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New members of fluorescent 1,8-naphthyridine-based BF_2 compounds: Selective binding of BF_2 with terminal bidentate N^N^O and N^C^O groups and tunable spectroscopy properties

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Intensely luminescent 1,8-naphthyridine-BF_2 complexes **1–9** containing terminal bidentate N^N^O and/or N^C^O groups are synthesized and structurally characterized by X-ray diffraction, electrospray ionization mass spectrometry, ^1H and ^{19}F NMR spectroscopy and elemental analysis. Complexes **1–4** are synthesized from 2-acetamino-1,8-naphthyridine derivatives by a facile route. Selective bonding modes and the chemical stability of complexes **5** and **6** obtained by reacting $BF_3{\cdot}Et_2O$ with 1,8-naphthyridine derivatives bearing dual-functional groups (N^C^O and N^N^O) are investigated by crystal structure analysis and time-dependent density functional theory calculations. The products containing a BF_2 core bound to a N^C^O chelating group are energetically favorable and can expand the range of derivatives by substitution at the 2-position. In this regard, a free -NH_2 group at the 2-position of complex **7** obtained from **5** can be functionalized under a variety of pH conditions to generate complexes **8** and **9** bearing flexible coordination arms that can be used to recognize certain transition metals. The photophysical properties of the complexes are examined in solution and solid state at room temperature. Compared with those of the starting naphthyridine-based compounds, the naphthyridine-BF_2 complexes display desirable light-absorbing properties and intense solution and solid-state emission with large Stokes shifts. Complex **4** in solution exhibited an emission quantum yield of 0.98. In complexes **5–9**, the binding sites for the BF_2 core change from N^N^O to N^C^O, which leads to red shifts of absorption and emission, excellent chemical stability and high emission quantum yields.

Introduction

Boron-dipyrromethene (BODIPY) dyes possess large molar extinction coefficients and Stokes shifts, high emission quantum yields and sharp fluorescence peaks ranging from the blue to near infrared region.[1] As a result, these dyes have received an upsurge of interest, and show promise in applications including photoelectric functional materials,[2] biomolecular labels,[3] sensors,[4] light-harvesting systems,[5] and photodynamic therapy agents.[6] 1,8-Naphthyridine derivatives are well known because of their wide range of applications as fluorescent biological probes.[7] A number of studies on 1,8-naphthyridine rings have shown that the N atoms in these compounds can effectively bind with transition metal ions and the nitrogenous bases of DNA through hydrogen bonding, so 1,8-naphthyridyl derivatives may find use in fluorescent materials, medicinal chemistry and biological fields.[8] Some multidentate dinucleating ligands bearing 1,8-naphthyridine groups can be used to link two metal ions in a similar manner to the *syn, syn* coordination mode of bridging carboxylate groups encountered in a variety of bimetallic centers in biology.[9] Recently, investigation of the photophysical properties of fluorescent naphthyridine derivatives and their Zn(II) and Cu(I) complexes has revealed that their ππ* or metal-to-ligand charge transfer excited states can be tuned by hydrogen-bonding sites leading to intra- or intermolecular interactions.[10] A previous report demonstrated that a 1,8-naphthyridine derivative with pyrrole moieties can be used to detect sugars through changes in absorption and fluorescence.[11] The well-known interaction between the nitrogenous bases of DNA and 1,8-naphthyridyl derivatives is very useful to quantitatively understand the forces involved in helix formation of nucleic acids.[12]

However, naphthyridine-based BF_2 complexes have seldom been explored. Our group reported the first complex with a bis(BF_2) core containing 1,8-naphthyridine moieties,

