

# NJC

Accepted Manuscript



This article can be cited before page numbers have been issued, to do this please use: T. M. H. VUONG, J. Weimmerskirch-Aubatin, J. Lohier, N. Bar, S. Boudin, C. Labbe, F. Gourbilleau, H. NGUYEN, T. T. Dang and D. Villemin, *New J. Chem.*, 2016, DOI: 10.1039/C6NJ00726K.



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



## ARTICLE

## Blue highly fluorescent boron difluoride complexes based on phthalazine-pyridine

Thi Minh Ha Vuong,<sup>a</sup> Jennifer Weimmerskirch-Aubatin,<sup>b</sup> Jean-François Lohier,<sup>a</sup> Nathalie Bar,<sup>a</sup> Sophie Boudin,<sup>c</sup> Christophe Labbé,<sup>b</sup> Fabrice Gourbilleau,<sup>b</sup> Hien Nguyen,<sup>d</sup> Tung Thanh Dang,<sup>d</sup> Didier Villemin.<sup>†a</sup>

Received 00th January 20xx,  
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Three new boron difluoride complexes based on phthalazine-pyridine, denoted **(6)**, **(7)** and **(8)** have been synthesized and their photophysical and electrochemical properties have been studied. Solutions of these new BF<sub>2</sub>-complexes exhibit an intense blue fluorescence under UV at low concentrations. Fluorescence Quantum Yields (QY) have been determined by PhotoLuminescence (PL) spectroscopy and decay times ( $\tau$ ) by semi-empirical methods. QY of **(6)**, **(7)** and **(8)** vary from 25% to 79%. HOMO and LUMO energy levels have been estimated by cyclic voltammetry and PL spectroscopy. The HOMO and LUMO energy levels, at  $\sim$ -5.3 eV and  $\sim$ -2.3 eV respectively, make these new complexes interesting candidates for blue emitters in OLED applications.

### Introduction

The design and synthesis of functionalised aza-BODIPY complexes have attracted a huge interest in diverse research fields<sup>1</sup>. Particularly, aza-BODIPY has been thoroughly investigated to apply in optoelectronic devices such as fluorescent sensors,<sup>2</sup> fluorescent indicators,<sup>3</sup> and fluorescent switches,<sup>4</sup> laser dyes,<sup>5</sup> organic photovoltaic cells<sup>6</sup> and OLEDs.<sup>7</sup> The families of boron complexes are based on N<sup>+</sup>O, C<sup>+</sup>O, and N<sup>+</sup>N chelates rigidified by a boron fragment.<sup>2</sup> There are many types of boron complexes with various rings, the five- and six-membered rings are the most common ones. Among them, the six-membered ring type I boron complexes (scheme 1) have been synthesized by the condensation of pyridine

derivatives with subsequent chelation of the resulting Schiff base.<sup>8</sup> They exhibit weak fluorescent quantum yields in solution due to their vibrational deactivation but important ones in solid state as a result of aggregation-induced emission.<sup>8a, b, e</sup> Most of compounds of type II have been synthesized based on various palladium-catalysed cross-coupling reactions as a key step.<sup>9</sup> Their boron complexes exhibit large Stokes shifts along with high quantum yields both in solution and in solid state.<sup>9a, b, e</sup> In the case of type III complexes, it is difficult to give a synthetic step/procedure for their synthesis because of the different constructions in both sides of the six-membered ring. Interestingly, in this type III,<sup>10</sup> Kobayashi *et al* reported the synthesis of pyrrolopyrrole aza-boron difluoridepyrroles based on modified diketopyrrolopyrroles and azapyrrolopyrroles.<sup>10b, c, g, i</sup> Their important electronic delocalization over the  $\pi$ -conjugated backbone made these boron complexes highly fluorescent in the red and near infrared regions.<sup>10a-c, i</sup> The azaboron diquinomethene complexes<sup>10h</sup> have been reported as highly fluorescent blue and green emitters. Basing on the above-mentioned studies, in this work, we describe the synthesis as well as the photophysical and electrochemical properties of three new pyridine-iminophthalazine chelates of boron (III) synthesized through a new simple procedure.

<sup>a</sup> LCMT, ENSICAEN – CNRS - UNICAEN, 6 boulevard du Maréchal Juin, 14050 Caen, France.

<sup>b</sup> CIMAP, ENSICAEN – CNRS - CEA - UNICAEN, 6 boulevard du Maréchal Juin, 14050 Caen, France.

<sup>c</sup> CRISMAT, ENSICAEN – CNRS - UNICAEN, 6 boulevard du Maréchal Juin, 14050 Caen, France.

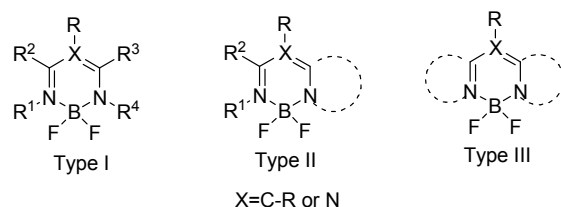
<sup>d</sup> Hanoi University of Education, Faculty of Organic Chemistry, 136 Xuan Thuy Street, Cau Giay District, Hanoi, Vietnam.

<sup>†</sup> Corresponding Author. Email: villemin@ensicaen.fr.

