# **β-Iminoenamine-BF<sub>2</sub> Complexes: Aggregation-Induced Emission and Pronounced Effects of Aliphatic Rings on Radiationless Deactivation**

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Abstract: The synthesis, photophysical, and electrochemical attributes of a novel class of boron difluorides containing an aromatic-fused alicyclic/ hetero-alicyclic ring built on a  $\beta$ -iminoenamine chromophoric backbone are reported. The compounds displayed large Stokes shifts (86–121 nm), and were emissive in the solid state. The quantum yields obtained in solution at room temperature were unusually lower by an order of magnitude compared to those in the solid state. Some of the tested compounds displayed aggregation-induced emission (AIE). Single crystal XRD analyses revealed a lack of interplanar  $\pi$ - $\pi$  interactions,

**Keywords:** aggregation-induced emission  $\cdot$  boron  $\cdot$  chromophores  $\cdot$ luminescence  $\cdot \pi - \pi$  interactions which are presumed to be absent owing to non-planarity of the alicyclic component in the molecule. For most of the studied compounds, time-dependent DFT (TD-DFT) calculations invariably reveal intramolecular charge transfer ( $\pi$ - $\pi$ \*) characteristics with the frontier orbitals concentrated on the boron-nitrogen heterocycle. The participation of boron and fluorine atoms was found to be negligible.

#### Introduction

Stable tetracoordinate organoboron complexes are of current scientific interest owing to their potential utility as functional luminophores for an array of applications.<sup>[1]</sup> This is further evident from the significant amount of research directed towards the boron–dipyrromethene (BODIPY) class of molecules. Incorporation of a boron atom is perceived to stabilize the N,N-monoanionic chelate by an effective delocalization of the negative charge. Although BODIPY dyes have evolved as a privileged class of molecules for a wide

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variety of applications,<sup>[2]</sup> the solid-state luminescence properties in most of their derivatives have been found to be poor when compared to those in solution, primarily owing to quenching of emission due to intermolecular  $\pi$ - $\pi$  stacking interactions. A prominent strategy to avoid such quenching has been to introduce a sterically imposing substituent at the meso-carbon of the dipyrrin core.<sup>[3]</sup> Apart from the dipyrrin framework, several groups have focused their attention in developing newer classes of boron-based fluorophores to achieve superior solid-state luminescence properties. The groups of Yamaguchi,<sup>[1e,4]</sup> Wang,<sup>[1a,b,5]</sup> Piers,<sup>[1f,6]</sup> and others<sup>[4c-f]</sup> have developed highly luminescent fluorophores that are mainly based on boron. In this study, we have aimed to explore the photophysical nature of yet a new class of flurophores, namely, the β-iminoenamine-boron difluorides with a fused aliphatic ring unit. They are akin to the popular "nacnac" ligands or the  $\beta$ -diketiminate systems, which have a "formal" 6-membered ring and a chelating  $\mu^2$ -H proton bridged to the nitrogen atoms.<sup>[7]</sup> The initial choice of the chelate was for the following reasons: 1) Desymmetrization of the chromophoric coordination sphere about the nitrogen atom bound to boron (unlike in the case of the dipyrrin core) has been recently realized to effect larger Stokes shifts.<sup>[6]</sup> 2) Introduction of an aliphatic ring in the chromophoric backbone can disrupt deleterious stacking interactions owing to its non-planar conformation. 3) Ease of introduction of diverse functional groups, which can eventually modulate the ground/excited states, which lead to intriguing luminescence properties. Gardinier et al. have elegantly compared the electronic properties of difluoroboron complexes bearing  $\beta$ -diketonate,  $\beta$ -ketoiminate, and  $\beta$ -diiminate

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1

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ligands,<sup>[8]</sup> which bear close resemblance to the system under investigation. Similarly, Mu et al. and other research groups have investigated the photoluminescence (PL) properties of anilido-imine-BF<sub>2</sub> compounds.<sup>[9]</sup> The observed luminescence in this case was attributed to  $\pi^*-\pi$  transition of their conjugated chelating anilido-imine ligands. Very recently, Piers et al. have described similar compounds that exhibit large Stokes shifts and good photostability.<sup>[6]</sup>

Herein, we have tried to exploit the basic skeleton of the borylated  $\beta$ -iminoenamine by encompassing it with either 1,2-dihydronaphthalene, 2*H*-chromene, or 2*H*-thiochromene in its chromophoric backbone. Functional variation of the substituents in the aromatic unit and also changes in the heteroatom of the fused aliphatic unit led to novel compounds with tunable emission properties. In line with our expectations, some of the synthesized compounds exhibited bright luminescence in the crystalline state and in the aggregated state in solution (AIE phenomenon), but were almost nonemissive in various solvent media. Combined photophysical, NMR spectroscopy, and single crystal X-ray diffraction studies have suggested that the aliphatic part of the molecule is primarily responsible for the varied emission behavior in this class of compounds.