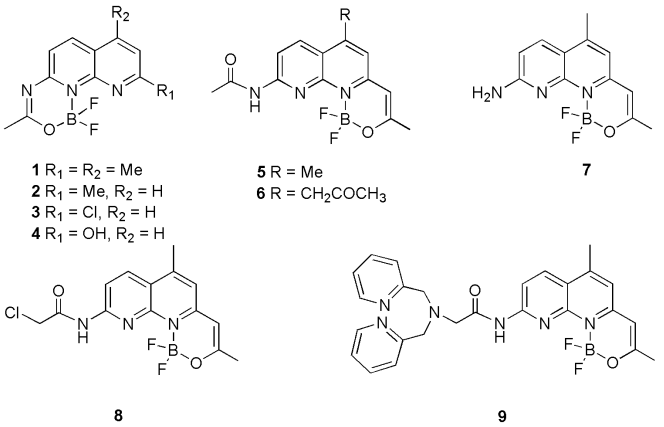
which displayed intense yellow-green emission and two-photon absorption and emission properties in solution, but exhibited weak solid-state emission.[13] In a subsequent study, 1,8-naphthyridine-BF_2 derivatives with strong emission both in solution and the solid state were obtained by binding the BF_2 core with N^N^N groups.[14] Spectroscopic investigation showed that these compounds exhibit unusual aggregation-induced blue-shifted emission in mixtures of DMSO and water, and solvent-influenced photoluminescence in crystalline states. Recent advances have provided a new approach to synthesize 1,8-naphthyridine-based BF_2 complexes containing N^N^O groups.[15] These compounds displayed weak to moderate fluorescence in the solid state, and a large Stokes shift was achieved by introducing an electron-donating group onto the phenyl ring. Along these lines, we found that the hydrogen atoms of methyl groups located on adjacent naphthyridine-N atom can be substituted by acetyl groups, which is accompanied by a 1,3-hydrogen transfer from the $–CH_2–$ group to a carbonyl-O atom resulting in a enolic configuration. In addition, formation of an isomer exhibiting tautomerization has also been observed during the formation of 2-acetamino-1,8-naphthyridine derivatives.[16] This would allow novel 1,8-naphthyridine-based BF_2 derivatives that are expected to exhibit a variety of interesting structures and spectroscopic properties to be produced. In this context, we report the synthesis and molecular structures of fluorescent 1,8-naphthyridine-based complexes containing terminal bidentate N^N^O and/or N^C^O groups and a BF_2 core. Selective bonding modes and the photochemical stability of the obtained complexes as well as their photophysical properties are investigated in detail by crystal structure analysis and time-dependent density functional theory (TD-DFT) calculations.

Results and discussion

Synthesis and crystal structures of 1,8-naphthyridine-BF_2 complexes

We previously prepared a bis(BF_2) complex containing two central five-membered NN^NB rings by reacting 1,2-bis(5,7-dimethyl-1,8-naphthyridin-2-yl)hydrazine with BF_3•Et_2O in the presence of 2,6-lutidine.[13] Extending on this previous work, 1,8-naphthyridine-based complexes with six-membered N^N^NB rings were prepared by coordinating both naphthyridine-N and pyridine-N atoms to BF_2 cores. As we reported previously, N,O-chelated BF_2 complexes with push-pull groups have a large Stokes shift resulting from photoinduced intramolecular charge transfer.[15] A facile way to synthesize new 1,8-naphthyridine-BF_2 complexes is by reaction of 2-acetamino-1,8-naphthyridine derivatives with BF_3•Et_2O (**1–4**, Scheme 1).

2,4-Dimethyl-7-amino-1,8-naphthyridine in acetic anhydride was heated under reflux to afford two unexpected compounds in which the hydrogen atoms of the methyl groups at 2 and/or 4 positions were substituted by acetyl groups except that $–NH_2$ at the 7-position is usually changed to acetylamino.[16] It is also surprising to react 1,8-naphthyridine derivatives bearing various coordination modes with BF_3•Et_2O. The BF_2 core in these complexes is only coordinated to the N^C^O chelating group rather than the N^N^O one (**5** and **6**, Scheme 1). The chemical stability of the new family of 1,8-naphthyridine-based complexes with BF_2 cores is remarkable; hydrolyzing **5** in potassium hydroxide in mixed ethanol and water affords **7** as a yellow powder in 80% yield. We wondered whether the free $–NH_2$ of **7** could be functionalized to further extend this new family. Therefore, we reacted complex **7** with 2-chloroacetyl chloride in chloroform in the presence of potassium carbonate, which gave light yellow product **8** with a high yield of 85%. Yellow complex **9** containing a di-(2-picoly)amine moiety was produced when **8** was used as a starting material (Scheme 1).



Scheme 1 Molecular structures of 1,8-naphthyridine-based complexes.

Single crystals of complexes **1**, **4**, and **6–9** suitable for X-ray diffraction analysis were grown by slow evaporation of dichloromethane solutions, which allowed their molecular structures and packing modes in the solid state to be studied. The crystallographic parameters and data are summarized in the ESI† (Table S1). Perspective drawings of the molecular structures of these materials are depicted in Figure 1. Crystal structures of the complexes show that the coordination geometry around each boron atom is a slightly distorted tetrahedron with each boron atom coordinated to the oxygen of an acetyl group and a naphthyridyl nitrogen atom as well as two fluorine ligands. Complexes **1–4** have similar structures; the geometric configuration of the central bridging N atom on the boron-containing ring was converted from sp^3 hybridization in the precursor to sp^2 when a BF_2 core was coordinated to the N^N^O group.[14] The most obvious difference between complexes **1** and **4** in their solid-state structures is their packing modes: for the former, adjacent molecules pack in a head-to-tail manner to form a two-dimensional layer structure in the *ac* plane, while the latter is arranged in a face-to-face fashion to form an infinite chain along the *a* axis direction with a uniform intermolecular distance of ca. 3.31 Å (Figure 2).