Electronic Supplementary Information (ESI) available: Crystallographic data for the structure reported in this paper have been deposited with Cambridge Crystallographic Data Centre (CCDC) as supplementary publication number (CCDC 1030686) See DOI: 10.1039/x0xx00000x

## ARTICLE

## New Journal of Chemistry

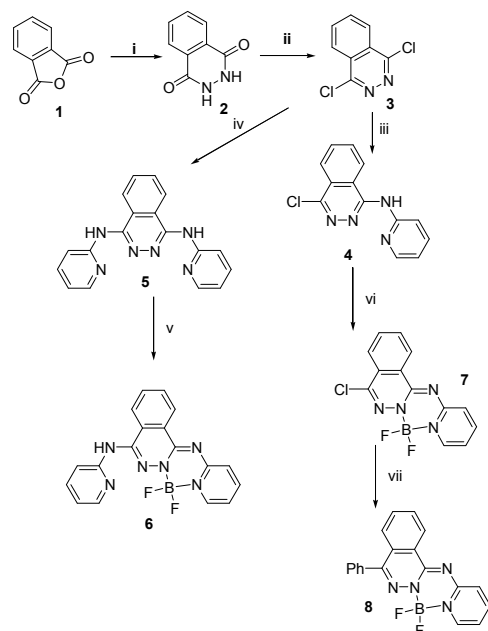


**Scheme 1: Various six-membered rings of *N,N* chelation modes.**

## Results and discussion

### Synthesis

The synthetic approaches for boron (III) complexes are depicted in scheme 2. Two *N,N* bi-dentate ligands (**4**) and (**5**) based on 2-aminopyridine and phthalazine were obtained after three classical steps. The first step is the synthesis of 2,3-*N,N*-dihydrophthalazine-1,4-dione (**2**) by condensation of phthalic anhydride and hydrazine in acetic acid. Continuously, compound (**2**) was reacted with phosphoryl chloride to give 1,4-dichlorophthalazine (**3**). Then, 1-chloro-4-(2'-pyridyl)aminophthalazine (**4**) and 1,4-di(2'-pyridyl)aminophthalazine (**5**) were obtained by suitable equivalent addition of sodium hydride and 2-aminopyridine. By sequential treatment of (**4**) and (**5**) with boron trifluoride etherate in the presence of triethylamine in toluene, BF<sub>2</sub>-complexes (**6**) and (**7**) were synthesized with a yield of approximately 40 %. Substitution of chloro group of complex (**7**) by a phenyl group to complex (**8**) was achieved via a Suzuki Palladium-catalysed cross coupling.<sup>11</sup> All new compounds were structurally characterized by <sup>1</sup>H, <sup>11</sup>B, <sup>9</sup>F, <sup>13</sup>C NMR and HRMS spectroscopies.



**Scheme 2: Synthesis of boron difluoride complexes based on phthalazine-pyridine:** i) NH<sub>2</sub>NH<sub>2</sub>·H<sub>2</sub>O (1.1 eq), acetic acid, 120°C, 4h, (yield 93%); ii) POCl<sub>3</sub> (4.0 eq), 110°C, 1h (yield 83%); iii) 2-aminopyridine (1.1 eq), NaH (4.0 eq), dioxane, 60°C, 16h (yield 47%); iv) 2-aminopyridine (2.1 eq), NaH (4.8 eq), dioxane, 60°C, 16h (yield 59%); v) and vi) Et<sub>3</sub>N (0.5 mL), BF<sub>3</sub>·Et<sub>2</sub>O (1.5 mL), THF/toluene, reflux, overnight (yield 41%); vii) C<sub>6</sub>H<sub>5</sub>B(OH)<sub>2</sub> (1.1 eq), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (5% mmol), K<sub>2</sub>CO<sub>3</sub> (2.0 eq), Dioxane/H<sub>2</sub>O 4/1, MW 110°C, 60 min (yield 75%).

### Crystal structure

Structure of complex (**6**) drawn in Figure 1 was unambiguously characterized by X-ray crystallography analysis. Crystal data are given in the experimental section.

In the molecule, the opposite atoms B1 and N5 deviate from the mean N2 C8 N5 C14 N6 B1 ring plane (R.M.S. deviation of fitted atoms = 0.1092) by 0.1136 (9) and 0.1731 (9) Å respectively, which leads to a boat-shaped deformation. The dihedral angle between pyridine ring and pyridazine ring is 14.546 (69)°.

The B-F and B-N bond lengths are inequivalent with distances of 1.3652 (17) and 1.3913 (18) Å and 1.5387 (18) and 1.5568 (18) Å respectively.

The crystal structure of complex (**6**) showed several intermolecular interactions. Four hydrogen bonds between complexes and water molecules (Figure 2 bottom) are presents and summarised in Table 1.

**Table 1: Hydrogen-bond geometry (Å, °)**

D—H...A	D—H	H...A	D...A	D—H...A
O1—H7...N5	0.90 (2)	2.04 (2)	2.934 (2)	175.5 (19)
O1—H8...N4 <sup>i</sup>	0.84 (2)	2.09 (2)	2.899 (2)	161 (2)
O1—H8...O1 <sup>ii</sup>	0.84 (2)	2.55 (2)	2.940 (2)	109.7 (18)
N3—H1...O1 <sup>iii</sup>	0.86 (2)	2.21 (2)	3.043 (2)	161.4 (15)

Symmetry codes: (i) 1+x, y, z; (ii) 2-x, 1-y, -z; (iii) 1-x, 1-y, -z.

An additional strong CH...Halogen interaction [C18-H18...F2 = 2.28 Å] is also present, the distance between the atoms involved is far less than the sum of the Van der Waals radii of these atoms, i.e. 2.67 Å. The cohesion of organic molecules within the crystal is finally reinforced by π-π intermolecular interactions between phthalazine rings, the distance from plane to plane being 3.435 Å (Figure 2 up).

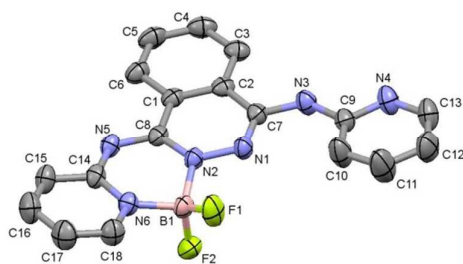


Figure 1: Structure of complex (6). Selected bond lengths (Å), angles (°) and dihedral angles (°): N6-B1 1.5568(18), N2-N1 1.3759(14), N2-B1 1.5387(18), N3-H1 0.860(18), B1-F1 1.3652(17), B1-F2 1.3913(18), F1-B1-F2 110.64(12), N1-N2-B1 113.22(10), N2-B1-N6 105.79(10).