## **Results and Discussion**

#### Synthesis and Characterization

Iminoenamines suitable for complexation were realized in two steps starting from the appropriate  $\alpha$ -tetralone/(2*H*)benzopyran-4-one/(2*H*)-benzthiopyran-4-one (Scheme 1). Vilsmeier–Haack formylation of the ketones furnished their respective  $\beta$ -chlorovinyl aldehydes (**1a–1e**), which upon treatment with 2.0 equivalents of substituted aryl amines in the presence of *p*-toluenesulfonic acid (PTSA) gave the desired iminoenamines (**2a–2n**) in the yield range of 65–92%. This route was previously established in our group and was used for the synthesis of condensed heterocycles such as acridines/quinolines.<sup>[10]</sup>

Detailed synthetic procedures for the preparation of new iminoenamines (2a-2n) are provided in the Supporting Information. We envisaged that the iminoenamines that are potential systems for electrocyclic ring closure should readily react with Lewis acidic BF<sub>3</sub>·Et<sub>2</sub>O to form stable boron compounds. As expected, treatment of iminoenamines with BF<sub>3</sub>·Et<sub>2</sub>O in the presence of excess base such as Et<sub>3</sub>N or disopropylamine (DIPA; to mop up the nascent HF generated) yielded the desired products in modest to good yields of 70–95% (Scheme 2). The reaction was also found to proceed with the hydrochloride salt of the iminoenamines in a one-pot sequence, which does not require prior neutralization. All of the products **3a-3f**, **4a-g**, and **5** were stable to



Scheme 2. Synthetic route to iminoenamine-BF2 complexes.

air and moisture and were fully characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, and HRMS experiments. Some of the diagnostic features in the <sup>1</sup>H NMR spectra of these boron compounds include the disappearance of the signal intensity, owing to the proton of the free amine and coupling between iminomethine and boron with  ${}^{3}J_{H-B}$  around 3.7 Hz. Broad multiplets in both <sup>11</sup>B NMR and <sup>19</sup>F NMR spectra were also observed owing to the coupling between boron and fluorine atoms. In certain cases, for example, the <sup>11</sup>B NMR spectrum of **4g** exhibited a triplet ( ${}^{1}J_{B-F} = 29.9 \text{ Hz}$ )



Scheme 1. Synthetic route to iminoenamines.

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Figure 1. X-ray structure of 4g with selective atomic numbering scheme, thermal ellipsoids are set at 50% probability (left). Crystal packing diagram of 4g (right).

and nearly the same coupling constant was observed in the  $^{19}\mathrm{F}\,\mathrm{NMR}$  spectrum  $(^{1}J_{\mathrm{B-F}}{=}\,30.0\,\mathrm{Hz})$  with a well-resolved quartet pattern.

#### **X-ray Diffraction Studies**

As expected, the coordinatively saturated boron atom adopted a pseudo-tetrahedral geometry on the plane defined by the imine and amido nitrogen flanked by the two fluorine atoms, above and below the plane (Figure 1 and see the Supporting Information, Figure S7). Selected bond distances and bond angles are provided in the Supporting Information together with other relevant crystallographic data (see the Supporting Information, Tables S1 and S2). The Nimine-B-Namido bite angles were in the expected standard range when compared to the previously reported<sup>[6,9]</sup> anilidoimine complexes. Similar to boron-dipyrromethene compounds,<sup>[2]</sup> the average distances of the boron atom to the nitrogen atom of the imine (B(1)-N(1)=1.54 Å) and to the amine nitrogen (B(1)-N(2)=1.55 Å) were similar, thus suggesting an effective delocalization of the positive charge of the iminium ion. The aliphatic ring in all the three cases adopted a puckered conformation owing to the sp<sup>3</sup>-hybridized nature of the carbon or oxygen atom, with the atoms exhibiting torsional angles approximately in the range of 55.8-59.2°. Also, the dihedral angles between the mean planes defined by the N-bonded arene and the boron heterocycle were invariably greater than 35° (see the Supporting Information, Table S1). These facts demonstrate low elements of symmetry and planarity in these molecules. Close examination of the crystal packing structures revealed more interesting aspects. Although no specific pattern in the arrangement or arene  $\pi$ - $\pi$  stacking was evident (closest  $\pi$ - $\pi$ interplanar distance was greater than 3.8 Å), significant intermolecular CH…F and CH… $\pi$  interactions  $^{[2i,11]}$  were observed in the lattices of these compounds. Especially in compound 3e, CH…F distances in the order of approximately 2.46 Å were observed. In addition to conferring increased stability, these interactions could affect photophysically relevant electronic states of the molecule.

