increased investigation of organic boron-fluorine complexes as fluorescent dyes, especially BODIPY dyes. These compounds exhibit a large number of advantages over other dyes, such as high fluorescence quantum yield and absorption coefficient, excellent chemical- and photochemical-stability, long excited-state lifetimes, a large two-photon cross-section for multiphoton excitation, good solubility, and narrow emission spectra, which may result in attractively high color purity. However, typical BODIPY dyes have two serious disadvantages: propensity to self-quenching and small Stokes shift.<sup>1c,2</sup> The high structural planarity allows them to pack closely in solid state or similar aggregates, resulting in concentration-induced fluorescence quenching; whereas, the small Stokes shift allows reabsorption of the emission, resulting in lowered fluorescence intensity. Dyes with solid-emissive properties and large Stokes shifts are actually very important for practical applications, such as photoelectric conversion,<sup>3</sup> OLED,<sup>4</sup> and molecular switches.<sup>5</sup> But only a limited number of organic solidemissive BODIPYs have been reported, and practical applications of BODIPYs in photoelectric conversion and electroluminescence materials are rare.<sup>6</sup> In order to obtain solid-emissive BODIPYs with large Stokes shift, some efforts have been made to decrease the energy lost via non-radiative decay processes.<sup>7</sup> One promising strategy is to introduce bulky groups into the BODIPY core structure to hinder close stacking of the chromophore.<sup>8</sup> There is also evidence that rigidification of the chromophore can enlarge the Stokes shift.<sup>9</sup> However, further work is needed to produce high performance solid-emissive BODIPY dyes.

Recently, it was reported that the molecules with intermolecular interactions (such as C-H…F-B, C-H…O, C…C, and C…N) can emit fluorescence in the solid state, even though those molecules have close lattice packing and no rigid side chains.<sup>10</sup> Some BODIPY derivatives can even crystallize in different forms to emit different fluorescence.<sup>10c,11</sup> In these cases, the strategy of molecular design is to use modified structures with non-pyrrole-based ligands to alleviate stacking-induced fluorescence quenching, and facilitate an efficient intramolecular charge transfer (ICT) process that increases the Stoke shift. With these factors in mind, we have designed a new class of boron 2-(2'-pyridyl)imidazole complexes (BOPIMs), and found that they exhibited a large Stokes shift.<sup>12</sup> However, terminally attached groups would affect the electronic environment of the chromophore core, which may affect ICT process and induce photophysical change of BOPIM dyes. In this report, we extend our work, by describing the synthesis, X-ray single structures, and photophysical properties of two BOPIM dyes with a different number of phenyl rings as electron-donating groups.



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## 2. Results and discussion

## 2.1. Design and synthesis

2-(2'-Pvridvl)imidazole was adopted to coordinate with boronfluoride to form the BOPIM chromophore. In order to inhibit intermolecular planar  $\pi - \pi$  interactions, which would result in aggregate formation, phenyl rings were introduced at the end as bulky steric groups and also act as electron-donating groups. On the one side, the steric groups can prohibit the free rotation of phenyl ring around the  $\delta$  bonds to reduce the energy lost. On the other side, electron-rich phenyl rings extend the  $\pi$  system, which would facilitate the charge-transfer transition. These two compounds were synthesized by standard method starting from commercially available 2-pyridinecarboxaldehyde and  $\alpha$ -diketone, according to previously reported procedure as listed in Scheme 1.<sup>13</sup> After treatment with  $BF_3 \cdot Et_2O$  under basic condition, compounds 1 and 2 were obtained as yellow solids with moderate yield (25% and 32%, respectively) after purification by column chromatography. These two compounds have been characterized thoroughly by <sup>1</sup>H NMR, <sup>13</sup>C NMR, HRMS, and X-ray single crystallographic analysis.

