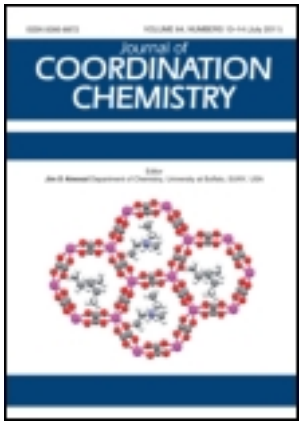

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Synthesis, crystal structures, and photophysical properties of dibromo-2-(2′-pyridyl)imidazole and its corresponding boron-fluorine complex

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Published online: 26 Sep 2011.

To cite this article: Miaofu Mao, Ronghua Zhang, Shuzhang Xiao & Kun Zou (2011) Synthesis, crystal structures, and photophysical properties of dibromo-2-(2′-pyridyl)imidazole and its corresponding boron-fluorine complex, Journal of Coordination Chemistry, 64:19, 3303-3310, DOI: 10.1080/00958972.2011.618836

To link to this article: http://dx.doi.org/10.1080/00958972.2011.618836

Journal of Coordination Chemistry
Vol. 64, No. 19, 10 October 2011, 3303–3310

Synthesis, crystal structures, and photophysical properties of dibromo-2-(2′-pyridyl)imidazole and its corresponding boron–fluorine complex

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(*Received 4 May 2011; in final form 12 August 2011*)

2-(2′-Pyridyl)imidazole **L1** and its corresponding boron–fluorine complex, **1**, were synthesized and their crystal structures correlated with their photophysical properties. **L1** forms a rigid supramolecular network through hydrogen bonds and halogen bond in the single crystal, which induces amplified spontaneous emission in crystals; it emits rather poor fluorescence in solution and powder states. Its boron chelate **1** emits intense fluorescence in solution since boron chelate is an excellent chromophore, and it exhibits large Stokes shift (136 nm in acetonitrile), due to the charge-transfer transition from the electron-donating π system to the electron-accepting boron moiety. Interestingly, **1** is also highly fluorescent in amorphous powder and crystal states; C–C rotation between pyridyl and imidazole groups is inhibited by the formation of a five-member ring containing BF_2, and the formation of intermolecular non-covalent bonds is the key factor. Solid emission with large Stokes shift makes it a valuable chromophore for synthesis of functional materials.

Keywords: BF_2 chelate; Fluorescence; Crystalline-induced emission; Solid emission

1. Introduction

The development of solid-emissive materials is of great interest for applications in light-emitting diodes [1–8], photoelectric conversion [9–14], memory [15], etc. Most organic dyes are highly fluorescent in dilute solutions but weakly luminescent or even non-emissive in solid states. One factor is that they pack tightly in amorphous solid phase and crystalline state and another key factor is the energy lost *via* rotational movements, which leads to significant self-quenching of the emission and limits their applications. Only a limited number of organic solid-emissive materials have been reported. In order to obtain solid-emissive materials for various applications, various techniques have been adopted, such as dendritic substituent protection [16–20], cross-dipole stacking [21], aggregation-induced emission [22–29], intramolecular charge-transfer (CT) transition [30, 31], J-aggregate formation [32], and non-planar intermolecular interactions

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958972.2011.618836

to result in rigid structures such as C–H···F–B, C–H···O, C···C, C···N interactions and hydrogen bonds [33, 34], because non-planar intermolecular interactions can help rigidify the structures to prevent rotational movement, keeping fluorescence in the solid state. In some cases, aggregate-induced fluorescence enhancement was observed due to the restriction to intramolecular motions [35–37]. In this work, we report a known ligand **L1** which shows weak fluorescence in both solution and as a powder. However, the formation of intermolecular hydrogen bond and a halogen bond in crystals makes it emit visibly enhanced fluorescence in crystals. The corresponding boron–fluorine complex, **1**, was prepared by treatment of **L1** with $BF_3 \cdot Et_2O$ under basic condition, as we reported previously [38]. BF_2 chelate is a highly fluorescent chromophore, showing intense fluorescence in solution. However, intense emissions were also observed in crystal and powder states due to non-covalent intermolecular interactions, proved by X-ray single crystal measurement. Photophysical properties of these two compounds were studied in various organic solvents and elucidated by the structural analyses of their single crystals.