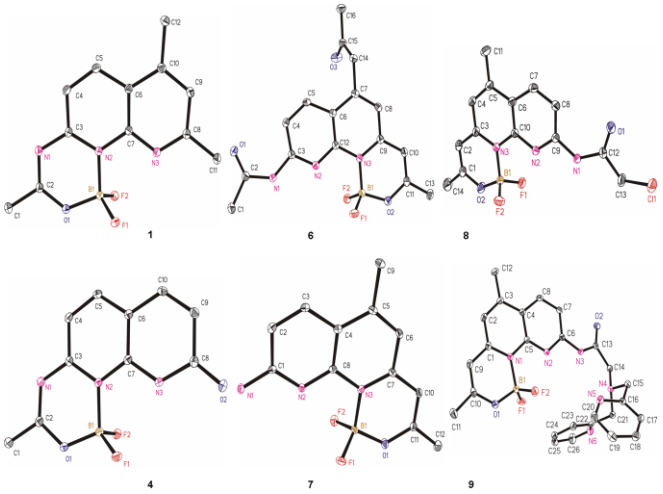


Fig. 1 Perspective views of the labeling schemes for compounds **1**, **4**, and **6–9**. All hydrogen atoms and solvent molecules have been omitted for clarity.

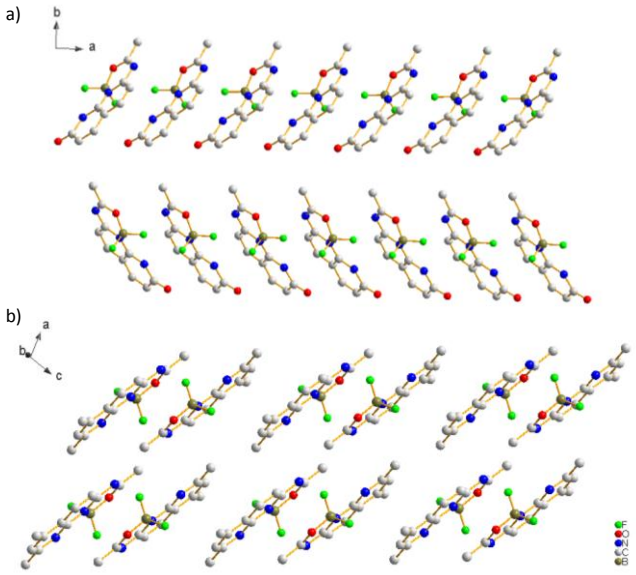


Fig. 2 Packing diagrams for compounds **4** (a, top) and **1** (b, bottom) showing different π-stacking modes.

The most interesting structural feature of complexes **5**–**9** is the selective binding of the BF_2 core with dual-functional groups N^C^O and N^N^O. X-ray analysis revealed that a BF_2 core is coordinated to the end N and O atoms of the N^C^O chelating group instead of the N^N^O chelating one, which results from the transformation from keto to enol form during complexation. For complexes **1**, **4**, and **6**–**9**, B–F, B–N and B–O bond lengths are in the ranges of 1.372(2)–1.400(2), 1.586(1)–1.595(3) and 1.445(2)–1.448(1) Å, respectively, which are comparable with those reported for a difluoro(amidopyrazinato-O,N) boron derivative.[17] The average C–O bond length of 1.323(2) Å in the boron-containing rings is considerably longer than a normal C=O double bond (*ca*. 1.22 Å), and close to a typical C–O single bond (*ca*. 1.34 Å). Meanwhile, the original N–C=O and C–C=O single bond distances (1.39 and 1.52 Å, respectively) were shortened markedly to an average of 1.300(2) Å in **1** and **4** and 1.350(3) Å in **6** and **7**, respectively, revealing the character of N=C–O and C=C–O double bonds. Similar behavior has been observed in the synthesis of dyes with fused perylene tetracarboxylic diimide and BODIPY analogue structures.[18] The N–B–O, F–B–F, N–B–F and F–B–O bond angles of 108°, 111°, 111° and 109°, respectively, all fall within normal limits, and both the naphthyridyl rings and boron-containing six-membered ring are nearly coplanar except for in complexes **4** and **8**. Structural investigation of complex **4** in Figure 1 showed that the hydrogen atom on the hydroxyl group of the naphthyridine ring transfers to an adjacent naphthyridine N atom to form a keto configuration. Boron centers in **4** and **8** are tilted out of plane from the naphthyridine ring compared with those of other complexes with BF_2 cores so that the trigonal NOB plane and the adjacent naphthyridyl ring are not coplanar, the dihedral angle varies from 22.6° in **4** to 6.2° in **8**.

