# Synthesis of Pyridine *N*-Oxide–BF<sub>2</sub>CF<sub>3</sub> Complexes and Their Fluorescence Properties

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**Abstract:** Pyridine *N*-oxide–BF<sub>2</sub>CF<sub>3</sub> and  $-BF_2C_2F_5$  complexes and their derivatives were synthesized. Most of the complexes show fluorescence both in solution and in the solid state. By expanding the  $\pi$ -conjugated skeleton, the color of the fluorescence could be changed dramatically. A fluorophore with a high solvent dependency could also be produced. Since such compounds can be synthesized on a gram scale in high yield, and are stable to oxygen, water, and heat, the complexes hold great potential as organic functional materials.

Pyridine, quinoline, and their related skeletons are important partial structures, not only of natural products<sup>[1]</sup> and drugs,<sup>[2]</sup> but also of functional materials.<sup>[3]</sup> Their higher electron-accepting ability compared with other heteroaromatic rings is particularly noteworthy, and makes these rings important components of n-type semiconducting materials for organic electronics.<sup>[4]</sup> We are interested in producing more electron-deficient pyridine and quinoline derivatives. Conventional approaches to obtain such compounds are derivation of the pyridines and quinolines to pyridinium salts and pyridine and quinoline N-oxides. Another promising method for producing more electron-deficient pyridine and quinoline rings is the activation of pyridine and quinoline Noxides using a Lewis acid. Several examples of pyridine Noxide-borane complexes have been reported, some of which show an enhanced electron-accepting property.<sup>[5]</sup> These ex-

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amples, however, contain thermally labile intermolecular pyridine *N*-oxide–borane complexes. Recently, Murakami and co-workers reported intramolecular complexes of pyridine *N*-oxide with boranes that have an improved stability.<sup>[5f]</sup> Here we report the successful synthesis of pyridine *N*oxide–BF<sub>2</sub>CF<sub>3</sub> complexes and their derivatives as highly electron-deficient compounds. These intermolecular complexes are stable to oxygen, water, and heat. In addition, most of the complexes fluoresce not only in solution but also in the solid state.<sup>[6-8]</sup>

First, we investigated the complex formation of 4-phenylpyridine *N*-oxide (**2a**) with various borane compounds, including BF<sub>3</sub>·OEt<sub>2</sub>, BF<sub>2</sub>C<sub>6</sub>F<sub>5</sub>, and BF<sub>2</sub>(4-CF<sub>3</sub>C<sub>6</sub>F<sub>4</sub>) (see the Supporting Information). In all cases, we observed quantitative conversion of **2a** to the corresponding borane complex. These products, however, were unstable under standard aqueous workup conditions or silica gel column chromatography. Their stability was highly dependent on the substituents on the boron center. Pyridine *N*-oxide complexes with BF<sub>2</sub>C<sub>6</sub>F<sub>5</sub> and BF<sub>2</sub>(4-CF<sub>3</sub>C<sub>6</sub>F<sub>4</sub>) were more stable than those with BF<sub>3</sub> (Figure S1, Supporting Information).

Based on the finding that borane reagents with higher Lewis acidity afford more stable products, we next tried the synthesis of a pyridine *N*-oxide complex with BF<sub>2</sub>CF<sub>3</sub>, which is a stronger Lewis acid than BF<sub>3</sub>. Thus, BF<sub>2</sub>CF<sub>3</sub>·OEt<sub>2</sub> (**1a**)<sup>[9]</sup> was prepared in situ by treating K[BF<sub>3</sub>CF<sub>3</sub>] with BF<sub>3</sub>·OEt<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> at 25 °C. Subsequent treatment of the mixture with **2a** for one hour afforded the 4-phenylpyridine *N*oxide–BF<sub>2</sub>CF<sub>3</sub> complex **3a** in 89% yield (Scheme 1). Complex **3a** is stable to air, water, and silica gel purification, and could be stored for at least 3 months.<sup>[10,11]</sup> When BF<sub>2</sub>Me, BF<sub>2</sub>(1-hexyn-1-yl), or BF<sub>2</sub>Ph was used in place of **1a**, a 4phenylpyridine *N*-oxide–BF<sub>3</sub> complex was obtained, thus indicating that Lewis acidic boranes stronger than BF<sub>3</sub> are es-



Scheme 1. Preparation of a  $BF_2CF_3$  complex with 4-phenylpyridine *N*-oxide (**2a**).