#### **Photophysical Studies**

All of the compounds were generally characterized by a well-separated intense low-energy absorption band in the range of 410–445 nm (see Table 1, Figure 2, and the Supporting Information, Figure S1) with molar extinction coefficients in the order of  $10^4 \text{M}^{-1} \text{cm}^{-1}$ . In addition, less intense



Figure 2. Electronic absorption spectra of 3a, 3d, 4c, and 4d.

bands, which indicate lower transition probability, were also observed in the wavelength range of 249-352 nm. Steadystate emission spectra measured in CH<sub>2</sub>Cl<sub>2</sub> at room temperature showed very weak emission intensities with low quantum yields in the range of  $10^{-2}$ - $10^{-4}$ . Compound 5 containing a sulfur atom was completely non-emissive in CH<sub>2</sub>Cl<sub>2</sub> at room temperature presumably owing to heavy atom photoinduced electron transfer.<sup>[12]</sup> The other emission profiles were Gaussian shaped, broad, and closely resembled the absorption bands (see Figure 3 and the Supporting Information, Figure S2). In the solid state, the emission profiles were relatively narrower and red-shifted. However, in the cases of 3c, 4a, 4d, 4e, and 4g a distinct blue shift was observed. The observed Stokes shifts were in an extraordinary range (86-121 nm) as compared to the typical 7-15 nm shift observed in BODIPY derivatives. Earlier observations with

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3

Table 1. Photophysical properties of compounds 3a-g, 4a-g, and 5

|     | RT solution (                      | CH <sub>2</sub> Cl | 2)   | Emissio                | $E_{\rm opt}^{\rm [f]} [eV]$ |                       |                       |      |
|-----|------------------------------------|--------------------|------|------------------------|------------------------------|-----------------------|-----------------------|------|
|     | Absorption                         | PL                 | τ    | $arPhi_{ m f}^{[a]}$ . | Stokes                       | $\lambda_{\max}[nm],$ | $\lambda_{\max}[nm],$ |      |
|     | $\lambda_{\max}[nm]$               | $\lambda_{emiss}$  | [ns] | x 10 <sup>-3</sup>     | shift <sup>[b]</sup>         | solid                 | PMMA                  |      |
|     | $(\varepsilon_{\rm max}/$          | [nm]               |      |                        | [nm]                         | $(\Phi_{ m f}$        | $(\Phi_{ m f}$        |      |
|     | [dm <sup>3</sup> mol <sup>-1</sup> |                    |      |                        |                              | solid) <sup>[c]</sup> | PMMA) <sup>[d]</sup>  |      |
|     | cm <sup>-1</sup> ])                |                    |      |                        |                              |                       |                       |      |
| 3a  | 348 (7706),                        | 541                | 0.3, | 0.97                   | 112                          | 562                   | 544                   | 2.47 |
|     | 429 (24996)                        |                    | 6.5  |                        |                              |                       |                       |      |
| 3b  | 337                                | 531                | _[e] | 6.20                   | 84                           | 555                   | 538                   | 2.44 |
|     | (14111),                           |                    |      |                        |                              |                       |                       |      |
|     | 447 (33670)                        |                    |      |                        |                              |                       |                       |      |
| 3c  | 317(7061),                         | 522                | 0.6, | 3.70                   | 101                          | 512                   | 514                   | 2.58 |
|     | 421(22590)                         |                    | 4.0  |                        |                              |                       |                       |      |
| 3 d | 324 (6168),                        | 520                | 1.3, | 2.61                   | 102                          | 543 (6.0)             | 522 (2.4)             | 2.59 |
|     | 418 (21 372)                       |                    | 9.1  |                        |                              |                       |                       |      |
| 3e  | 345 (6371),                        | 540                | 2.0  | 0.57                   | 116                          | 552 (2.4)             | 547 (1.6)             | 2.48 |
|     | 427 (20701)                        |                    |      |                        |                              |                       |                       |      |
| 3 f | 339 (1295),                        | 531                | _[e] | 54.01                  | 86                           | -                     | 545                   | 2.45 |
|     | 445 (36301)                        |                    |      |                        |                              |                       |                       |      |
| 4a  | 338 (5221),                        | 515                | _[e] | 4.10                   | 103                          | 506                   | 510                   | 2.65 |
|     | 412 (15870)                        |                    |      |                        |                              |                       |                       |      |
| 4b  | 337 (7971),                        | 539                | 0.9, | 0.78                   | 121                          | 553 (6.4)             | 539 (1.7)             | 2.53 |
|     | 418 (24464)                        |                    | 8.0  |                        |                              |                       |                       |      |
| 4 c | 335 (7849),                        | 534                | _[e] | 3.15                   | 101                          | 538                   | 540                   | 2.51 |
|     | 433 (21294)                        |                    |      |                        |                              | (0.003)               |                       |      |
| 4 d | 340 (7041),                        | 522                | 0.7, | 3.20                   | 112                          | 496                   | 527 (6.4)             | 2.62 |
|     | 410 (20904)                        |                    | 17.0 |                        |                              |                       |                       |      |
| 4e  | 344 (7511),                        | 518                | 0.4, | 6.65                   | 105                          | 504                   | 527 (10.0)            | 2.62 |
|     | 413 (22715)                        |                    | 6.3  |                        |                              |                       |                       |      |
| 4 f | 331 (8433),                        | 523                | 0.6  | 6.91                   | 110                          | 526                   | 514 (5.7)             | 2.57 |
|     | 413 (31 059)                       |                    |      |                        |                              |                       |                       |      |
| 4g  | 328 (7550),                        | 521                | 0.1  | 3.60                   | 110                          | 503                   | 511 (1.0)             | 2.67 |
|     | 411 (26740)                        |                    |      |                        |                              |                       |                       |      |
| 5   | 352                                | -                  | -    | -                      | -                            | 566                   | -                     | 2.49 |
|     | (12541),                           |                    |      |                        |                              |                       |                       |      |
|     | 428 (31510)                        |                    |      |                        |                              |                       |                       |      |