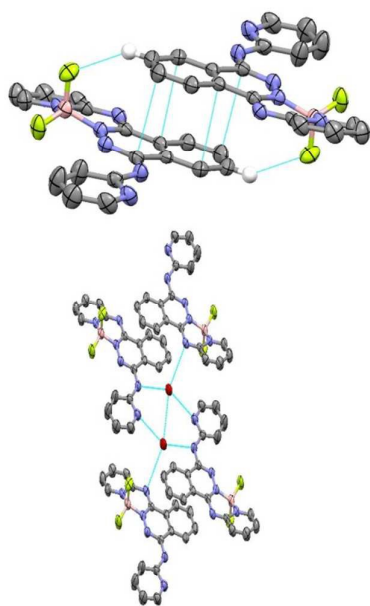


Figure 2: Intermolecular interactions in crystals of (6).

## Photophysical properties

### Quantum yield determination

The relative Quantum Yields (QY)  $\Phi$  of the boron (III) complexes (6), (7), (8) were determined by the following formula:<sup>12</sup>

$$\frac{\Phi_x}{\Phi_R} = \frac{A_R}{A_x} \times \frac{E_x}{E_R} \times \frac{n_x^2}{n_R^2} \quad (1)$$

where subscripts  $x$  and  $R$  refer to the sample and the reference respectively,  $A$  is the absorbance at the excitation wavelength,  $E$  is the integrated PhotoLuminescence (PL) intensity and  $n$  is the refractive index of the solvent at the excitation wavelength. To determine the QY, two conditions must be satisfied: i) the reference and the sample must absorb and emit light in the same wavelength range,<sup>13</sup> ii) the excitation wavelength must be identical for the reference and the sample. To fulfil these requirements a reference

solution of anthracene in absolute ethanol was chosen and the complexes (6), (7) and (8) were dissolved in chloroform. The QY reported by Dawson *et al.*<sup>14</sup> for anthracene in ethanol was considered as reference. The absorbance spectra of the complexes (6), (7), (8) and anthracene are displayed on Figure 3.

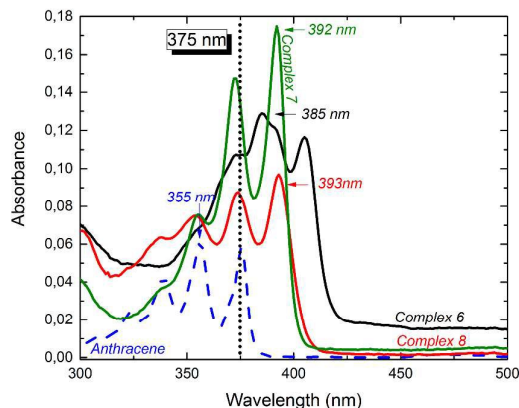


Figure 3 : Room Temperature (RT) absorbance spectra of reference (anthracene) and complexes (6), (7), (8) solutions. For each solution, the most intense peak is indicated.

The absorbance spectra are composed of main peaks at 373 nm, 385 nm 391 nm and 405 nm wavelengths for complex (6), at 355 nm, 372 nm and 392 nm for complex (7), and at 336 nm, 350 nm, 373 nm, and 393 nm for complex (8). For each spectrum, the maximum absorbance peak wavelength is indicated in Figure 3. The optical gap energies deduced from the absorption edges are 2.98 eV, 3.09 eV and 3.07 eV for the complexes (6), (7), (8), respectively (Table 3). The substitution of the chloro-group of complex (7) by the pyridylamino- or the phenyl-group in complexes (6) and (8) increases the number of molecular orbitals and consequently reduces the optical gap energy, as shown by the trend  $\Delta E_{\text{opt}}(7) > \Delta E_{\text{opt}}(8) > \Delta E_{\text{opt}}(6)$ .

Figure 4 represents the PL Excitation (PLE) and PL spectra of the reference (anthracene), complexes (6), (7) and (8) solutions. The shapes of the PLE spectra are almost identical to the shape of the absorbance spectra in Figure 3. The maximum absorption wavelengths for the anthracene, complexes (6), (7) and (8) are similar to the maximum excitation ones, i.e. at 355 nm, 385 nm, 391 nm, and 392 nm respectively. The emission bands of complexes (6), (7), and (8) have almost the same shape, with sharper peaks for the complex (7). The maximum PL peaks for the anthracene, complexes (6), (7) and (8) are recorded at 398 nm, 420 nm, 398 nm and 400 nm respectively. The Stokes shifts for complexes (6), (7), and (8) are 2165  $\text{cm}^{-1}$ , 449  $\text{cm}^{-1}$  and 510  $\text{cm}^{-1}$ , respectively.

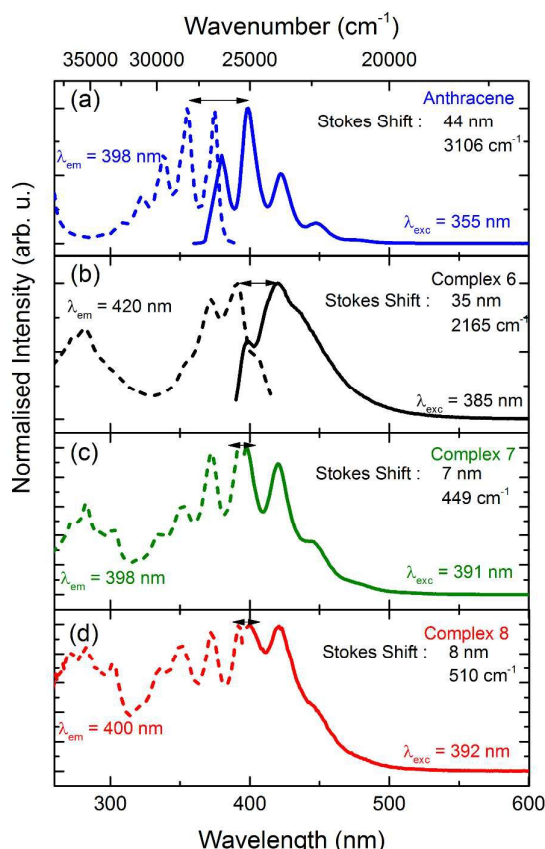


Figure 4 : RT PLE (dash line) and PL (continue line) spectra of (a) anthracene, (b) complex (6), (c) complex (7) and (d) complex (8). The value of the excitation or emission wavelengths and the Stokes shift are indicated.