Theoretical investigation of selective binding of a BF_2 core to an N^C^O group

To elucidate the energetics of the competing reactions of BF_2 coordination to N^N^O and N^C^O functional groups, all geometrical structures of compounds **1**–**9** were optimized at the SCRF(PCM/Bader)-B3LYP/6-311++G(d,p) level in CH_2Cl_2 solution, with single-point energy and molecular orbitals calculated at the TD-DFT(SCRF(PCM/Bader)-B3LYP/6-311++G(d,p)) level (see ESI†).[19]. The calculated total molecular energies were **1**: -929.0195794, **2**: -889.6912072, **3**: -1309.9836741, **4**: -925.6231234, **5**: -1081.728235, **6**: -1234.413745, **7**: -929.0267231, **8**: -1541.3428219, and **9**: -1710.024192 au. Comparison of the total molecular energies indicates that the stability of compounds **1**–**4** with a six-membered N^N^OB ring follows the order **3** > **1** > **4** > **2**, whereas for compounds **5**–**9** adopting a coordination mode of N^C^OB, the single-point energy follows the order **9** > **8** > **6** > **5** > **7**. Additionally, compared with the binding modes determined by structural analysis for compounds **5**, **6**, **8** and **9** bearing dual-functional ligands, structures of their

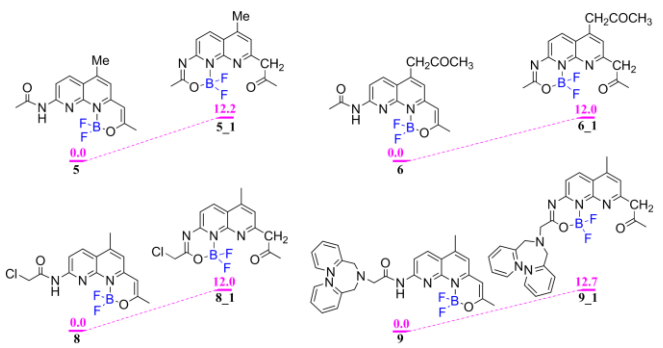


Fig. 3 The calculated molecular relative energies (kcal/mol) of **5**, **6**, **8** and **9** and their corresponding compounds,

corresponding compounds **5_1**, **6_1**, **8_1** and **9_1** with chelating coordination modes of N^N^OB were also optimized by DFT. Their calculated molecular energies have respective values of -1081.7074081, -1234.393237, -1541.3226127 and -1710.0025523 au, which are higher than those of the compounds **5**, **6**, **8** and **9**. This implies the former are structurally unstable relative to the latter. Therefore, **5**, **6**, **8** and **9** were obtained as reaction products in the competing reaction (Figure 3)

Table 1 Spectroscopic data for compounds **1**–**9**

Complexes	Medium (298 K)	λ_{abs}/nm (ε/dm^3 mol^{-1} cm^{-1})	λ_{em}/nm	ϕ_f	τ/ns	Stokes shift/nm
1	CH_2Cl_2	344 (23 930), 361 (30 740)	384	0.02	< 0.5	23
	solid state		503		0.7	
2	CH_2Cl_2	343 (19 100), 360 (23 250)	383	0.03	< 0.5	23
	solid state		415		0.8	
3	CH_2Cl_2	345 (27 600), 362(34 550)	385	0.20	< 0.5	23
	solid state		416		0.8	
4	CH_2Cl_2	365 (29 250), 383 (31 500)	408	0.98	3.3	25
	solid state		453		1.2	
5	CH_2Cl_2	390 (33 027), 410 (37 243)	426, 446	0.26	2.4, 3.8	10
	CH_3OH	388 (37 444), 407 (41 108)	424, 443	0.46		17
	solid state		458, 498		1.4, 5.4	
6	CH_2Cl_2	392 (42 438), 412 (45 920)	435, 450			23
7	CH_2Cl_2	390 (20 149), 412 (30 099)	423, 443	0.75	2.2, 3.5	11
	CH_3OH	392 (21713), 413 (31 104)	429, 445	0.34		16
	solid state		448, 512		1.1, 4.1	
8	CH_2Cl_2	391 (24 337), 412 (25 867)	428, 447	0.84	3.8, 5.7	16
	CH_3OH	389 (24 694), 408 (26 173)	428, 445	0.68		20
	solid state		459, 510		2.0, 7.5	
9	CH_2Cl_2	392 (30 301), 413(35 524)	428, 446	0.23	1.5, 3.4	8
	CH_3OH	390 (40 993), 410 (44 491)	428, 447	0.31		18
	solid state		484, 511		2.0, 5.8	