[a] Quantum yield determined with fluorescein in 1N NaOH as a standard. [b] Calculated from the difference of the absorption and emission maxima. [c] Quantum yield determined in the solid state. [d] Quantum yield determined from PMMA thin films with a 2 wt % doped concentration. [e] Multiexponential decay. [f] Optical band-gap calculated from the absorption edge.

anilido-amine systems<sup>[1c,9]</sup> also revealed similar trends, which could be attributed to the deviation from the  $C_2$ -symmetric



see that the solid crystals of most compounds were highly fluorescent when irradiated with a hand-held UV-lamp (excitation approx. 365 nm, see the Supporting Information, Figure S4). For compounds **3e**, **4f**, and **4g**, which exhibited monoexponential decay lifetimes, the calculated<sup>[13a]</sup> radiative  $(K_r)$  and non-radiative  $(K_{nr})$  rates were in the ranges of  $10^5$ –  $10^6$  s<sup>-1</sup> and  $10^8$ – $10^9$  s<sup>-1</sup>, respectively. The magnitude of  $K_{nr}$ suggests a significant degree of radiationless deactivation in solution.

The absolute quantum yield of **3e** in the solid state (crystalline form) was found to be 2.4% when measured by an integrating sphere apparatus. This value is significantly higher than that observed in  $CH_2Cl_2$  (Table 1). In the solid state, one would normally expect electron-transfer quenching owing to exciton-phonon coupling, which originates from close interatomic distances, as proposed by Langhals et al.<sup>[13b]</sup> As discussed earlier, compounds for which singlecrystal XRD data were examined, such as 3e, showed CH…F and CH… $\pi$  interactions, but were devoid of  $\pi$ - $\pi$  interactions. The presence of CH···F and CH··· $\pi$  interactions and absence of  $\pi$ - $\pi$  interactions was presumed to have some influence on the quantum yield by altering the ground-state properties of the luminophore. To verify this hypothesis, we recorded the absorption spectra of 3e, 4a, 4c, 4d, and 4g in the solid state by using a diffuse reflectance method. Indeed bathochromic shifts of various magnitudes (5-72 nm) were observed for these compounds (see the Supporting Information, Figure S5). For example, the largest change in the absorption maximum  $(\lambda_{max})$  was found for 4c, which showed a significant shift from 433 nm in CH<sub>2</sub>Cl<sub>2</sub> to 505 nm in the solid state. Such phenomenon has been previously attributed

to an increase in exciton coupling.<sup>[14]</sup>

To ascertain if similar beneficial self-organizing aggregates can be triggered in solution, we further carried out experiments with **4d**. For a solution of **4d** in tetrahydrofuran (THF), the PL spectra were obtained with an increasing concentration of deionized water as shown in Figure 4. A steady increase in the relative emission intensity was observed with increasing water concentration owing to the formation of partially soluble aggregates. At 80–90% (v/



Figure 3. Emission spectra of 3d (left) and 4e (right) in CH<sub>2</sub>Cl<sub>2</sub>, thin films, and in the solid state are recorded at room temperature.