QY of complexes (6), (7) and (8) have been determined using the formula (1) and the absorption and photoemission data of anthracene, (6), (7) and (8) complexes. In order to optimize the excitation wavelength for all the solutions, a compromise excitation wavelength of 375 nm was chosen. This choice is carefully detailed in supplementary data. The estimated QY ( $\Phi$ ) equals to 25%, 52% and 79% for complexes (6), (7) and (8) respectively (Table 2). We can notice that the substitution of a phenyl group from complex (8) by a pyridylamino- or a chloro-group to complexes (6) and (7) decreases the fluorescence QY. Similarly to the aza-boron-diquinomethene complexes reported by Wang *et al.*,<sup>10h</sup> the substitution by a more electro-withdrawing or donating group decreases the QY. Compared to QY of other type (III) molecules,<sup>10a-c,h,i</sup> complexes (6) and (7) exhibit medium QY and complex (8) is highly luminescent.

#### Semi-empirical determination of the decay time

Based on absorption and photoluminescence data, luminescence decay time of complexes (6), (7) and (8) were estimated using the Strickler-Berg formula:<sup>15</sup>

$$\frac{1}{\tau_0} = \frac{\Phi}{\tau} = 2,880 \times 10^{-9} n^2 \frac{\int I(\nu) d\nu}{\int \nu^{-3} I(\nu) d\nu} \int \frac{A}{c \times d \times \nu} d\nu \quad (2)$$

where  $\tau_0$  is the radiative decay time (s), in absence of non-radiative recombination mechanisms,  $\Phi$  is the quantum yield,  $\tau$  is the measurable decay time,  $n$  is the refractive index of the solvent at the excitation wavelength  $\lambda_{exc}$ ,  $I(\nu)$  is the intensity of the fluorescence spectrum,  $A$  is the absorbance,  $c$  is the concentration in  $\text{mol} \cdot \text{cm}^{-3}$  and  $d$  is the length of the container in cm. The frequency  $\nu$  is in  $\text{cm}^{-1}$ . The integration on the absorbance is not done on the whole absorption spectrum, but only from 300 nm to the absorption edge. In order to test the validity of this formula, the semi-empirical decay time of anthracene was estimated first. The calculations led to the values  $\tau_0 = 6.0$  ns and  $\tau = 1.7$  ns, which are of the same order than the experimental value,  $\tau_{exp} = 5$  ns, measured for anthracene in ethanol by Lampert *et al.*<sup>16</sup> Similar calculations applied to the complexes (6), (7), and (8) solutions, led to  $\tau_{(6)} = 0.9$  ns,  $\tau_{(7)} = 3.1$  ns and  $\tau_{(8)} = 3.1$  ns respectively (Table 2). The decay times, estimated for complexes (6), (7) and (8) are of the same order than the ones measured for similar molecules.<sup>10h,i</sup> These results have to be confirmed by appropriated decay time measurements, since the temporal detection limit of our equipment is higher than these values of decay times.

Table 2 : Relative Quantum Yield (QY) and semi-empirical decay times ( $\tau$ ) calculated for anthracene and complexes (6), (7) and (8).

	$\tau_0$ (ns)	$\tau$ (ns)	$\Phi$ (%)
Anthracene	6.0	1.7	28 <sup>14</sup>
Complex (6)	3.6	0.9	25
Complex (7)	6.0	3.1	52
Complex (8)	4.0	3.1	79

#### Electrochemical properties

HOMO and LUMO energy levels have been estimated from cyclic voltammetry. Cyclic Voltammograms (CV) of (6), (7) and (8) complexes are shown on Figure 5. The oxidation and reduction peaks of ferrocene/ferrocenium ( $\text{Fc}/\text{Fc}^+$ ) used as reference are observed at 0.16 V and 0 V respectively. The (6), (7) and (8) complexes exhibit subtle oxidation peaks located at  $E_{\text{peak max}}^{\text{oxy}} = 0.90$  V, 1.12 V and 0.85 V respectively and reduction peaks located at  $E_{\text{peak max}}^{\text{red}} = -0.50$  V,  $-0.54$  V and  $-0.54$  V respectively (Table 3). In order to confirm the attribution of the latter peaks to complexes (6), (7) and (8), CV of complex free solutions and of more concentrated complex solutions have been recorded (corresponding CV are reported in supplementary materials). The absence of oxidation and reduction peaks of complexes for the free complex solutions and the presence of more intense peaks for the more concentrated complex solutions confirm the previous attribution. The HOMO and LUMO energy levels of (6), (7) and (8) complexes have been deduced from the potentials of the oxidation peak onsets versus  $\text{Fc}/\text{Fc}^+$   $E_{\text{peak onset vs Fc}}^{\text{oxy}}$  (V) and from the optical gap energies  $\Delta E_{\text{opt}}$ , estimated from the absorption edges (Table 3).



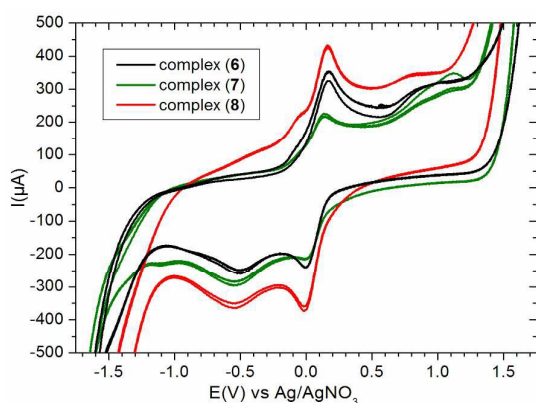
The HOMO and LUMO energy levels are close for complexes (6), (7) and (8) with  $E_{\text{HOMO}} \sim -5.3$  eV and  $E_{\text{LUMO}} \sim -2.3$  eV. We can notice that the substitution of the phenyl group of complex (8) by a more electron donating or withdrawing group as the pyridylamino- or chloro- group in complex (6) or (7) stabilizes the HOMO level as shown by the trend  $E_{\text{HOMO}}(8) > E_{\text{HOMO}}(6) > E_{\text{HOMO}}(7)$ .