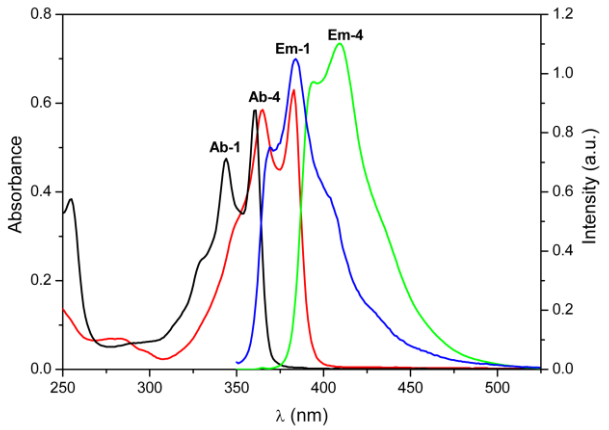


Fig. 4 Electronoc absorption and emission spectra of compounds **1** and **4** in dichloromethane solution.

Spectroscopic properties of 1,8-naphthyridine-based complexes with BF_2 cores

The spectroscopic properties of compounds **1**–**9** both in solution and solid state at room temperature were investigated, the spectral data are summarized in Table 1. The salient feature of the absorption spectra for compounds **1**–**4** in dichloromethane solution is the strong bands between 300 and 400 nm with almost the same profiles (Figures 4) and extinction coefficients in the range of 19100–31500 dm^3 mol^{-1} cm^{-1}. However, the absorption bands of **4** are red-shifted compared with those of the other three analogous compounds. Complexes **1**–**3** in dichloromethane solution emit at about 384 nm with emission lifetimes of less than 0.5 ns and quantum yields of 0.02–0.20, whereas **4** displays intense lower-energy emission with λ_{max} at 408 nm and a fluorescence quantum yield of up to 0.98. The small Stokes shift and short emission lifetimes of complexes **1**–**3** suggests their emissive states are of singlet $^1(\pi–\pi^*)$ character. The solid-state emissions (Figure 5) of compounds **1**–**4** are quite different from those in solution, which is contributed to different molecular stacking, as shown above in the packing diagrams (Figure 2).

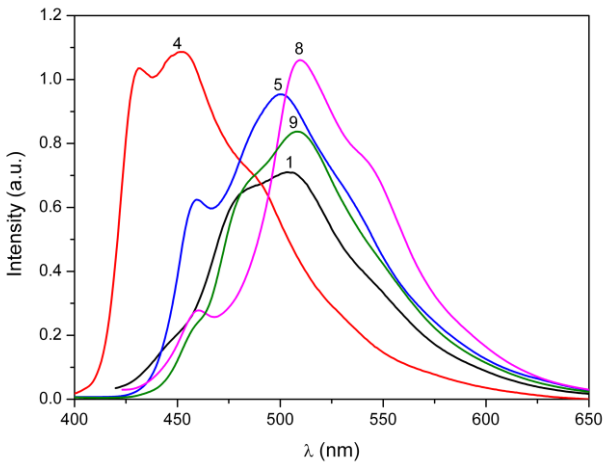


Fig. 5 Solid-state emission spectra of compounds **1**, **4**, **5**, **8** and **9**, excitation upon 350 nm (**1**) and 400 nm, respectively.

In comparison, absorption spectral profiles of complexes **5**–**9** obtained by selectively coordinating $BF_3{\cdot}Et_2O$ to N^C^O functional groups are similar to those of **1**–**3** but exhibit a

marked red shift from ca. 361 to 412 nm in dichloromethane solution. Compounds **5**–**9** (Figure 6) exhibit strong emissions whether in dichloromethane or methanol solution with quantum yields of 0.23–0.84, and emission spectra display a red shift of 60 nm compared with those of **1**–**3**. These naphthyridine-BF_2 complexes exhibited intense photoluminescence in the solid state at room temperature. Compared with the emissions of compounds **2** and **3**, compound **1** and **5**–**9** bearing an alkyl group at the 4-position of the naphthyridine ring display broad low-energy solid-state emissions (Table 1). The emissions centered at 415 nm for the former extended to ca. 510 nm for **7**–**9**.