## 2.2. Single X-ray crystallography

X-ray single crystal measurement for compound **1** indicates that the phenyl ring at the end of imidazole ring can rotate freely around the C–C  $\delta$  bond, even under low temperature (liquid nitrogen). It's not surprising since there is no much steric hindrance for this phenyl ring. However, intermolecular non-covalent interactions (C1-H1···N3: 2.470 Å, C7-H7···B1: 2.706 Å) are apparent to provide a rigid structure in crystal state (Fig. 1). These non-covalent interactions of BOPIMs can be more clearly elaborated in the crystal structure of compound 2. Moreover, there is almost no overlap between intermolecular chromophore cores. The hindrance of intermolecular overlap of the chromophores is mainly due to the twisted benzene rings on the end of the chromophore. Meanwhile, the F–B–F group acts as a bifurcated acceptor with an angle of 111.7°, and F1 atom forms C–H…F–B contact with the neighboring donor molecule (C-H…F: 3.24 Å, 151°). However, F2 interacts with C2, C3 on pyridine ring to form triangle structure with 3.11 and 3.15 Å, respectively. Due to these non-covalent interactions, aggregate formation through planar  $\pi - \pi$  stacking is inhibited.

## 2.3. Photophysical properties

The absorption and emission data of compounds **1** and **2** in various solvents were listed in Table 1. Compared to typical BODI-PYs with insensitivity to environment, these two BOPIM dyes exhibit significant solvent-dependent properties, known as 'solvatochromism'. As revealed from UV–vis absorption spectra, both of these two dyes show multiple absorptive bands in all organic solvents and the absorption bands shift significantly to solvent polarity (Fig. 2A, D). In non-polar solvents such as hexane, the dyes show the longest absorptive wavelength. The center of the absorption band is located at 412 nm for compound **1** and 427 nm

for compound **2** in hexane referenced to SO-S1 transition, which indicates that the introduction of more electron-donating groups can result in red-shift of the absorption. With increasing of the solvent polarity, absorption bands significantly blue-shift.

The emission properties are more complicated since environment polarity is only one of the influencing factors. For compound **1**, the emission is solvent-dependent. The longest wavelength of emissive bands is observed at 514 nm in acetonitrile, while the shortest emission wavelength is observed in cyclohexane (486 nm). Quite different behavior was observed for compound 2, although there is no big structural difference between these two dyes. The longest wavelength of emissive bands is at 537 nm in THF, while the shortest emission wavelength is at 498 nm in acetonitrile. This means that the phenyl rings at the end of imidazole contribute a lot for the fluorescence of these dyes, which is also proved by comparison of these two dyes to BOPIMs with no phenyl rings.<sup>12</sup> The effect of terminal groups on their photophysical properties can be explained by ICT mechanism. Photoexcitation of a 'push-pull'  $\pi$ electron system will generate an electric field with the positive pole at electron donor region and negative pole at acceptor. BOPIM 1 has one phenyl ring as electron donor, which can rotate freely along the  $C-C \delta$  bond. In polar solvent, the emission is mainly from twisted intramolecular charge transfer. In contrast, the presence of two twisted phenyl rings in 2 prohibits their rotation due to the steric effect, resulting in a different solvent-dependent emission character with that of **1**.

It's observed that the fluorescence quantum yields in polar solvent are significantly lower than those in apolar solvents for both dyes. Since there is no sign of aggregate formation as revealed by concentration-dependent fluorescent spectra (Fig. 2C, F), the low quantum yield in polar solvent is mainly due to the strong intramolecular charge transfer characteristics. And for compound 2, aggregate-induced fluorescent quenching is much less than that of compound **1** as expected, indicating that the steric effect plays important role to prevent aggregation. These two dyes also exhibit less intense fluorescence in polar solvents due to ICT characteristics, which results in red-shift of the emission in polar solvent. The sensitive photophysical response to media, along with the high fluorescence yield will make BOPIM dyes suitable sensors for communicating local environmental properties. On the other hand, large Stokes shifts (>75 nm) in all the studied solvents were observed for synthesized BOPIMs, which would induce suppression of Forster-type energy transfer, thus helps to alleviate concentrationinduced emission quenching. Especially in polar solvents, the observed Stokes shifts are more than 120 nm. Such big Stokes shifts were rarely reported for boron chelates till now.<sup>10,14</sup> Since fluorescent probes are regularly applied in biological environment, BOPIMs with large Stokes shifts in polar condition are of popular interest for bio-imaging study.

It's interesting to note that these two compounds are highly fluorescent in solid state and in crystals. In the solid film prepared by evaporation of a concentrated THF solution, the SO–S1 transition band in absorption turns slightly broader. The intense emission peaks were observed at 513 nm for **1**, and 524 nm for **2**. However, the emissions become narrower compared to those in chloroform





Fig. 1. Single crystal structures, intermolecular interactions of compounds 1 and 2.