2. Experimental

2.1. *General*

All starting materials were obtained from commercial suppliers and used as received. Moisture sensitive reactions were performed under an atmosphere of nitrogen and solvents were treated by standard methods. ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR were recorded on Bruker 400 or Varian 300 NMR spectrometers. MS data were recorded on a Waters Quattro Micro API MS spectrometer. UV-Vis and fluorescence spectra were obtained on Hitachi U-3010 and F-4500, respectively. The fluorescence quantum yield is calculated using anthracene as reference. Single crystals suitable for X-ray measurements were obtained by slow evaporation of their chloroform solutions, and single-crystal X-ray diffraction (XRD) data were collected on a Bruker APEX II CCD diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 298 K.

2.2. *Synthetic procedure of 2-(2′-pyridyl)-4,5-dibromoimidazole (L1)*

To a solution of 2-(2′-pyridyl)imidazole [39] (1.45 g, 0.01 mol) in chloroform (100 mL) was added bromine (3.2 g, 0.02 mol) in chloroform (20 mL) dropwise at room temperature. The reaction mixture was allowed to stir at room temperature overnight, and the resulting suspension was washed with aqueous $NaHCO_3$ and then extracted by chloroform. The organic phase was collected and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the target product was obtained as a yellow solid (85%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.51 (d, $J = 5.10$ Hz, 1 H), 8.18 (d, $J = 7.80$ Hz, 1 H), 7.86 (m, 1 H), 7.34 (m, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 148.6, 138.0, 124.0, 120.4. MS: m/z: 300 $[M]^+$. Anal. Calcd for $C_8H_5Br_2N_3$: C, 31.72; H, 1.66; N, 13.87. Found: C, 30.87; H, 1.65; N, 12.74.

2.3. *Synthetic procedure of boron 2-(2′-pyridyl)-4,5-dibromoimidazole (1)*

In a stirred mixture of **L1** (2.4 g, 8 mmol) and Et_3N (5 mL) in anhydrous CH_2Cl_2 (25 mL), $BF_3 \cdot OEt_2$ (5.6 mL, 44 mmol) was added dropwise at 0°C. After addition of $BF_3 \cdot OEt_2$, the reaction mixture was allowed to warm to room temperature and stirred at room temperature overnight. The organic phase was washed with water several times, dried on Na_2SO_4, and evaporated *in vacuo*. Then the obtained crude residue was subjected to column chromatography on a silica gel column to provide a yellow solid (38%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.43 (d, $J = 5.60$ Hz, 1H), 8.23 (t, $J = 7.80$ Hz, 1H), 7.92 (d, $J = 8.00$ Hz, 1H), 7.58 (t, $J = 6.60$ Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 145.4, 141.8, 123.9, 117.7. ^{19}F NMR ($CDCl_3$, 376 MHz): $\delta -148.5$, -148.9. HRMS calcd for $C_8H_5BBr_2F_2N_3$ $[M+H]^+$ 349.8911, found 349.8915. Anal. Calcd for $C_8H_4BBr_2F_2N_3$: C, 27.39; H, 1.15; N, 11.98. Found: C, 28.33; H, 1.13; N, 11.74.

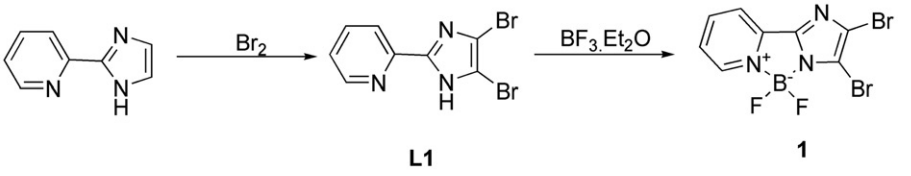
3. Results and discussion

3.1. *Synthesis*

Compound **L1** 2-(2′-pyridyl)-4,5-dibromoimidazole was obtained by treating 2-(2′-pyridyl)imidazole with bromine according to reported procedure [38, 40], as shown in scheme 1. This compound has been characterized by ^{1}H NMR, ^{13}C NMR, HRMS, and X-ray single crystal diffraction. After treatment with $BF_3 \cdot Et_2O$, the corresponding boron chelate **1** can be obtained as a yellow solid in 38% yield after purification by column chromatography [38]. These compounds have been fully characterized by ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, HRMS, and X-ray single crystal diffraction. **L1** and **1** show quite different resonance patterns because the existence of BF_2 obviously changes the electron density of the pyridyl ring. As shown in figure 1, downfield shift for H3, H2, and upfield shift for H1 were observed, due to electron deficiency of boron. ^{19}F NMR of **1** can further prove the presence of BF_2. There are two resonances according to ^{19}F NMR of **1** (figure 1, inset), indicating the existence of two fluorines, and that the chemical environments of these fluorines are slightly different.