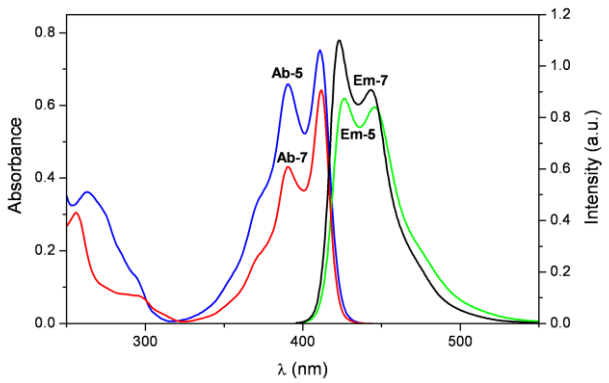


Fig. 6 Electronoc absorption and emission spectra of compounds **5** and **7** in dichloromethane solution.

TD-DFT calculations of **1**–**9** indicated their highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) are mainly localized on the naphthyridine ligand with some of the HOMO on the BF_2 core(Figure S1 and Table S1 in ESI†). Figure 7 shows that the complex **7** formed by reacting $BF_3{\cdot}Et_2O$ with naphthyridine derivatives with functional groups N^C^O shifted both HOMO and LUMO to higher energy. However, the effect on HOMO level was larger than that on the LUMO, so longer wavelength absorption was observed upon the complex.

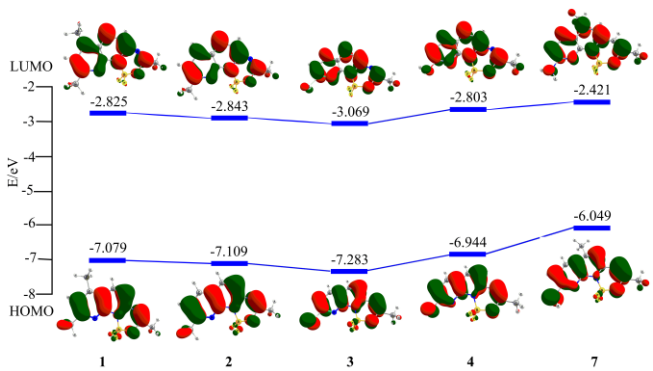


Fig. 7 Molecular orbital energy diagrams and isodensity surface plots of the frontier orbitals of **1**–**4** and **7**.

Experimental

Synthesis and characterization of 1-4

Complexes **1-4** were prepared by reaction of corresponding 7-acetamino-1,8-naphthyridine (2 mmol) derivatives with $BF_3{\cdot}Et_2O$ (3 mL) in dichloromethane (50 mL) containing 2,6-lutidine (2 mL) for 3 h at room temperature under nitrogen atmosphere. Water (20 mL) was added to remove excess $BF_3{\cdot}Et_2O$, and the dissolved product in the aqueous phase was extracted with dichloromethane (3 × 30 mL). The incorporated organic phase was evaporated under vacuum to give a crude product. The product was purified by column chromatography on silica gel using dichloromethane/ethyl acetate (v/v, 25/1) as an eluent.

Characterization of 1: Yield: 60%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.52 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.28 (s, 1H), 2.79 (s, 3H, C*H*$_3$), 2.69 (s, 3H, C*H*$_3$), 2.41 ppm (s, 3H, C*H*$_3$); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -129.94 ppm (d, *J* = 22.7 Hz, BF_2); ESI-MS: *m/z* 264 $[M+H]^+$; elemental analysis calcd. for $C_{12}H_{12}BF_2N_3O$ (263.1): C 54.79, H 4.60, N 15.97; found: C 54.61, H 4.54, N 16.08.

Characterization of 2: Yield: 51%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.31 (d, *J* = 8.0 Hz, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 2.86 (s, 3H, C*H*$_3$), 2.42 ppm (s, 3H, C*H*$_3$); ESI-MS: *m/z* 250 $[M+H]^+$; elemental analysis calcd. for $C_{11}H_{10}BF_2N_3O$ (249.0): C 53.05, H 4.05, N 16.87; found: C 53.21, H 4.06, N 16.97.

Characterization of 3: Yield: 49%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.24 (d, *J* = 8.0 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 2.32 ppm (s, 3H, C*H*$_3$); ESI-MS: *m/z* 308 $[M+K]^+$; elemental analysis calcd. for $C_{10}H_7BClF_2N_3O$ (269.4): C 44.58, H 2.62, N 15.60; found: C 44.73, H 2.70, N 15.97.

Characterization of 4: Yield: 32%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 1H), 6.72 (d, *J* = 8.0 Hz, 1H), 2.38 ppm (s, 3H, C*H*$_3$); ESI-MS: *m/z* 252 $[M+H]^+$; elemental analysis calcd. for $C_{10}H_8BF_2N_3O_2$ (251.0): C 47.85, H 3.21, N 16.74; found: C 48.12, H 3.25, N 16.88.