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4

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Figure 4. PL spectra of **4d** in THF/H<sub>2</sub>O mixtures  $(1.0 \times 10^{-5} \text{ M}, \text{ excited at } 410.0 \text{ nm})$  with different volumes of H<sub>2</sub>O ( $f_w$ ).

v) ratios, the aggregates of the compound were visible as tiny dots when observed under the UV lamp (see the Supporting Information, Figure S4). A similar phenomenon was also observed in the case of 4c (see Supporting Information, the Figure S6). This observation is consistent with the phenomenon of AIE.<sup>[15a]</sup> Aprahamian and co-workers have recently reported AIE phenomenon in BF<sub>2</sub>-hydrazone complexes.<sup>[15b]</sup> To gain more insight, increasing weight percent concentrations of 4d were doped onto thin films with PMMA (PMMA =

poly(methyl methacrylate)) as the host matrix. The quantum yields obtained with 2.0, 4.0, 10.0, and 40.0 wt % loadings were 6.4, 5.0, 4.0, and  $2.0 \times 10^{-3}$ %, respectively, thereby indicating a trend opposite to aggregation induced in solution.

Based on the observations of the two above experiments, the following tentative conclusions can be drawn: first, the increased luminescence observed by slow incremental precipitation (AIE phenomenon) probably occurs because of photophysically favorable preorganization due to spontaneous forces of self-organization; and second, under forced situations such as doping a small weight% of the dye in PMMA, similar phenomenon need not be observed due to the possibility of molecular motions in the matrix. The solidstate molecular structures revealed a significant loss of planarity in the molecule, and in addition, one can also expect single bond-free rotation of the arenes about the nitrogen atoms in solution. We reasoned that these symmetry lowering factors can contribute more to the lowering of quantum yields in solution. However, it was intriguing to note that the anilido-difluoride system recently reported showed good quantum yields in solution,<sup>[6]</sup> despite having similar Nbonded arenes. A notable variation that is unique to the current system is that it incorporates an acyclic ring (benzopyran or chromene) in the chelating backbone. It was therefore hypothesized that the rapid conformational changes (ringflipping) at ambient temperature could significantly contribute in accelerating the rates of non-radiative decay. Supporting this notion, low variable temperature (VT)-NMR recorded for **4e** at 233 K revealed decoalescence of the resonance signal, which corresponds to the methylene protons at  $\delta = 4.87$  ppm owing to the "frozen-out" conformation (see Figure 5a, highlighted region). Further, VT photoluminescence of **4b** (in 2-methyltetrahydrofuran) under rigorous exclusion of oxygen was also undertaken. As shown in Figure 5b, the compound exhibited maximum relative intensity at 77 K; this decreases with an increase in temperature. Even at 175 K, most of the emission intensity is lost, further confirming that conformational dynamics are a key factor



Figure 5. a) Low VT-NMR of 4e in  $[D_8]$ THF, (\*) denotes solvent impurity (CH<sub>2</sub>Cl<sub>2</sub>). b) VT-photoluminescence spectrum of 4b recorded in 2-methyltetrahydrofuran.

responsible for quenching of fluorescence intensity in this class of molecules. To further clarify the photoluminescence behavior of the compounds in the crystalline state and in the PMMA matrix, we measured the absolute quantum yields of selected complexes **3d**, **3e**, and **4b** both in PMMA thin films (2 wt% doped) and in the solid state. In the PMMA matrix, quantum yields of 2.4, 1.6, and 1.7% were obtained for **3d**, **3e**, and **4b**, respectively. In the case of solids, marginally incremental values of 6.0, 2.4, and 6.4% were observed for **3d**, **3e**, and **4b**, respectively.

It is presumed that, although the quantum yields increased roughly tenfold in moderately rigid PMMA matrix as compared to in solution, the molecular motions are not entirely restricted and therefore it still exhibits a lower value as compared to that in the solid state. Such unrestricted molecular motions have been reported previously.<sup>[16]</sup> The excited-state lifetime for many compounds could be best fitted biexponentially containing a short subnanosecond and a longer nanosecond term. Such biexponential decay has been previously observed for molecules with conformational flexibility and also for aggregation-induced luminophores that display flipping kinetics.<sup>[9d]</sup> To gain some ideas about the electrochemical behavior of these compounds and their