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Scheme 2. Synthesis of various pyridine N-oxide-BF<sub>2</sub>CF<sub>3</sub> complexes 3.

sential to produce the desired pyridine *N*-oxide–borane complexes based on this synthetic protocol.

This synthetic method is applicable to the preparation of the BF<sub>2</sub>CF<sub>3</sub> complexes with various pyridine *N*-oxide derivatives, as summarized in Scheme 2. Pyridine *N*-oxides bearing electron-donating or electron-withdrawing groups, as well as sterically encumbered derivatives, smoothly produced the corresponding BF<sub>2</sub>CF<sub>3</sub> complexes **3b–n** in moderate to excellent yields. Ring-fused analogues, such as quinoline, isoquinoline, acridine, and benzo[*h*]quinoline *N*-oxides, also produced the corresponding BF<sub>2</sub>CF<sub>3</sub> complexes **3o–t** in yields of 60–94%. The BF<sub>2</sub>C<sub>2</sub>F<sub>5</sub> complex **4** was also obtained, with a yield of 87%.

Notably, the synthesis can be performed on a gram scale. Treatment of 750 mg of 4-phenylpyridine *N*-oxide (**2a**) with  $BF_2CF_3$  produced 1.17 g of **3a** in 92 % yield, which is comparable to the yield shown in Scheme 1 (**2a**: 145 mg).

Among the  $BF_2CF_3$  complexes thus produced, the structure of the acridine derivative **3r** was determined by singlecrystal X-ray structure analysis (Figure 1). The oxygen atom in the acridine *N*-oxide coordinates to the boron center of  $BF_2CF_3$ . The distance between the oxygen atom and the

atom is 1.514(3) Å, boron which is significantly shorter than a typical B-O coordination bond (e.g., B–O in 1.719 Å).<sup>[12]</sup> BF<sub>3</sub>·OMe<sub>2</sub>, The boron center adopts a slightly distorted tetrahedral geometry with a tetrahedral character (%THC) of 87%.[13] This finding indicates a strong Lewis acid-base interaction between BF<sub>2</sub>CF<sub>3</sub> and acridine N-oxide moieties.

The series of pyridine Noxide-borane complexes thus prepared has several useful characteristics. First, complexation of pyridine N-oxides with more Lewis acidic boranes enhances the thermal stability (Table S1, Supporting Information). In addition, increasing the Lewis basicity of the pyridine N-oxides improves the stability. For example, the 4-phenylpyridine N-oxide complex with the more Lewis acidic  $BF_2C_2F_5$  has a significantly higher decomposition point of 275°C than that of the BF<sub>2</sub>CF<sub>3</sub> congener (162°C). The decomposition point of 3c (176°C) is also higher than that of 3b



Figure 1. ORTEP drawing of acridine N-oxide–BF<sub>2</sub>CF<sub>3</sub> complex **3r** (50% probability for thermal ellipsoids. Hydrogen atoms are omitted for clarity).

(139 °C). Natural bond orbital (NBO) calculations (MP2/6-31+G(d)//B3LYP/6-31G+(d)) suggested that the Wiberg bond index (WBI) of the B–O bond increases as the Lewis acidity of the fluoroboron moiety increases (WBI for pyridine *N*-oxide complexes with BF<sub>3</sub>, BF<sub>2</sub>CF<sub>3</sub>, and BF<sub>2</sub>C<sub>2</sub>F<sub>5</sub> were 0.4711, 0.5226, and 0.5304, respectively), consistent with the observed trend of the thermal stability of these complexes. The NBO analyses also indicated that O–B

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bonds in the pyridine *N*-oxide complexes with highly Lewis acidic  $BF_2CF_3$  and  $BF_2C_2F_5$  have significant covalent bond properties, whereas the corresponding  $BF_3$  complex induces a coordination interaction (see the Supporting Information).

Second, complexation with the highly Lewis acidic fluoroalkylborane enhances the electron-accepting character of the pyridine *N*-oxide-containing  $\pi$ -electron systems. The cyclic voltammetry of 4-phenylpyridine *N*-oxide–BF<sub>2</sub>CF<sub>3</sub> complex **3a** showed an irreversible reduction peak with a peak potential of -1.87 V (vs. Fc/Fc<sup>+</sup>) in THF (Figure S2, Supporting Information).<sup>[14]</sup> The LUMO energy level estimated by the onset potential of the reduction peak was -3.30 eV.