Synthesis and characterization of 5

2,4-Dimethyl-7-amino-1,8-naphthyridine (0.346 g, 2.0 mmol) in acetic anhydride (10 mL) was heated under reflux with vigorous stirring for 20 h under an atmosphere of nitrogen. The solution changed from colorless to black. The resulting solution was concentrated and the crude product was purified by column chromatography on silica gel using chloroform/acetone (v/v, 20/1) as an eluent to give an orange solid. ESI-MS: *m/z* 258 $[M+1]^+$. The obtained ligand (0.202 g, 0.8 mmol) was dissolved in dichloromethane (60 mL). A mixture of $BF_3{\cdot}Et_2O$ (3 mL) and 2,6-lutidine (2 mL) was added dropwise to the solution with an isobaric funnel under an atmosphere of nitrogen at room temperature. After 5 h, dichloromethane was removed under vacuum, and the resulting mixture was extracted with chloroform and water (v/v, 2/1; 3 × 20 mL). The organic phase was dried over anhydrous Na_2SO_4 and the solvent was evaporated to give a

yellow solid. The crude product was purified by column chromatography on silica gel using dichloromethane/ethanol (v/v, 300/1) as an eluent to afford a light yellow powder. Yield: 36% (0.088 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.76 (br s, 1H, N*H*), 8.47 (d, *J* = 8.0 Hz, 1H, Napy-*H*,), 8.19 (d, *J* = 8.0 Hz, 1H, Napy-*H*), 6.84 (s, 1H, Napy-*H*), 5.65 (s, 1H, C=C*H*), 2.65 (s, 3H, Napy-CH_3), 2.29 (s, 3H, CH_3), 2.23 ppm (s, 3H, CH_3); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -128.40 (d, *J* = 13.40 Hz, BF_1), -128.47 ppm (d, *J* = 13.40 Hz, BF_2); ESI-MS: *m/z* 306 $[M+H]^+$; elemental analysis calcd. for $C_{14}H_{14}BF_2N_3O_2$ (305.1): C 55.12, H 4.63, N 13.77; found: C 55.31, H 4.79, N 13.88.

Synthesis and characterization of 6

Complex **6** was synthesized and purified by a procedure similar to that used for **5** except that the reaction time for ligand synthesis was extended to 36 h. Yield: 17%. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.80 (br s, 1H, NH), 8.47(d, *J* = 8.5 Hz, 1H, Napy-*H*), 8.04 (d, *J* = 8.5 Hz, 1H, Napy-*H*), 6.87 (s, 1H, Napy-*H*), 5.70 (s, 1H, C=C*H*), 4.09 (s 2H, Napy-CH_2), 2.33 (s 3H, CH_3), 2.30 (s, 3H, CH_3), 2.25 ppm (s, 3H, CH_3); ESI-MS: *m/z* 348 $[M+H]^+$; elemental analysis calcd. for $C_{16}H_{16}BF_2N_3O_3$ (347.1): C 55.36, H 4.65, N 12.11; found: C 55.12, H 4.53, N 12.23.

Synthesis and characterization of 7

A solution containing potassium hydroxide (0.340 g) in ethanol (20 mL) and water (5 mL) was added to a solution of complex **5** (0.070 g, 0.23 mmol) in dichloroethane (200 mL) with stirring under an atmosphere of nitrogen. The reaction mixture was heated under reflux for 5 h. Water (20 mL) was added, the organic phase was dried over anhydrous Na_2SO_4 and the solvent was evaporated to give a yellow solid. The crude product was purified by column chromatography on silica gel using dichloromethane/methane (v/v, 200/1) as an eluent to afford a yellow powder. Yield: 80% (0.048 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.89 (d, *J* = 12.0 Hz, 1H, Napy-*H*), 6.69 (d, *J* = 8.0 Hz, 1H, Napy-*H*), 6.64 (s, 1H, Napy-*H*), 5.55 (s, 1H, C=C*H*), 5.43 (s, 2H, NH_2), 2.55 ppm (s, 3H, Napy-CH_3), 2.18 ppm (s, 3H, CH_3). ^{19}F NMR (376 MHz, $CDCl_3$): δ = -129.17 (d, *J* = 15.0 Hz, BF_1), -129.25 ppm (d, *J* = 15.0 Hz, BF_2); ESI-MS: *m/z* 264 $[M+H]^+$; elemental analysis calcd. for $C_{12}H_{12}BF_2N_3O$ (263.1): C 55.12, H 4.63, N 13.77; found: C 55.31, H 4.79, N 13.88.