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5

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suggests the involvement of the imine part of the compound

in the reduction process. From the onset of the first reduction peak,<sup>[17a]</sup> the LUMO energy values were calculated to

be in range between -2.33 eV to -2.87 eV for the measured

compounds. These values were in general agreement-both

in terms of trend and magnitude-with those obtained by

**Theoretical Calculations** 

To better understand the luminescent properties of the synthesized  $\beta$ -iminoenamine-BF<sub>2</sub> complexes, DFT calculations in the gas phase and TD-DFT calculations in CH<sub>2</sub>Cl<sub>2</sub> (using the CPCM polarizable conductor calculation mode)<sup>[18]</sup> were

carried out for the selected molecules 3a-3c, 4c, and 4e with the Gaussian 03 program package<sup>[19]</sup> using the hybrid functional B3LYP<sup>[20]</sup> in conjunction with the Pople-type

According to the TDDFT calculations, the calculated UV/ Vis spectra of the studied compounds closely reproduce the

experimental results with a well-separated low-energy intense absorption band appearing in the range 410–445 nm

DFT calculations discussed later on.

basis set  $6-311 + G(2d,p) [6-311G^*]$ .<sup>[21]</sup>

band gaps, cyclic voltammetry studies were carried out for selected compounds **3b–3d**, **3f**, **4a**, **4c**, **4e**, and **4g**. Most compounds exhibited a prominent quasi-reversible first reduction wave when recorded at 25 °C in CH<sub>2</sub>Cl<sub>2</sub> with 0.1 M  $[nBu_4N][PF_6]$  as the supporting electrolyte; the anodic part of the wave described by the anodic current ( $i_a$ ) was notably less intense than expected. An example is shown in Figure 6



Figure 6. Cyclic voltammogram of **4a** in 0.1 M [*n*Bu<sub>4</sub>N][PF<sub>6</sub>]; Au electrode; scan rate = 100 mV s<sup>-1</sup>; 20 °C; CH<sub>2</sub>Cl<sub>2</sub>; LUMO [eV]=-( $E_{red}-E_{Fe/Fe+}$ +4.8).<sup>[17]</sup>

and others are shown in the Supporting Information (Figure S8). Irreversible oxidation peaks were observed for 3c and 4c within the electrochemical window of CH<sub>2</sub>Cl<sub>2</sub>; the other less prominent oxidation waves could not be assigned with certainty. Among the compounds with a dihydronaphthalene backbone (3b-3d, 3f), those containing a p-nitrophenyl substituent such as 3b and 3f, displayed reduction peak potentials with lower negative values of -1.43 V and -1.46 V when compared to **3c** and **3d** that contain a fluorine atom as the substituent (Table 2). Among the chromene derivatives (4a, 4c, 4e, and 4g), compound 4a without any substituent on the phenyl ring showed a peak potential at -1.95 V. In comparison, compound **4c** with a *p*-nitrophenyl substituent, and 4e with a m-fluorine substituent showed relative ease of reduction with potentials at -1.45 V and -1.80 V, respectively. Compound 4g containing a methyl substituent shifted towards more negative reduction potentials at -1.98 V as expected. The above trend tentatively

Table 2. Electrochemical data of selected complexes.

|     | Reduction<br>E <sub>p,c</sub> [V] | Onset reduction $E_{\rm red,onset}$ [V] | Oxidation $E_{p,a}$ [V] | LUMO <sup>[a]</sup> [eV] |
|-----|-----------------------------------|---|-------------------------|--------------------------|
| 3b  | -1.43                             | -1.26                                   | _                       | -2.83                    |
| 3c  | -1.93                             | -1.74                                   | +1.02                   | -2.35                    |
| 3 d | -1.98                             | -1.67                                   | -                       | -2.43                    |
| 3 f | -1.46                             | -1.29                                   | -                       | -3.81                    |
| 4a  | -1.95                             | -1.72                                   | -                       | -2.38                    |
| 4c  | -1.45                             | -1.23                                   | +1.37                   | -2.87                    |
| 4e  | -1.80                             | -1.51                                   | -                       | -2.61                    |
| 4g  | -1.98                             | -1.76                                   | _                       | -2.33                    |

[a] LUMO [eV] =  $-(E_{red}-E_{Fc/Fc+}+4.8)$ .

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and less intense bands in the range 249–352 nm (see the Supporting Information, Figure S9). The calculated  $\lambda_{max}$  in-

creases in the order of 393 (413 nm) for 4e > 401 (421) for 3c > 421 (429) for 3a > 445 (433) for 4c > 468 (447) nm for 3b (Table 3). The calculated values are in good agreement with the experimental values (in brackets), the general trend is well respected, but it is worth noting that the calculated values are underestimated by 10–20 nm for compounds containing F- or OCH<sub>3</sub>-substituted phenyl rings, while they are overestimated by about 20 nm for the NO<sub>2</sub>-containing compounds 3b and 4c.

