



## Structure–property correlation of solid-emissive boron–fluorine derivatives

Qiong Cao, Shuzhang Xiao\*, Miaofu Mao, Xiaohong Chen, Sa Wang, Ling Li, Kun Zou

Hubei Key Laboratory of Natural Products Research and Development, College of Chemistry and Life Science, China Three Gorges University, Hubei Yichang 443002, PR China

### ARTICLE INFO

#### Article history:

Received 24 May 2012

Received in revised form

21 July 2012

Accepted 26 July 2012

#### Keywords:

BOPIM

Fluorescence

Solid-emission

Supramolecular interaction

Structure–property relationship

### ABSTRACT

A series of solid-emissive BOPIM (boron 2-(2-pyridyl)imidazole complex) dyes, bearing electron-donating or -withdrawing substituents (methoxy, hydrogen, or nitro), are facilely synthesized. The compounds were characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and MS. X-ray single crystal diffractions of BOPIM **1** and **2** indicate that nonplanar rigid structures were formed through intermolecular non-covalent interactions. Due to these non-covalent interactions, these dyes exhibit intense fluorescence in solution and also in solid state. According to  $^1\text{H}$  NMR analysis, electronic effect of the substitutes plays an important role in contribution to these BOPIMs' electronic states. The photophysical measurements reveal that electron-donating groups (methoxy) lead to significant bathochromism of the absorption and emission. In contrast, electron-withdrawing moieties (nitro) play the reverse role. However, BOPIM **3** bearing nitro groups emits long wavelength fluorescence in solid state, probably due to the formation of intermolecular hydrogen bond. This work elucidates the spectroscopic structure–property relationship of solid-emissive BOPIMs, which would be valuable for design of solid-emissive dyes.

© 2012 Elsevier B.V. All rights reserved.

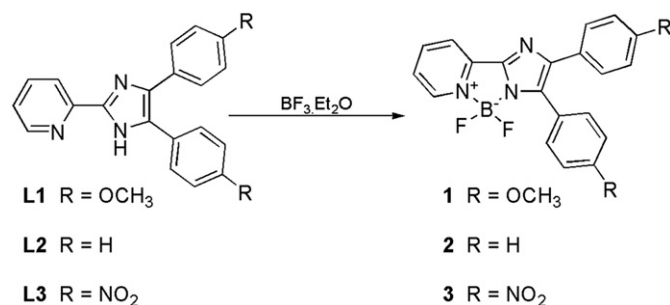
### 1. Introduction

Fluorescent dyes have been under wide research because of their applications in various research fields, especially for these probes sensitive to environment and solvent polarity [1–5]. Among all these chromophores reported till now, organic boron–fluorine complexes (known as BODIPY) attract great interest, due to their large number of advantages over other dyes. They usually have high fluorescence quantum yield and absorption coefficient, excellent chemical- and photochemical-stability, plus a large number of BODIPYs exhibit environment-sensitive properties. However, typical BODIPYs are non-emissive in solid state, due to their high planarity which results in concentration-induced quenching [6–10]. And they usually have small Stokes shift, inducing reabsorption of the emission. To keep BODIPYs' emission in solid state for practical applications in light-emitting devices, it's essential to decrease the aggregate formation due to the  $\pi$ – $\pi$  stacking of the chromophore. Some strategies have proved to be effective, such as attaching bulky groups on BODIPY core structure to inhibit intermolecular planar  $\pi$ – $\pi$  interaction [11–14], introducing rigid side chain on the chromophore core to enlarge the Stokes shift [15]. Recently it's found that boron–fluorine derivatives with intermolecular interactions (such as  $\text{C–H}\cdots\text{F–B}$ ,  $\text{C–H}\cdots\text{O}$ ,  $\text{C}\cdots\text{C}$  and  $\text{C}\cdots\text{N}$ )