**Table 3 :** Electrochemical characteristics of complexes (6), (7) and (8)

	$E_{\text{peak max}}^{\text{red}}$ (V)	$E_{\text{peak max}}^{\text{oxy}}$ (V)	$E_{\text{peak onset}}^{\text{oxy}}$ (V)	$E_{\text{peak onset vs Fc}}^{\text{oxy}}$ (V)	$\Delta E_{\text{opt}}$ (eV)	$E_{\text{HOMO}}$ (eV) <sup>a</sup>	$E_{\text{LUMO}}$ (eV) <sup>b</sup>
(6)	-0.50	0.90	0.63	0.55	2.98	-5.35	-2.37
(7)	-0.54	1.12	0.66	0.58	3.09	-5.38	-2.29
(8)	-0.54	0.85	0.57	0.49	3.07	-5.29	-2.22

$$^a E_{\text{HOMO}}(\text{eV}) = -e(E_{\text{peak onset vs Fc}}^{\text{oxy}}(\text{V}) + 4.8)$$

$$^b E_{\text{LUMO}}(\text{eV}) = E_{\text{HOMO}}(\text{eV}) + \Delta E(\text{eV})$$



**Figure 5 :** Cyclic voltammograms of acetonitrile solutions of (6), (7) and (8) complexes ( $2.10^{-3}$  M), ferrocene ( $10^{-3}$  M) and TBAP (0.1 M).

## Conclusions

In this article, we described an efficient synthesis of new boron difluoride  $\text{BF}_2$ -complexes based on phthalazine-pyridine which performed high intensive emission in solution. The photophysical properties of these novel emitters could be finely tunable through the various substitution at the 1-position of the phthalazine core. Then, the resulting complexes and their photophysical properties are currently being studied and will be attempted to apply in OLED devices.

## Experimental

### 1. Synthesis and NMR characterisations

All chemicals and solvents were purchased from chemical suppliers and were used as received, unless otherwise mentioned.

Purification of products was performed by column flash chromatography on Geduran® Si 60 silica gel (40-63  $\mu\text{m}$ ) from Merck with analytically pure solvents. For analytical thin layer

chromatography (TLC), silica gel-coated substrates "60 F254" from Merck were used and compounds were detected by illumination with UV lamp ( $\lambda = 254$  or  $365$  nm).

Microwave irradiation were done with a monowave 300 Anthon Paar cavity at 2450MHz.

$^1\text{H}$  and  $^{13}\text{C}$  NMR experiments were recorded in the listed deuterated solvents (internal standard) on Bruker Spectrometers Avance 400. Multiplicity of NMR signal was denoted as br (broad), m (multiplet), s (singlet), d (doublet), t (triplet). Mass analyses were carried out on LCMS QTOF Micro WATERS machine.

### 2,3-Dihydrophthalazine-1,4-dione (2)

A mixture of phthalic anhydride (7.40 g, 50.0 mmol), hydrazine hydrate (2.80 mL, 55.0 mmol, 1.1 eq) was heated to  $120^\circ\text{C}$  in acetic acid for 4h. Then, the reaction mixture was cooled to room temperature and filtered to give a white solid (7.52 g, 93 %).  $^1\text{H}$ -NMR (DMSO, 400 MHz)  $\delta = 11.53$  (br s, 2H), 8.06 (m, 2H), 7.87 (m, 2H).

### 1,4-Dichlorophthalazine (3)

2,3-Dihydrophthalazine-1,4-dione (2) (7.52 g, 46.4 mmol) was heated to  $110^\circ\text{C}$  in 18mL (4 eq) of phosphoryl chloride. After one hour, the reaction mixture was cooled to room temperature and added dropwise to crushed ice. The formed precipitate was filtered, washed with  $\text{H}_2\text{O}$ , and then dried in vacuum to give a white solid (7.64 g, 83%).  $^1\text{H}$ -NMR (DMSO, 400 MHz)  $\delta = 8.34$  (m, 2H), 8.27 (m, 2H).  $^{13}\text{C}$ -NMR (DMSO, 100 MHz)  $\delta = 155.2, 136.2, 127.1, 126.1$ .

### 1-Chloro-4(2'-pyridyl)aminophthalazine (4)

Sodium hydride (60 % in mineral oil) (1.60 g, 40.0 mmol) was carefully added into a mixture of 1,4-dichlorophthalazine (3) (1.99 g, 10 mmol) and 2-aminopyridine (1.034 g, 11.0 mmol, 1.1 eq) in 25 mL of freshly distilled dioxane. The resulting mixture was stirred at  $60^\circ\text{C}$  for 16h. Then, it was quenched carefully with water and was acidified with aqueous hydrochloric acid 1M. After that, the mixture was washed with  $\text{CHCl}_3$  (50 mL x3), and the organic phase was concentrated in vacuum. The crude product was then purified by silica-gel column chromatography (eluted with Cyclohexane/AcOEt: 3/1) to give the expected product as a white solid (1.21 g, 47%).  $^1\text{H}$ -NMR (DMSO, 400 MHz)  $\delta = 10.02$  (s, 1H), 8.72 (d,  $J = 7.8$  Hz, 1H), 8.36 (d,  $J = 4.4$  Hz, 1H), 8.24 (d,  $J = 7.8$  Hz, 1H), 8.19 (d,  $J = 7.7$  Hz, 2H), 8.08 (m, 2H), 7.82 (td,  $J = 7.7$  Hz, 1.6, 1H), 7.08 (t,  $J = 6.0$  Hz, 1H).  $^{13}\text{C}$ -NMR (DMSO, 100 MHz) 153.7, 153.0, 148.4, 138.3, 134.2, 134.2, 133.8, 126.3, 125.2, 124.4, 121.4, 118.8, 115.0.