3.2. *Crystal structures*

Suitable crystals of **L1** and **1** have been obtained by slow evaporation of their chloroform solutions (figure 2). According to the crystallographic measurement of **L1**, there is no intramolecular hydrogen bond between N1 and H2A on imidazole due to the



Scheme 1. Synthesis of **L1** and its boron chelate **1**.

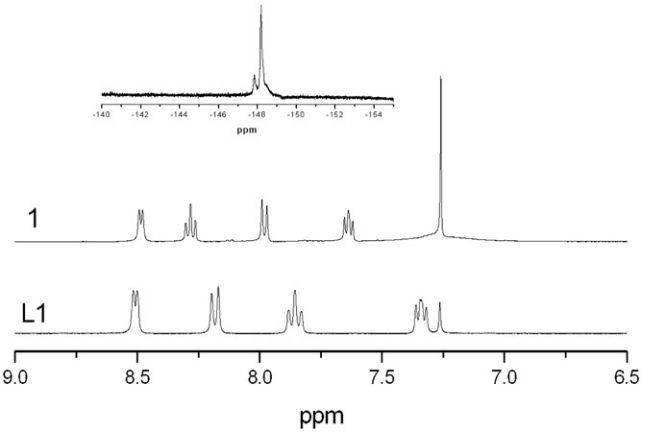


Figure 1. ^{1}H NMR of **L1**, **1**, and ^{19}F NMR of **1** (inset).

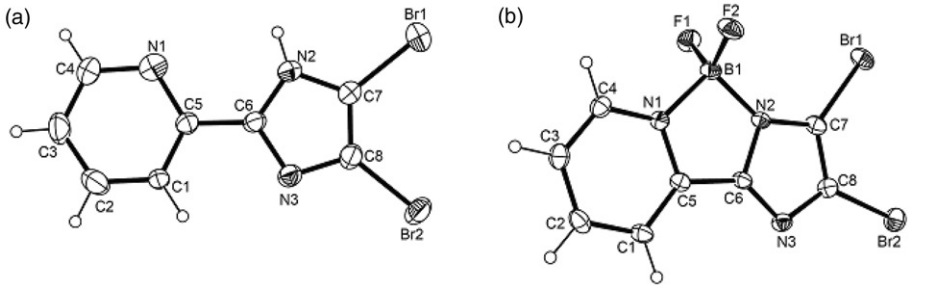


Figure 2. Single-crystal structures of (a) **L1** and (b) **1**.

long distance between these two atoms, measured to be 2.77 Å. Instead, multiple intermolecular interactions are present. First of all, H2A interacts with Br2 on an adjacent molecule to form a halogen bond, and meanwhile Br2 interacts with N2, forming a triangular structure (H2A···Br···N2 angle is 4.23°). As a result, the pyridine ring and imidazole ring are in different planes with a plane torsion angle of 11.7°. Most importantly, H1 interacts with adjacent H1, N3, C1 to form a steady tetrahedral structure (distances between H1···H1 2.00 Å, H1···N3 2.13 Å, H1···C1 2.84 Å). Its packing can be described as a herringbone pattern (figure 3a). The formation of intermolecular triangular and tetrahedral structures helps to rigidify the intermolecular packing, thus prohibiting planar π–π stacking.

For **1**, the F–B–F group is a bifurcated acceptor with an angle of 112.64°. With adjacent donors, F2 forms C–H···F–B with a distance of 2.53 Å. The boron is in the same plane containing N1, N2, C5, and C6 and the chromophore core is near-planar with the twisted angle between pyridine and imidazole rings being 1.57°, which shows the good planarity of the main molecular plane. Adjacent molecules were linked by C–H···F–B interactions to form non-parallel interlayered structure, preventing intermolecular π–π stacking. Besides C–H···F–B interaction, F1 forms halogen bonds with Br1 and Br2 with the distances of 3.27 Å and 3.08 Å, respectively. There is only slight overlap between intermolecular chromophore cores due to the rigid