Third, introduction of the BF<sub>2</sub>CF<sub>3</sub> moiety gives rise to fluorescence emission. During the synthesis of **3a**, we found that **3a** showed a purple fluorescence in acetonitrile solution,<sup>[8b,c,15]</sup> whereas 4-phenylpyridine and its *N*-oxide **2a** showed quite weak fluorescence (in CH<sub>3</sub>CN, 4-phenylpyridine, and 4-phenylpyridine *N*-oxide,  $\Phi_{\rm F} < 0.005$ ). Although pyridine *N*-oxide–BF<sub>2</sub>CF<sub>3</sub> complexes **3b–h** showed virtually no fluorescence, the other aryl-, alkenyl-, and alkynyl-substituted complexes **3i–n** as well as the ring-fused derivatives **3o–t** also showed intense emissions, presumably due to the effective extension of  $\pi$ -conjugation. The photophysical properties of several BF<sub>2</sub>CF<sub>3</sub> complexes, **3a**, **3m**, and **3r**, are summarized in Table 1. Both **3a** and **3m** showed only subtle

Table 1. Photophysical data of various pyridine N-oxide-BF<sub>2</sub>CF<sub>3</sub> complexes **3a**, **3m**, and **3r** 

Cmpd	Solvent	Absorptio $\lambda_{abs}$ $[nm]^{[a]}$	n $\epsilon/10^4$ [M <sup>-1</sup> cm <sup>-1</sup> ]	Emission $\lambda_{em}$ [nm]	$\Phi_{ m F}$	Stokes shift [cm <sup>-1</sup> ]
3a	THF	290	2.14	355 <sup>[b]</sup>	0.0094 <sup>[e]</sup>	6300
	MeCN	289	2.15	360 <sup>[b]</sup>	$0.35^{[e]}$	6800
3 m	THF	330	2.91	439 <sup>[c]</sup>	0.10 <sup>[f]</sup>	7500
	MeCN	329	2.93	449 <sup>[c]</sup>	$0.0075^{[f]}$	8100
3r	THF	438	0.25	455 <sup>[d]</sup>	0.53 <sup>[f]</sup>	900
	MeCN	438	0.22	456 <sup>[d]</sup>	0.53 <sup>[f]</sup>	900

[a] The longest wavelength absorption band. [b] Excited at 270 nm. [c] Excited at 290 nm. [d] Excited at 310 nm. [e] Determined using 2-aminopyridine in aq. H<sub>2</sub>SO<sub>4</sub> ( $\Phi_{\rm F}$ =0.66) as a standard.<sup>[16]</sup> [f] Determined using quinine in aq. H<sub>2</sub>SO<sub>4</sub> ( $\Phi_{\rm F}$ =0.55) as a standard.<sup>[17]</sup>

positive solvatochromism in their fluorescence spectra, which indicates that these molecules contain comparable dipole moments between the ground state and the excited state. Their fluorescence quantum yields ( $\Phi_F$ ) are dependent on the solvent polarity. Compound **3a** had significantly higher  $\Phi_F$  of 0.35 in the more polar solvent acetonitrile than in THF ( $\Phi_F$ =0.0094), whereas  $\Phi_F$  of **3m** decreased with increasing solvent polarity ( $\Phi_F$ =0.10 and 0.0075 in THF and acetonitrile, respectively), although the reason remains unclear. On the other hand, acridine *N*-oxide–BF<sub>2</sub>CF<sub>3</sub> complex **3r** displayed completely different features compared to those of **3a** and **3m** (Figures S6 and S7, Supporting Information). Both absorption and the fluorescence properties of **3r** are almost independent on the solvent. Compound **3r**  showed the highest  $\Phi_{\rm F}$  of 0.53 among the pyridine *N*-oxide– BF<sub>2</sub>CF<sub>3</sub> complexes. These features might be attributable to the rigid molecular skeleton that prohibits a structural change both in ground and singlet excited states.

Because **3a** has a high electron-accepting ability, we anticipated that the introduction of an electron-donating group to this skeleton should render the molecule with interesting photophysical properties.<sup>[18]</sup> Indeed, 4-(4-diphenylamino)phenylpyridine *N*-oxide–BF<sub>2</sub>CF<sub>3</sub> complex **3k** showed a significant extent of solvatochromism in fluorescence (Figure 2).