### 1,4-Di(2'-pyridyl)aminophthalazine (5)

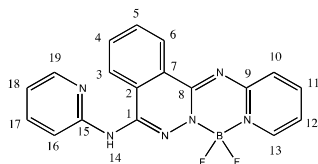
Sodium hydride (60 % in mineral oil) (1.60g, 24.0 mmol) was carefully added into a mixture of 1,4-dichlorophthalazine (3) (0.98 g, 5 mmol) and 2-aminopyridine (0.98 g, 10.5 mmol, 2.1 eq) in 25 mL of distilled dioxane. The resulting mixture was stirred at  $60^\circ\text{C}$  for 16h. Then, it was quenched carefully with water and was acidified with aqueous hydrochloric acid 1M. After that, the solvent was removed and the residue was

## ARTICLE

## New Journal of Chemistry

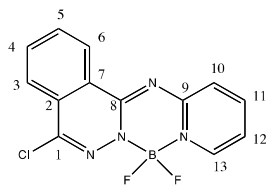
washed with  $\text{CHCl}_3$  to eliminate the non-reacted 2-aminopyridine. The crude product was then purified by silica-gel column chromatography (eluted with  $\text{AcOEt}/\text{MeOH}$ : 10/1) to give product as a white solid (0.71 g, 59%).  $^1\text{H-NMR}$  ( $\text{CD}_3\text{OD}$ , 400 MHz)  $\delta$  = 8.98 (dd,  $J$  = 6.1, 3.3 Hz, 2H), 8.58 (d,  $J$  = 5.7 Hz, 2H), 8.37 (dd,  $J$  = 6.1, 3.3 Hz, 2H), 8.32 (t,  $J$  = 7.2 Hz, 2H), 7.98 (d,  $J$  = 8.7 Hz, 2H), 7.52 (dd,  $J$  = 7.2 Hz, 5.2 Hz).  $^{13}\text{C-NMR}$  ( $\text{CD}_3\text{OD}$ , 100 MHz) 150.7, 148.8, 143.4, 140.5, 135.4, 124.4, 121.8, 119.6, 116.1,  $[\text{M}+\text{H}]^+$  calcd: 315.1358, found: 315.1366.

## Complex (6)



To 1,4-(2'-pyridyl)aminophthalazine (**5**) (0.31 g, 1.0 mmol) in toluene/THF was added 0.5 ml of  $\text{Et}_3\text{N}$ , and then subsequently added of  $\text{BF}_3\cdot\text{OEt}_2$  (1.5 mL) through syringe. The reaction mixture was heated to reflux overnight. After cooling down to room temperature, the reaction mixture was extracted with  $\text{AcOEt}$  (30 mL  $\times$  3). The organic layers were combined, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and evaporated to dryness under vacuum. The crude product was purified by column chromatography on silica gel (Cyclohexane/ $\text{AcOEt}$ : 1/1) to give the final product as a yellow powder (0.15g, 41%).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  = 8.89 (d,  $J$  = 7.8 Hz, 1H, H6), 8.50 (br s, 1H, H16), 8.21-8.12 (m, 2H, H13 and H19), 8.03 (br s, 1H, H3), 7.91 (t,  $J$  = 7.8 Hz, 1H, H4), 7.83 (t,  $J$  = 7.8 Hz, 1H, H5), 7.78 (t,  $J$  = 8.3 Hz, 1H, H17), 7.72 (t,  $J$  = 8.7 Hz, 1H, H11), 7.32 (d,  $J$  = 8.7 Hz, 1H, H10), 6.98 (t,  $J$  = 6.8 Hz, 1H, H12), 6.92 (t,  $J$  = 6.4 Hz, 1H, H18).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz) 153.7 (C9), 152.6 (C15), 149.3 (C8), 147.4 (C19), 145.5 (C1), 140.3 (C11), 139.3 (C17), 137.4 (C13), 133.8 (C4), 132.4 (C5), 127.9 (C7), 127.8 (C6), 123.3 (C10), 122.6 (C2), 121.2 (C3), 117.9 (C18), 115.4 (C12), 113.7 (C16).  $^{19}\text{F-NMR}$  ( $\text{CDCl}_3$ , 376 MHz) -137.61 (br, 2F),  $^{11}\text{B-NMR}$  ( $\text{CDCl}_3$ , 128 MHz) 1.03 (t,  $J$  = 25.27 Hz, 1B),  $[\text{M}+\text{H}]^+$  calcd: 363.1341, found: 363.1349.

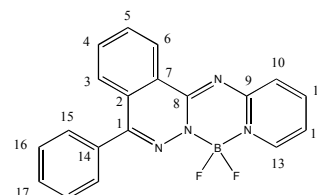
## Complex (7)



To 1-chloro-4-(2'-pyridyl)aminophthalazine (**4**) (0.51g, 2.0 mmol) in  $\text{CHCl}_3$  was added 0.5 mL of  $\text{Et}_3\text{N}$ , and then subsequently added of  $\text{BF}_3\cdot\text{OEt}_2$  (1.5 mL) through syringe. The reaction mixture was heated to reflux overnight. After cooling down to room temperature, the reaction mixture was extracted with  $\text{AcOEt}$  (30 mL  $\times$  3). The organic layers were combined, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and evaporated to dryness under vacuum. The crude product was purified by column chromatography on silica gel (Cyclohexane/ $\text{AcOEt}$ : 3/1) to give final product as a yellow

powder (0.27g, 41%).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  = 9.00 (d,  $J$  = 7.4 Hz, 1H, H6), 8.45 (br s, 1H, H13), 8.26 (d,  $J$  = 7.4 Hz, 1H, H3), 8.09 (t,  $J$  = 7.4 Hz, 1H, H4), 8.05 (t,  $J$  = 7.4 Hz, 1H, H5), 8.02 (t,  $J$  = 7.0 Hz, 1H, H11), 7.58 (d,  $J$  = 8.6 Hz, H10), 7.26 (t,  $J$  = 7.0 Hz, 1H, H12).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz) 153.5 (C9), 150.8 (C8), 145.9 (C1), 141.4 (C11), 138.0 (C13), 134.3 (C4), 133.4 (C5), 127.9 (C7), 127.3 (C2), 127.2 (C6), 125.6 (C3), 123.6 (C10), 116.8 (C12).  $^{19}\text{F-NMR}$  ( $\text{CDCl}_3$ , 376 MHz) -135.68 (dd,  $J$  = 50.98 Hz,  $J$  = 25.49 Hz, 2F),  $^{11}\text{B-NMR}$  ( $\text{CDCl}_3$ , 128 MHz) 0.89 (t,  $J$  = 25.50 Hz, 1B),  $[\text{M}+\text{Na}]^+$  calcd: 327.0396, found: 327.0396.