can emit fluorescence in solid state with large Stokes shift, even though these molecules have neither bulky groups nor rigid side chains [16–21]. And the large Stokes shift is the result of efficient intramolecular charge transfer (ICT) from electron-rich groups to electron-accepting BOPIM skeleton. In these molecules, intermolecular non-covalent interactions provide a comparatively rigid structure, which exhibit non-planar packing mode. Boron 2-(2'-pyridyl)imidazole complex (BOPIM) is one class of these samples, which exhibit no aggregate in concentrated solution according to concentration-dependent fluorescence measurement [22]. And they emit intense fluorescence both in solutions and also in solid state with large Stokes shift [23–25]. The synthesis is facile, and the chromophore can be easily functionalized, which make it ideal candidate for construction of functional materials. However, the introduction of electron donating and withdrawing substituents to these conjugated groups can significantly change the electronic environment of the chromophore core, resulting in shift of the emission wavelength [3,26]. In this way, emission of BOPIMs may be tuned by attaching different electron-donor or acceptor. So it's necessary to investigate qualitatively the effect of chemical structure and substituent groups on fluorescence characteristics, concerning fluorescence intensity, emission wavelength, Stokes shift, etc. In this report, three solid-emissive BOPIM dyes are synthesized, bearing different electron-donating or -withdrawing groups (Scheme 1). Then we study their photophysical properties to elucidate the relationship between the chemical structure and the photophysical properties.

\* Corresponding author. Tel./fax: +86 717 6397478.

E-mail address: [shuzhangxiao@gmail.com](mailto:shuzhangxiao@gmail.com) (S. Xiao).



Scheme 1. Synthesis of BOPIM dyes.

## 2. Experimental

### 2.1. Materials

The corresponding ligands for synthesis of BOPIM dyes are prepared according to literature procedures [27]. BF<sub>3</sub>·OEt<sub>2</sub> is purchased from Aldrich. All other starting materials are obtained commercially as analytical-grade and without further purification. Moisture sensitive reactions were performed under an atmosphere of nitrogen. Anhydrous dichloromethane was obtained by distillation of commercial analytical-grade dichloromethane after treated with molecular sieve.

### 2.2. Measurements

<sup>1</sup>H NMR and <sup>13</sup>C NMR were recorded on Bruker 400 NMR or Varian 300 Mercury spectrometer. Chemical shifts are reported in parts per million with CDCl<sub>3</sub> as reference (7.26 ppm for <sup>1</sup>H NMR, and 77.0 ppm for <sup>13</sup>C NMR). MS data were recorded on a Waters Quattro Micro API LC-MS spectrometer (Waters, USA) or Applied Biosystems Voyager-DE STR mass spectrometer. UV–vis and fluorescent spectra were obtained on Hitachi U-3010 and F-4500, respectively. The fluorescent quantum yield is calculated using quinine bisulfate as reference. Single crystals suitable for X-ray measurements were obtained by slow evaporation of mixed organic solutions, and single-crystal X-ray diffraction data were collected on a Bruker APEX II CCD diffractometer with graphite monochromated Mo K α radiation (λ = 0.71073 Å) at 298 K.

### 2.3. Synthesis

The typical synthetic procedure of BOPIMs was described as following: in a stirred mixture of ligand (8 mmol) and Et<sub>3</sub>N (5 ml) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (25 mL), BF<sub>3</sub>·OEt<sub>2</sub> (5.6 mL, 44 mmol) was added dropwise at 0 °C. After the addition of BF<sub>3</sub>·OEt<sub>2</sub>, the reaction mixture was allowed to warm to room temperature and stir at room temperature overnight. The organic phase was washed with water several times, dried on Na<sub>2</sub>SO<sub>4</sub>, and evaporated in vacuo. Then the obtained crude residue was subjected to column chromatography on a silica gel column to provide products as solid.

#### 2.3.1. BOPIM 1

Orange solid (30%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 8.42 (d, J = 5.60 Hz, 1H), 8.16 (t, J = 7.60 Hz, 1H), 8.06 (d, J = 8.00 Hz, 1H), 7.55 (m, 4H), 7.46 (t, J = 5.60 Hz, 1H), 6.92 (m, 4H), 3.84 (s, 3H), 3.82 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 159.41, 158.85, 145.81, 144.85, 144.53, 141.18, 133.76, 129.98, 129.30, 127.42, 123.30, 122.35, 117.47, 114.06, 113.77, 55.20. MS [M + H]<sup>+</sup>: 406.2 calcd. 406.1.