In all cases, the  $S_0 \rightarrow S_1$  transition (Table 3) has exclusively a HOMO $\rightarrow$ LUMO ( $\pi/\pi^*$ ) character. The HOMO of the compounds with electron-withdrawing groups (F, NO<sub>2</sub>) on the N-coordinated phenyl rings includes large contributions from the central β-diketiminato boron core C<sub>3</sub>N<sub>2</sub>B (61-64%), limited participation of the phenyl rings (20-25%), and of the fused aliphatic rings (13-19%) (Table 4 and see the Supporting Information, Figure S10). The presence of the electron-donating methoxy groups in 3a increases the participation of the substituted phenyl rings in the HOMO to 41%, thus decreasing the involvement of the rest of the molecule to 51% for the central core and to only 8% for the fused aliphatic cycle. The LUMO of 3a is even more localized on the central core (64%) but in a different pattern (see the Supporting Information, Figure S11). Indeed, while the HOMO shows antibonding  $\pi^*$  interactions between C3– C4–C5 and N2–N6, the LUMO exhibits antibonding  $\pi^*$  interactions between N2-C3, C5-N6, C3-C5, and N2-N6. These HOMO and LUMO shapes are also observed for 3c and 4e with contributions of the central ring of 62-64%. The fluorescent properties are thus mainly due to an intramolecular charge transfer located in the central heterocycle of these three species. It is important to note that the boron

Table 3. Selected singlet-singlet excited states with the corresponding TD-DFT vertical excitation energies (nm), transition coefficients, orbitals involved in the transitions, oscillator strengths (f), and molecular orbital energies (eV) for compounds **3a**, **3b**, **3c**, **4c**, and **4e**.

| Complex               | 3a                      | 3 b                     | 3c                      | 4c                    | 4e                      |
|-----------------------|-------------------------|-------------------------|-------------------------|-----------------------|-------------------------|
| $S_0 \rightarrow S_1$ | $H \! \rightarrow \! L$ | $H \! \rightarrow \! L$ | $H \! \rightarrow \! L$ | $H{\rightarrow}L$     | $H \! \rightarrow \! L$ |
|                       | (100%)                  | (100%)                  | (100%)                  | (100%)                | (100%)                  |
|                       | 421.4 (0.550)           | 473.4 (0.606)           | 400.7                   | 449.4 (0.533)         | 391.6                   |
|                       |                         |                         | (0.584)                 |                       | (0.505)                 |
| $S_0 \rightarrow S_2$ | $H-1 \rightarrow L$     | $H \rightarrow L + 1$   | H-1→L                   | $H \rightarrow L + 1$ | H-1→L                   |
|                       | (100%)                  | (100%)                  | (100%)                  | (100%)                | (100%)                  |
|                       | 363.4 (0.186)           | 433.5 (0.176)           | 328.7                   | 410.6 (0.126)         | 345.8                   |
|                       |                         |                         | (0.175)                 |                       | (0.129)                 |
| $S_0 \rightarrow S_n$ | n=8                     | n=3                     | n = 10                  | n=3                   | n=3                     |
|                       | $H \rightarrow L + 3$   | $H \rightarrow L + 2$   | $H-2 \rightarrow L$     | $H-1 \rightarrow L$   | $H-2 \rightarrow L$     |
|                       | (61%)                   | (100%)                  | (57%)                   | (65%)                 | (100%)                  |
|                       | 274.4 (0.115)           | 365.1 (0.145)           | 264.1                   | 387.0 (0.128)         | 328.6                   |
|                       |                         |                         | (0.146)                 |                       | (0.093)                 |
| $S_0 \rightarrow S_n$ | n = 10                  | n=4                     |                         | n=4                   | n=9                     |
|                       | $H-6 \rightarrow L$     | $H-1 \rightarrow L$     |                         | $H \rightarrow L+2$   | $H-6 \rightarrow L$     |
|                       | (51%)                   | (82%)                   |                         | (70%)                 | (62%)                   |
|                       | 267.9 (0.129)           | 351.9 (0.197)           |                         | 362.3 (0.136)         | 263.6                   |
|                       |                         |                         |                         |                       | (0.159)                 |
| Exp./                 | 429, 348                | 447, 337                | 421, 317                | 433, 335              | 413, 344                |
| Calcd <sup>[a]</sup>  | 421, 363                | 468, 355                | 401, 329                | 445, 357              | 393, 343                |
| LUMO                  | -2.20                   | -3.17                   | -2.33                   | -3.19                 | -2.49                   |
| (eV)                  |                         |                         |                         |                       |                         |
| НОМО                  | -5.61                   | -6.23                   | -5.87                   | -6.42                 | -6.17                   |
| (eV)                  |                         |                         |                         |                       |                         |

[a] The calculated values were obtained from the TD-DFT/CPCM UV/Vis spectra drawn by GaussView.