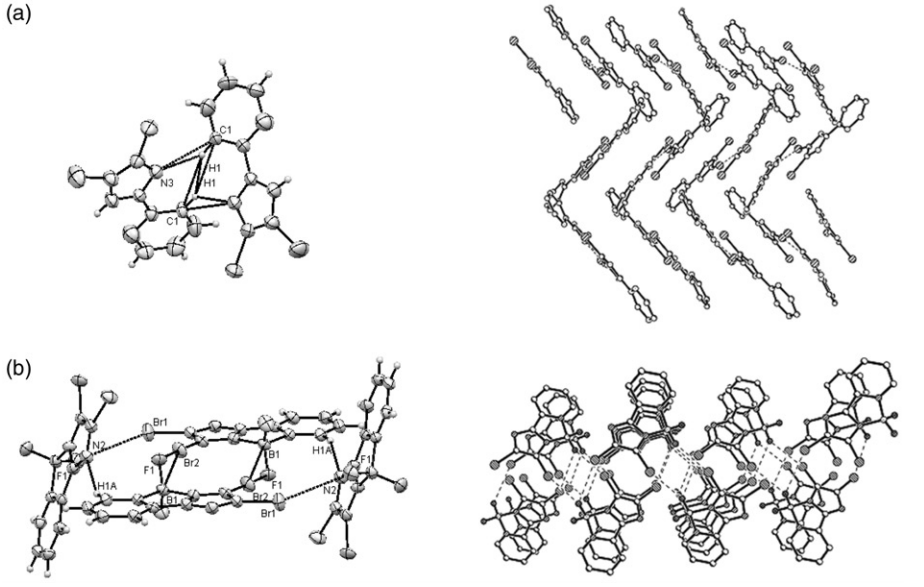


Figure 3. Crystal packing diagram of (a) **L1** and (b) **1**.

supramolecular network, and all of the molecules are induced to array parallel with identical conformation and orientation in the crystal (figure 3b). The formation of these non-covalent bonds produces a rigid 3-D structure, which inhibits planar π–π stacking of the chromophores.

3.3. *Photophysical properties*

L1 absorbs in the ultra-violet region and exhibits weak emission in organic solvents (figure 4a). In acetonitrile, the maximum emission was observed at 360 nm with fluorescence quantum yield less than 0.001, which is reasonable since **L1** contains no highly emissive chromophore. In the solid state, similar fluorescence was observed (figure 4b). However, visible enhanced fluorescence was obtained in crystals and the fluorescence quantum yield in a crystal is measured as 0.03 by the integrating sphere method. Compared to fluorescence quantum yield in the solid state, the crystals exhibit more than 30-fold enhancement. This can be explained by rigidification of the structure by supramolecular interactions as proved by X-ray single crystal measurement, which helps alleviate the energy lost *via* rotational movement around a single bond; the rigid structure only exists in crystal, which explains the fluorescence quenching as a powder. The fluorescence would disappear after crystals are ground into powders, which is typical force-induced emission change. In order to investigate the different emission, XRD of the crystals and powders are performed. The diffraction curves of the crystals show much fewer peaks, indicating molecules are packed tightly in the crystal. Thus, the observed mechanochromic luminescence should be attributed to disruption of intermolecular non-covalent bonds, such as hydrogen bonds and halogen bonds, resulting in a less ordered polymorph [41].