Figure 2. Fluorescent spectra of 4-(4-diphenylamino)phenylpyridine N-oxide-BF<sub>2</sub>CF<sub>3</sub> complex **3k** in various solvents.

Varying the solvent from cyclohexane to  $CH_2Cl_2$  induced a red shift of more than 80 nm (see the Supporting Information for details). According to the density functional theory (DFT) calculation at the B3LYP/6-31+G\* level of theory, the HOMO of **3k** is localized on the 4-Ph<sub>2</sub>NC<sub>6</sub>H<sub>4</sub> moiety, while the LUMO mainly localizes on the pyridine moiety (Figure 3). The time-dependent DFT (TD-DFT) calculation at the same level of theory indicated that the emission of **3k** occurs from an excited state generated by the intramolecular charge-transfer (ICT) transition from the HOMO to the LUMO.



Figure 3. Kohn–Sham molecular orbitals of 3k calculated at the B3LYP/  $6\mathchar`-31+G\mathchar`-16$  level.

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The  $BF_2CF_3$  complexes also showed intense fluorescence, even in the solid state. Powder samples of **3a**, **3m**, **3r**, and **3k** showed purple, blue, green, and yellow fluorescence with emission maxima at 354, 394, 497, and 545 nm, respectively (Figure 4). The quantum yields were 0.51, 0.25, 0.28, and



Figure 4. Fluorescence spectra of 3a, 3m, 3r, and 3k in the solid state. Inset: Photographs taken under irradiation with a hand-held UV lamp.

0.11 for **3a**, **3m**, **3r**, and **3k**, respectively. Therefore, a wide range of fluorescence colors was covered, even in the solid state, simply by changing the structure of the *N*-heteroaromatic moiety of the  $BF_2CF_3$  complexes. Notably, compound **3m** showed a much narrower emission band in the solid state than in solution (full width at half maximum, 75 nm and 42 nm in THF and in the solid state, respectively), which is beneficial for producing a pure blue emission color.

#### Conclusions

In summary, using a simple synthetic method, a series of Noxide-BF2CF3 and -BF2C2F5 complexes of pyridines, quinoline, acridine, and their derivatives can be synthesized as a new category of highly electron-deficient pyridines and related compounds. Most of the complexes showed fluorescence not only in solution but also in the solid state. By expanding the  $\pi$ -conjugated systems, the color of the fluorescence could be changed dramatically. Cyclic voltammetry measurements indicated that the reduction potential was low enough to be a good electron acceptor. In fact, a fluorophore exhibiting a large solvatochromism could be produced by introducing an electron-donating group into the pyridine skeleton. Because the pyridine N-oxide-BF<sub>2</sub>CF<sub>3</sub> complexes and their derivatives can be synthesized on a gram scale in high yield, and are stable to oxygen, water, and heat, the complexes hold great potential as organic functional materials. Our findings provide useful insights for the field of fluorescent materials. It is expected that such compounds could be used as organic electroluminescence materials.

#### **Experimental Section**

#### Preparation of 4-Phenylpyridine N-oxide-BF2CF3 Complex

BF<sub>3</sub>·OEt<sub>2</sub> (595 μL, 4.82 mmol, 1.1 equiv) was added to a mixture of potassium trifluoro(trifluoromethyl)borate (848 mg, 4.82 mmol, 1.1 equiv) in CH<sub>2</sub>Cl<sub>2</sub> (9.0 mL), and the mixture was stirred at 25 °C for 20 min. Then, 4-phenylpyridine *N*-oxide (750 mg, 4.38 mmol) was added to the reaction mixture and the mixture was stirred at 25 °C for 3 h. After dilution of the reaction mixture with CH<sub>2</sub>Cl<sub>2</sub>/acetone (1:1), the insoluble solid was filtered off and washed with CH<sub>2</sub>Cl<sub>2</sub>/acetone (1:1). Subsequently, the solvent was removed under reduced pressure, and the crude product was purified by column chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>, then CH<sub>2</sub>Cl<sub>2</sub>/ acetone, 20:1) to give difluoro((4-phenylpyridin-1-ium-1-yl)oxy)(trifluoromethyl)borate (**3a**, 1.17 g, 92 % yield).

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**Keywords:** boranes • charge transfer • fluorescence • Lewis acid–base interaction • pyridine *N*-oxide

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