Dye	Solvent	UV		$\lambda_{em}$ (nm)	ν (nm)	$\Phi_{\rm F}$
		$\lambda_{abs}$	ε			
1	Hexane	327	24,580	487	75	0.32
		412	26,500			
	Cyclohexane	329	24,120	486	74	0.33
		412	26,550			
	THF	312	22,270	509	115	0.22
		394	27,350			
	Chloroform	369	24,220	501	132	0.24
	Dioxane	312	23,080	509	115	0.24
		394	27,140			
	Acetonitrile	298	20,170	514	130	0.21
		384	25,300			
	Methanol	297	20,550	503	121	0.17
		382	28,050			
	Solid	393	~	513	120	0.12
2	Hexane	278	15,630	515	88	0.30
		338	14,880			
		427	23,480			
	Cyclohexane	277	14,910	517	88	0.34
		339	14,410			
		429	24,390			
	THF	310	14,110	537	130	0.17
		404	17,200			
	Chloroform	268	20,370	528	140	0.30
		388	35,560			
	Dioxane	273	16,580	510	123	0.26
		387	50,390			
	Acetonitrile	363	28,610	498	135	0.19
	Methanol	264	16,380	534	143	0.10
		291	18,690			
		391	19,900			
	Solid	402	~	524	122	0.18

solution (Fig. 3), which is quite unusual and exciting because typical dyes exhibit spectral broadening in solid state. It needs to note that there appears two emissive peaks for compound **1** in solid state (Fig. 3A), due to a minimal aggregate formation, while this phenomenon is not observed at all for BOPIM **2**, indicating that the existence of two steric bulky groups is essential for efficient aggregate prohibition. Because of the aggregate prohibition, both dyes emit high fluorescence in solid state, and also in crystal state. As can be seen from Fig. 4, intense fluorescence was observed in amorphous powder and also in a single crystal under 365 nm light irradiation for both dyes. In fact, the fluorescent intensity is so high that it even can be visibly seen under day-light excitation. The

absolute fluorescent quantum yield of **1** and **2** in solid film is estimated to be 0.12 and 0.18 by integrating sphere method, which makes them ideal solid-emitting materials for various applications. The lower fluorescent quantum yield of **1** compared to **2** is mainly due to the fast rotation of the phenyl ring and less electron density. The solid-emissive property is the result of the abnormal noncovalent intermolecular interactions, which inhibits the concentration-induced quenching, as proved by X-ray single crystal analysis and fluorescence measurement.

## 2.4. DFT calculation

To better understand the correlation of spectra and electron properties, molecular orbital calculations for compound **2** were carried out on the density functional theory (DFT) level employing the Gaussian 03 programs. Geometric parameters from X-ray diffraction analysis were used for the calculation (Fig. 5). It indicated that the HOMO distribution was donated by all atomic orbitals in the aromatic rings, while LUMO was mainly contributed by the part of BOPIM chromophore. Therefore, efficient intramolecular charge transfer (ICT) process could be a key factor for large Stokes shift and solvent-reliant photophysical properties.<sup>15</sup>

## 3. Conclusions

In conclusion, we synthesized two novel BOPIM derivatives, starting from simple ligands reported previously. The dyes exhibit high fluorescent intensity and large Stokes shift in all organic solvents studied. Due to the intermolecular non-planar interactions, which inhibit concentration-induced quenching, they exhibit highly solid-emissive property. And introduction of bulky steric groups is essential for prohibition of aggregate formation. Solidemissive BOPIMs with large Stokes shift will make them suitable candidates for application of OLED, memory, fluorescent probes, etc.

## 4. Experimental section

## 4.1. General

All starting materials were obtained from commercial supplies and used as received. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on Varian or Bruker instrument, using CDCl<sub>3</sub> or DMSO- $d_6$  as solvents. Chemical shifts are reported in parts per million with CDCl<sub>3</sub> or TMS (when DMSO- $d_6$  is adopted as solvent) as reference (in CDCl<sub>3</sub>: 7.26 ppm for <sup>1</sup>H NMR, and 77.0 ppm for <sup>13</sup>C NMR). The fluorescent quantum yield is calculated using anthracene as reference in solution, integrating sphere method in solid state. UV–vis and fluorescent measurements were carried out on Hitachi U-3010 and F-4500, respectively. MS data were recorded on a Waters Quattro Micro API MS spectrometer.