Table 4. HOMO and LUMO compositions (%) for compounds 3a, 3b, 3c, 4c, and 4e.

| Atom |     | <b>B</b> 1 | N2 | C3 | C4 | C5 | N6 | total C3BN2 | phenyls |
|------|-----|------------|----|----|----|----|----|-------------|---------|
| LUMO | 3a  | 1          | 11 | 21 | 2  | 20 | 8  | 64          | 9       |
|      | 3b  | 0          | 2  | 6  | 1  | 6  | 1  | 16          | 79      |
|      | 3c  | 1          | 11 | 21 | 2  | 21 | 8  | 64          | 10      |
|      | 4 c | 1          | 2  | 6  | 1  | 6  | 1  | 17          | 78      |
|      | 4 e | 1          | 10 | 21 | 3  | 19 | 8  | 62          | 10      |
| HOMO | 3a  | 1          | 9  | 3  | 19 | 3  | 14 | 51          | 41      |
|      | 3b  | 1          | 10 | 4  | 26 | 5  | 18 | 64          | 20      |
|      | 3c  | 1          | 11 | 4  | 25 | 4  | 17 | 62          | 25      |
|      | 4 c | 1          | 8  | 4  | 28 | 4  | 16 | 61          | 20      |
|      | 4 e | 1          | 9  | 3  | 28 | 4  | 17 | 62          | 22      |

and fluorine atoms do not participate more than 1% to these frontier orbitals.

The lowest-energy absorption bands of 3b and 4c, experimentally observed at longer wavelengths, arise from the lowest excited states S1 and S2 that correspond to the HOMO→LUMO (100%)and  $HOMO \rightarrow LUMO +$ 1 (100%) transitions, respectively. The red-shift effect of the UV/Vis absorption is observed at the molecular orbital level by the narrow HOMO-LUMO gaps of 3.06 and 3.23 eV for 3b and 4c, in comparison with 3.41, 3.54, and 3.68 eV for 3a, 3c, and 4e, respectively. These small energy differences are mainly due to the low-energy LUMO and LUMO+1, which are delocalized over the substituted phenyl rings, and stabilized by the extended conjugation of the phenyl rings over the NO2 groups. These two unoccupied orbitals, ob-

served as LUMO+1 and LUMO+2 for 3a. 3c. and 4e, become LUMO and LUMO+1 for compounds 3b and 4c. The participation of the central six-membered ring into the LUMO of 3b and 4c drops to 16-17% and to as low as 2-4% into LUMO+1, thereby reducing significantly the spatial antibonding interactions over the molecule. On the contrary, the electron density is delocalized at 78-79% on the NO<sub>2</sub>-substituted phenyl rings, thus showing the influence of such an electron-withdrawing group and conjugated group on the fluorescent properties of this class of compounds. The calculated LUMO energies (see Table 3 and Table 2) were in line with the corresponding values obtained from the CV measurements, with the relative decrease in energy following the order of 3c > 4e > 3b > 4c.

### Conclusions

The synthesis, photophysical, and electrochemical aspects of a novel class of  $\beta$ -diketiminato-BF<sub>2</sub> molecules with an aromatic-fused alicyclic/hetero-alicyclic ring unit have been studied. They were found to display large Stokes shifts as compared to the popular boron-dipyrromethene complexes. The solid-state emission quantum yields were found to be superior compared to those in solvents at room temperature. From various experiments it is under-

stood that, the inclusion of a non-planar aliphatic core indeed improves the solid-state emission by preventing  $\pi$ - $\pi$ stacking, however, on the other hand, in solvents it simultaneously expedites non-radiative pathways owing to the rapid conformational motions. The significant CH…F CH… $\pi$  interactions observed in some of the solid-state molecular structures, apart from conferring structural rigidity to the compound, are also believed to alter the ground state of the molecule to a certain extent.

### **Experimental Section**

Synthetic and experimental procedures are described, crystallographic details and additional spectroscopy data of the molecules are provided in the Supporting Information. CCDC 880782 (3d), CCDC 880783 (3e), CCDC 880784 (4c), CCDC 880785 (4e), CCDC 880786 (4g) contain the supplementary crystallographic data (excluding structure factors) for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

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7

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Got it in one: A new class of  $\beta$ -iminoenamine-BF<sub>2</sub> complexes with a  $\pi$ - $\pi$  stacking disruptive alicyclic core exhibit solid-state fluorescence, large Stokes shifts, tunable emission, and aggregation-induced emission (AIE).



### **Aggregation-Induced Emission**

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9