#### 2.3.2. BOPIM 2

Yellow solid (32%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 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) δ 144.68, 141.26, 134.56, 130.66, 128.68, 128.59, 128.34, 128.14, 127.31, 122.78, 117.73. MS [M + H]<sup>+</sup>: 346.1 calcd. 346.1.

#### 2.3.3. BOPIM 3

Yellow solid (20%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 8.59 (m, 1H), 8.31 (m, 2H), 8.29 (m, 1H), 8.24 (m, 2H), 7.85 (m, 3H), 7.68 (m, 2H), 7.36 (m, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 149.03, 147.40, 147.25, 137.52, 128.41, 124.62, 124.23, 124.05, 120.50, 29.70. MS [M+2H]<sup>+</sup>: 437.2 calcd. 437.1.

## 3. Results and discussion

### 3.1. X-ray crystal structure

Crystals suitable for X-ray measurements were obtained by slow evaporation of mixed organic solutions. In the crystal structures of BOPIM 2 [25], intermolecular interactions (such as C–H···N, C–H···B, etc.) provide a rigid structure to inhibit planar π–π stacking in crystal state, which is also found for BOPIM 1 (Fig. 1). It's interesting that the unit cell of BOPIM 1 contains two molecules and they exhibit different intermolecular non-covalent interactions. In the crystal structure of BOPIM 1, F1 atom forms B–F···H–C contact with the methyl protons on the neighboring donor group (2.621 Å). However, F2 atom associates with phenyl proton H16 (2.465 Å), and also H31 on pyridine ring (2.376 Å). The protons on pyridine ring are also active, easily to form hydrogen bond with neighboring atoms, especially with B, F atoms. Thus triangle structure was formed between H1A on pyridine ring with B, and F atoms on neighboring molecule (distance: H1A–F4 2.38 Å, H1A–F3 2.653 Å, H1A–B2 3.009 Å). Although the chromophore containing imidazole and pyridine fused with B was almost planar, there is almost no overlap between neighboring chromophore cores, indicating that planar π–π stacking of the chromophores is inhibited by non-covalent interactions and the steric hindrance from twisted phenyl rings on the end of the chromophore. The solubility of BOPIM 3 in conventional organic solvents is poor, and the efforts to grow single crystal of 3 failed.

### 3.2. <sup>1</sup>H NMR analysis

To investigate the electronic effect of terminally electron donor (methoxy) and acceptor (nitro) on the chromophore, <sup>1</sup>H NMR analysis was carried out as shown in Fig. 2. To make a comparison, BOPIM 2 bearing terminal H atoms is chosen as reference. With electron donors attached (BOPIM 1), significant upfield shift was observed for all the protons on phenyl rings with the largest shift –0.46 ppm for H6, indicating that the existence of electron donor (methoxy group) enriches the electronic density of the phenyl rings, leading to a higher shielding effect on these protons. The protons on the chromophore core were only slightly affected, with upfield shift of resonance signal of H4 0.03 ppm, and H1 0.01 ppm. In contrast, the introduction of nitro group (BOPIM 3) lowers the electronic density of the whole π system on a large scale, and shifts most resonance signals to down-field pronouncedly, especially for these protons on phenyl rings. And the boron center is also highly electron deficient, resulting in the different electronic states of H5 with H5', and also H6 with H6'. These results indicate that the electronic density of the chromophore core can be tuned by the terminally attached electron donors and acceptors. And it needs to note that all the protons on BOPIM 3 exhibit multiple resonances (H1 for example), suggesting that nitro moieties on

Download English Version:

<https://daneshyari.com/en/article/1323138>

Download Persian Version:

<https://daneshyari.com/article/1323138>

[Daneshyari.com](https://daneshyari.com)