## 4.2. Ligand L1

The synthesis was performed according to previously reported procedure.<sup>13a</sup> <sup>1</sup>H NMR (DMSO- $d_6$ , 300 MHz):  $\delta$  8.61 (d, *J*=3.90 Hz, 1H), 8.12 (d, *J*=7.80 Hz, 1H), 7.90 (m, 3H), 7.75 (s, 1H), 7.38 (t, *J*=7.50 Hz, 3H), 7.22 (t, *J*=7.20 Hz, 1H).

#### 4.3. Ligand L2

The synthesis was performed according to previously reported procedure.<sup>13b</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  8.51 (d, *J*=5.00 Hz, 1H), 8.28 (d, *J*=8.00 Hz, 1H), 7.76 (t, *J*=8.80 Hz, 1H), 7.66 (d, *J*=7.00 Hz, 2H), 7.45 (d, *J*=6.80 Hz, 2H), 7.32 (m, 6H).

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Fig. 2. Absorption, and fluorescent spectra of compound 1 (A, B) and compound 2 (D, E) in various organic solvents (1.0×10<sup>-5</sup> M); concentration-dependent fluorescence in CHCl<sub>3</sub> for compound 1 (C) and compound 2 (F) (Ex: 365 nm).



Fig. 3. Normalized absorption and fluorescent spectra of  ${\bf 1}$  and  ${\bf 2}$  in chloroform solution and in solid state (Ex: 365 nm).



Fig. 4. Bright field images and fluorescent images (under 365 nm light) of compounds 1 (A) and 2 (B) in solid powder and in crystal state.



Fig. 5. Diagrams showing the HOMO and LUMO levels of compound 2.

## 4.4. Synthesis of BOPIMs

Ligand (2.18 mmol) was dissolved in anhydrous dichloromethane (20 mL), followed by addition of triethylamine (4.40 mL) under N<sub>2</sub>. This mixture was cooled by ice, and then  $BF_3 \cdot Et_2O$ (3.50 mL, 27.4 mmol) was added dropwise. Then the reaction mixture was allowed to stir at room temperature overnight. After quenching with water, the organic phase was separated and the aqueous phase was extracted with dichloromethane. The combined organic phases were washed with water, dried on Na<sub>2</sub>SO<sub>4</sub>, and evaporated in vacuo. The crude residue was subjected to a silica gel column to afford target products as yellow solid.

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4.4.1. BOPIM **1**. Yellow solid (28%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  8.46 (d, *J*=4.20 Hz, 1H), 8.18 (t, *J*=7.50 Hz, 1H), 8.00 (d, *J*=7.50 Hz, 1H), 7.82 (d, *J*=6.90 Hz, 2H), 7.59 (s, 1H), 7.47 (m, 3H), 7.33 (t, *J*=6.90 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  144.64, 141.23, 133.38, 129.00, 128.02, 125.79, 122.76, 117.59. HRMS calcd for C<sub>14</sub>H<sub>11</sub>BF<sub>2</sub>N<sub>3</sub> [M+H]<sup>+</sup> 270.1014, found 269.1050.

4.4.2. BOPIM **2**. Yellow solid (32%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  8.43 (d, *J*=5.40 Hz, 1H), 8.16 (m, 1H), 8.09 (d, *J*=7.80 Hz, 1H), 7.60 (m, 4H), 7.46 (m, 1H), 7.36 (m, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  144.68, 141.26, 134.56, 130.66, 128.68, 128.59, 128.34, 128.14, 127.31, 122.78, 117.73. HRMS calcd for C<sub>20</sub>H<sub>15</sub>BF<sub>2</sub>N<sub>3</sub> [M+H]<sup>+</sup> 346.1325, found 346.1315.

#### 4.5. X-ray structures

Single crystals suitable for X-ray analysis were obtained by slow evaporation of mixed organic solvents. These data (CCDC-842917 for **1**, and CCDC-804488 for **2**) can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

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## Supplementary data

<sup>1</sup>H NMR, <sup>13</sup>C NMR spectra of intermediates and BOPIM dyes, X-ray crystallography of the complexes. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2012.04.052.

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