## Complex (8)



The mixture of complex (**7**) (0.32 g, 1.0 mmol), phenyl boronic acid (136 mg, 1.1 mmol), bistrisphenylphosphine palladium (II) dichloride (70 mg, 0.05 mmol), and  $\text{K}_2\text{CO}_3$  (276 mg, 2 mmol) was dissolved in dioxane- $\text{H}_2\text{O}$  (4:1, 5.0 mL). The resulting mixture was subjected to microwave irradiation for 60 min at  $110^\circ\text{C}$ . After cooling down to room temperature, the reaction mixture was extracted with  $\text{CHCl}_3$  (20 mL  $\times$  3). The organic layers were combined, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and evaporated to dryness under vacuum. The crude product was purified by column chromatography on silica gel (Cyclohexane/ $\text{AcOEt}$ : 4/1) to give final product as a yellow powder (0.26 g, 75%).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  = 8.99 (d,  $J$  = 6.5 Hz, 1H, H6), 8.32 (d,  $J$  = 5.2 Hz, 1H, H13), 7.92-7.82 (m, 4H, H3, H4, H5 and H11), 7.75-7.69 (m, 1H, H15), 7.55-7.51 (m, 2H, H16 and H17), 7.50-7.45 (m, 1H, H10), 7.09 (t,  $J$  = 6.8 Hz, 1H, H12).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz) 153.7 (C9), 153.6 (C1), 150.8 (C8), 140.9 (C11), 137.8 (C13), 135.1 (C14), 133.5 (C4), 132.2 (C5), 130.0 (C15), 129.4 (C17), 128.6 (C16), 127.4 (C2), 127.3 (C7), 127.0 (C6), 126.7 (C3), 123.3 (C10), 116.1 (C12).  $^{19}\text{F-NMR}$  ( $\text{CDCl}_3$ , 376 MHz) -135.82 (dd,  $J$  = 50.38 Hz,  $J$  = 25.19 Hz, 2F).  $^{11}\text{B-NMR}$  ( $\text{CDCl}_3$ , 128 MHz) 1.28 (t,  $J$  = 25.34 Hz, 1B),  $[\text{M}+\text{H}]^+$  calcd: 369.1097, found: 369.1099.

## 2. Single crystal X Ray diffraction

Single crystals of (**6**) suitable for X-ray crystallographic analysis were obtained by slow evaporation of  $\text{CH}_2\text{Cl}_2$  solution. X-ray diffraction data collection were performed at 150 K with graphite-monochromatized  $\text{Mo K}_\alpha$  radiation ( $\lambda$  = 0.71073 Å) on a Bruker-Nonius Kappa CCD area detector diffractometer. Formula :  $\text{C}_{18}\text{H}_{15}\text{BF}_2\text{N}_6\text{O}$  ; Formula weight : 380.17 ; Crystal system : monoclinic ; Space group :  $P2(1)/n$  ; Cell parameters :  $a$  = 10.5846(4) Å,  $b$  = 7.6098(3) Å,  $c$  = 21.9235(10) Å,  $\alpha$  =  $\gamma$  =  $90^\circ$ ,  $\beta$  =  $100.651(2)^\circ$ ,  $V$  = 1735.44(12) Å<sup>3</sup> ;  $Z$  = 4 ; Calculated density = 1.455 g/cm<sup>3</sup> ;  $\mu$  = 0.110 mm<sup>-1</sup> ;  $R_{\text{int}}$  = 0.0252 ;  $R[F^2 > 2\sigma(F^2)]$  = 0.0388 ;  $wR(F^2)$  = 0.1076. Program(s) used to solve structure : SHELXS97. Program(s) used to refine structure : SHELXL-2014. Software used to prepare material for publication : SHELXTL. CCDC 1030686 contains the

supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

### 3. Absorbance and Photoluminescence measurements

The absorbance spectra were measured at room temperature on a Perkin-Elmer UV-Visible Spectrophotometer with a resolution of 1 nm. The PL and PLE spectra were measured at room temperature using a Horiba Jobin Yvon Fluorolog-3 spectrofluorimeter with a 450 W xenon lamp, with a resolution of 1 nm. Absorbance and photoluminescence spectra were measured on CHCl<sub>3</sub> solutions of complexes (6), (7) and (8) and on a reference solution of anthracene in absolute ethanol (4 mg dissolved in 250 mL of solvent). For QY and  $\tau$  calculations, refractive indexes  $n$  of ethanol<sup>17</sup> and chloroform<sup>18</sup> and reference QY of anthracene in ethanol<sup>14</sup> were considered.

### 4. Electrochemical measurements

Electrochemical measurements were performed with a VersaStat potentiostat using a three electrodes cell with a Pt working electrode, a Pt counter electrode and a Ag/AgNO<sub>3</sub> reference electrode (Ag in a 0.01 M AgNO<sub>3</sub> and 0.1 M TBAP (TetraButyl Ammonium Perchlorate) acetonitrile solution). The electrolytes were deoxygenated acetonitrile solutions of complexes (6), (7) or (8) (2.10<sup>-3</sup> M), TBAP (0.1 M) and ferrocene (10<sup>-3</sup> M), used as an internal reference. The cyclic voltammograms were recorded during 3 cycles between - 1.75 V (starting potential) and 1.75 V vs Ag/AgNO<sub>3</sub> at a 0.2 V/s scan rate.

### Acknowledgements

The authors wish to thank Karine Jarsalé for the mass spectroscopy spectra and Rémi Legay for NMR spectra analysis. We gratefully acknowledge financial support from the «Ministère de la Recherche et des Nouvelles Technologies», CNRS (Centre National de la Recherche Scientifique), the «Région Basse-Normandie» and the European Union (FEDER funding). The authors acknowledge the financial support of the french Agence Nationale de la Recherche (ANR), through the program "Investissements d'Avenir" (ANR-10-LABX-09-01), LabEx EMC<sup>3</sup> and the Vietnam National Foundation for Science and Technology Development (NAFOSTED 104.01-2012.26).