Synthesis and characterization of 8

A suspension containing potassium carbonate (0.300 g) in chloroform (20 mL) was added to a solution of complex **7** (0.262 g, 1.00 mmol) in chloroform (20 mL) with stirring under an atmosphere of nitrogen. After 15 min, a solution of 2-chloroacetyl chloride (0.16 mL) in chloroform was added dropwise to the above mixture with an isobaric funnel. The resulting mixture was evaporated to give a brown solid. The crude product was purified by column chromatography on silica gel using dichloromethane as the eluent to give a light yellow powder. Yield: 85% (0.289 g). ^{1}H NMR (400 MHz, DMSO-d_6) δ = 11.11 (s, 1H, N-*H*), 8.52 (d, *J* = 8.0 Hz, 1H, Napy-*H*), 8.11 (s, 1H, Napy-*H*), 7.24 (s, 1H, Napy-*H*), 5.94 (s, 1H, C=C*H*), 4,69 (s, 2H, CH_2), 2.66 (s, 3H, Napy-CH_3), 2.15 ppm (s, 3H, CH_3); ^{19}F NMR (376 MHz, DMSO-d_6): δ = -120.6 (d, *J* = 12.4 Hz); ESI-MS: *m/z* 264 $[M+H]^+$; elemental analysis calcd. for $C_{14}H_{13}BClF_2N_3O_2$ (339.5): C 49.52, H 3.86, N 12.38; found: C 49.83, H 3.89, N 12.52.

Synthesis and characterization of 9

Acetonitrile (80 mL) containing complex **8** (0.100 g, 0.30 mmol), potassium iodide (0.38 mmol), potassium carbonate (0.38 mmol), and di-(2-picoly)amine (0.40 mmol) was heated under reflux for 24 h with stirring under an atmosphere of nitrogen. The resulting mixture was evaporated to give an oily brown solid. The crude product was purified by column chromatography on silica gel using dichloromethane/methanol (v/v, 50/1) as the eluent to give a yellow powder. Yield: 60% (0.090 g). ^{1}H NMR (400 MHz, DMSO-d_6) δ = 11.43 (br s, 1H, N*H*), 8.67 (d, *J* = 4.0 Hz, 2H, Py-*H*), 8.51 (d, *J* = 8.0 Hz, 1H, Napy-*H*), 8.29 (d, *J* = 8.0 Hz, 1H, Napy-*H*), 7.74 (t, *J* = 8.0 Hz, 2H, Py-*H*), 7.51 (d, *J* = 8.0 Hz, 2H, Py-*H*), 7.26 (t, *J* = 4.0 Hz, 2H, Py-*H*), 7.24 (s, 1H, Napy-*H*), 5.95 (s, 1H, C=C*H*), 4.18 (s, 4H, CH_2), 3.58 (s, 2H, CH_2), 2.66 (s, 3H, Napy-CH_3), 2.17 ppm (s, 3H, CH_3); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -125.74 (d, *J* = 22.6 ppm Hz, BF_2); ESI-MS: *m/z* 503 $[M+H]^+$; elemental analysis calcd. for $C_{26}H_{25}BF_2N_6O_2$ (502.3): C 62.17, H 5.02, N 16.73; found: C 62.50, H 5.23 N 16.95.

Conclusions

Novel fluorescent 1,8-naphthyridine-BF_2 complexes were synthesized by introducing a BF_2 core onto 1,8-naphthyridine derivatives through N^N^O or/and N^C^O functional groups. In the case of 2-acetylamino-1,8-naphthyridine derivatives, the compound exhibits a chelating coordination mode and the 1,8-naphthyridine-BF_2 complex with six-membered chelate rings was formed through the terminal N and O atoms of the N^N^O group. In contrast, 1,8-naphthyridine derivatives bearing dual-functional groups show competitive chelation, namely a BF_2 core is coordinated to the end N and O atoms of N^C^O instead of N^N^O. The former displays enhanced emission and red shifts of absorption and emission maxima relative to the latte. This shows that 1,8-naphthyridine-BF_2 complexes formed by ketone ligands are more stable than those containing acetylamino groups. DFT calculation results support this conclusion. This work extends 1,8-naphthyridine-BF_2 chemistry, and offers many advantages, including easy synthesis, good stability and end functionalization with NH_2 groups to produce a new class of fluorescent materials suited for biomedical applications. The water solubility and biocompatibility of naphthyridine-based BF_2 compounds containing BF_2 cores coordinated with N^C^N, N^N^O and N^C^O groups still need improving, which we are currently attempting in our laboratory.

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Entry for the Table of Contents

Selective binding of the BF_2 core with N^N(C)^O groups of 1,8-naphthyridine-based compounds produces complexes with tunable absorption and luminescence properties