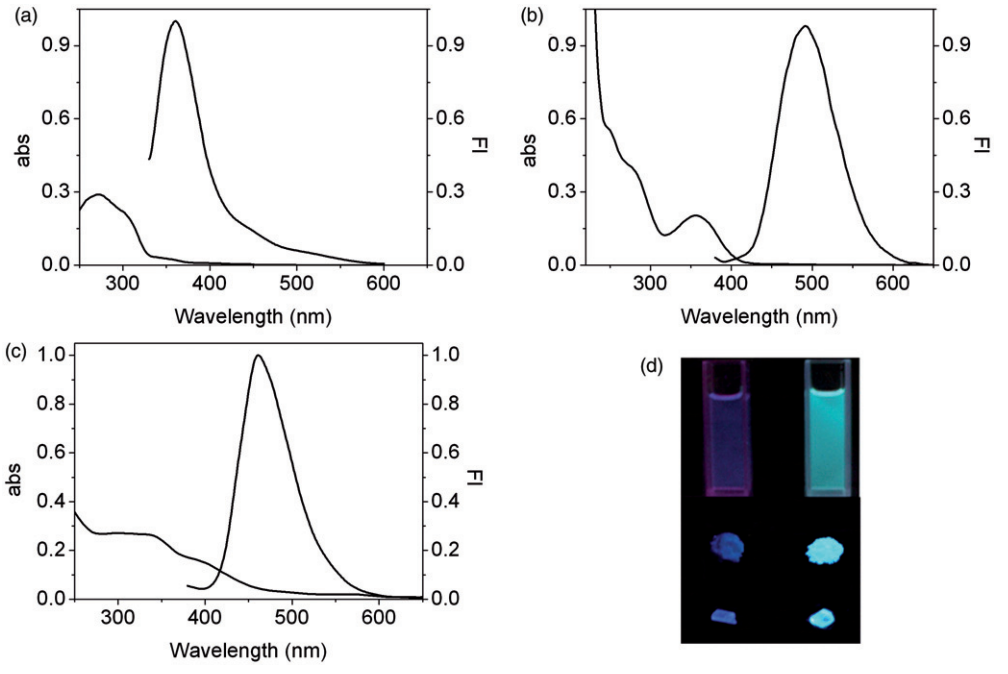


Figure 4. (a) Absorption and fluorescence spectra of **L1** in acetronitrile (1.0×10^{-5} molL^{-1}); (b) absorption and fluorescence spectra of **1** in acetronitrile (1.0×10^{-5} molL^{-1}); (c) absorption and fluorescence spectra of **1** in solid film; (d) fluorescent images of **L1** (left) and **1** (right) under 365 nm irradiation in solution, powder, and crystal states.

BF_2 chelate is known as an excellent fluorescent chromophore and **1** is highly fluorescent in regular organic solvents. Acetonitrile solution is yellow and the maximum absorption is located at 356 nm (ε 2.04×10^4 $(\text{mol L}^{-1})^{-1}\,\text{cm}^{-1}$) ascribed to S_0–S_1 transition. The maximum fluorescent emission is observed at 492 nm with fluorescent quantum yield estimated to be 0.32 and Stokes shift of 136 nm. This quite large Stokes shift compared to typical BODIPY dyes (normally 15–30 nm) is possibly due to the CT transition from the electron-donating π system to the electron-accepting boron [42]. Compared to the BF_2 chelate with Br substituted by H, the existence of two bromines greatly enlarges the Stokes shift, since BF_2 chelate with no Br only shows Stokes shift of 28 nm [38]. This indicates that p–π conjugation between Br and the aromatic rings increases electronic density of the π system, facilitating the CT transition.

As shown in figure 4(c) and (d), **1** exhibits intense fluorescence in solution, powder, and also crystal states, which have been rarely reported before. The maximum emission is at 461 nm. However, the BF_2 chelate with Br substituted by H does not show any solid emission similar to most other BODIPY dyes [38]. This indicates Br is requisite for solid emission. As revealed by single crystal XRD, the maintenance of fluorescence in the solid state is ascribed to the various supramolecular interactions, such as C–H $\cdots$ F–B, halogen bond between Br with adjacent F atom, etc. The existence of these non-covalent bonds makes the 3-D structure rigid, preventing formation of aggregates, thus maintaining fluorescence in the solid state. The fluorescence quantum

yield in power is measured to be 0.10; however, the number increases to 0.26 as a crystal. Similar to **L1**, **1** also shows much better fluorescence in crystal than in powder, due to the non-covalent interactions in crystal as revealed from X-ray single crystal structure. The solid-emissive property with large Stokes shift makes **1** an ideal intermediate for synthesis of multi-functional materials, since it contains two reactive bromines which are ready to undergo various coupling reactions. Efforts have been made to utilize **1** for synthesis of solid-emissive dyes. Attempts to substitute Br with alkyne by coupling failed, because this reaction needs basic conditions at high temperature, and **1** decomposes under such conditions. Optimization of the coupling reaction for **1** is still in progress.

4. Conclusion

We report the crystal structures of 2-(2′-pyridyl)-4,5-dibromoimidazole **L1** and its corresponding BF_2 chelate **1**. **L1** exhibits weak emission in solution and powder states, but visible enhanced fluorescence as a crystal, due to the formation of rigid structure by non-covalent bonds. Compound **1** is highly fluorescent in solution with large Stokes shift and supramolecular interactions maintain its fluorescence in solid and crystal states. The solid emission with large Stokes shift makes **1** a valuable chromophore for synthesis of multi-functional materials for various applications.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos 804487 for **L1** and 817253 for **1**. Copies of the data can be obtained free of charge from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-11223-336033; E-mail: deposit@ccdc.cam.ac.uk).

Acknowledgments

We are grateful for the financial support from the National Natural Science Foundation of China (21002059).

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