### Notes and references

- Loudet, A., Burgess, K., *Chem. Rev.*, 2007, **107**, 4891.
- Frath, D., Massue, J., Ulrich, G., Ziessel, R., *Angew. Chem. Int. Ed.*, 2014, **53**, 2290
- Boens, N., Leen, V., Dehaen, W., *Chem. Soc. Rev.*, 2012, **41**, 1130.
- Guo, Z., Park, S., Yoon, J., Shin, I., *Chem. Soc. Rev.*, 2014, **43**, 16.
- Ulrich, G., Ziessel, R., Harriman, A., *Angew. Chem. Int. Ed.*, 2008, **47**, 1184.
- Besette, A., Hanan, G. S., *Chem. Soc. Rev.*, 2014, **43**, 3342.

- Qian, G., Wang, Z. Y., *Chem. Asian J.*, 2010, **5**, 1006.
- (a) Hong, Y., Lam, J. W. Y., Tang, B. Z., *Chem. Commun.*, 2009, 4332; (b) Hong, Y., Lam, J. W. Y., Tang, B. Z., *Chem. Soc. Rev.*, 2011, **40**, 5361; (c) Liu, X., Ren, Y., Xia, H., Fan, H., Mu, Y., *Inorg. Chim. Acta.*, 2010, **363**, 1441; (d) Macedo, F. P., Gwengo, C., Lindeman, S. V., Smith, M. D., Gardinier, J. R., *Eur. J. Inorg. Chem.*, 2008, 3200; (e) Perumal, K., Garg, J. A., Blacque, O., Saiganesh, R., Kabilan, S., Balasubramanian, K. K., Venkatesh, K., *Chem. Asian J.*, 2012, **7**, 2670; (f) Ren, Y., Liu, X., Gao, W., Xia, H., Ye, L., Mu, Y., *Eur. J. Inorg. Chem.*, 2007, 1808; (g) Zhao, D., Li, G., Wu, D., Qin, X., Neuhaus, P., Cheng, Y., Yang, S., Lu, Z., Pu, X., Long, C., You, J., *Angew. Chem. Int. Ed.*, 2013, **52**, 13676.
- (a) Aranedá, J. F., Piers, W. E., Heyne, B.; Parvez, M., McDonald, R., *Angew. Chem. Int. Ed.*, 2011, **50**, 12214; (b) Esparza-Ruiz, A., Peña-Hueso, A., Nöth, H., Flores-Parra, A., Contreras, R., *J. Organomet. Chem.*, 2009, **694**, 3814; (c) Frath, D., Poirel, A., Ulrich, G., De Nicola, A., Ziessel, R., *Chem. Commun.*, 2013, **49**, 4908; (d) Liddle, B. J., Silva, R. M., Morin, T. J., Macedo, F. P., Shukla, R., Lindeman, S. V., Gardinier, J. R., *J. Org. Chem.*, 2007, **72**, 5637; (e) Morin, T. J., Lindeman, S. V., Gardinier, J. R., *Eur. J. Inorg. Chem.*, 2009, 104; (f) Nawn, G., Oakley, S. R., Majewski, M. B., McDonald, R., Patrick, B. O., Hicks, R. G., *Chem. Sci.*, 2013, **4**, 612; (g) Yang, Y., Su, X., Carroll, C. N., Aprahamian, I., *Chem. Sci.*, 2012, **3**, 610.
- (a) Fischer, G. M., Daltrozzi, E., Zumbusch, A., *Angew. Chem. Int. Ed.*, 2011, **50**, 1406; (b) Fischer, G. M., Ehlers, A. P., Zumbusch, A., Daltrozzi, E., *Angew. Chem. Int. Ed.*, 2007, **46**, 3750; (c) Fischer, G. M., Isomäki-Krondahl, M., Göttker-Schnetmann, I., Daltrozzi, E., Zumbusch, A., *Chem. Eur. J.*, 2009, **15**, 4857; (d) Kubota, Y., Tsuzuki, T., Funabiki, K., Ebihara, M., Matsui, M., *Org. Lett.*, 2010, **12**, 4010; (e) Liu, Q. D., Mudadu, M. S., Thummel, R., Tao, Y., Wang, S., *Adv. Func. Mater.*, 2005, **15**, 143; (f) Quan, L., Chen, Y., Lu, X.-J., Fu, W.-F., *Chem. Eur. J.*, 2012, **18**, 14599; (g) Shimizu, S., Iino, T., Araki, Y., Kobayashi, N., *Chem. Commun.*, 2013, **49**, 1621; (h) Wang, D., Liu, R., Chen, C., Wang, S., Chang, J., Wu, C., Zhu, H., Wacławik, E. R., *Dyes Pigm.*, 2013, **99**, 240; (i) Wiktorowski, S., Fischer, G. M., Winterhalder, M. J., Daltrozzi, E., Zumbusch, A., *Phys. Chem. Chem. Phys.*, 2012, **14**, 2921; (j) Zhou, Y., Xiao, Y., Li, D., Fu, M., Qian, X., *J. Org. Chem.*, 2008, **73**, 1571.
- Medda, F., Sells, E., Chang, H.-H., Dietrich, J., Chappeta, S., Smith, B., Gokhale, V., Meuliet, E.J., Hulme, C., *Bioorg. Med. Chem. Lett.*, 2013, **23**, 528.
- Williams, A. T. R., Winfield, S. A. & Miller, J. N. *Analyst*, 1983, **108**, 1067–1071.
- Fery-Forgues, S. & Lavabre, D. *J. Chem. Educ.*, 1999, **76**, 1260.
- Dawson, W. R. & Windsor, M. W. *J. Phys. Chem.*, 1968, **72**, 3251–3260.
- Strickler, S. J. & Berg, R. A. *J. Chem. Phys.*, 1962 **37**, 814–822.
- Lampert, R. A., Chewter, L. A., Phillips, D., O'Connor, D. V., Roberts, A. J., Meech, S. R., *Anal. Chem.*, 1983, **55**, 68–73.
- Kedenburg, S., Vieweg, M., Gissibl, T. & Giessen, H. *Opt. Mater. Express*, 2012, **2**, 1588–1611
- Samoc, A., *J. Appl. Phys.*, 2003, **94**, 6167–6174



## Graphical abstract

Synthesis and characterizations of three blue fluorescent phthalazine-pyridine boron complexes with quantum yields up to 79%.

