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Benzothiazole-enamide-based BF$_2$ Complexes: Luminophores Exhibiting Aggregation-induced Emission, Tunable Emission and High Efficient Solid-State Emission

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A series of benzothiazole-enamide-based boron difluoride complexes (Borebt1–6) were synthesized and characterized. These new luminophores were demonstrated to possess aggregation-induced emission, tunable, substituent-dependent emission profiles and large Stokes shift in solution. At the solid state, Borebt1–6 exhibited intense emission with high quantum yield of 0.21–0.37. The photophysical properties and AIE characteristics of these compounds were rationalized through X-ray crystal analysis, electrochemical studies and theoretical calculations. Furthermore, Borebt3–6 were capable of sensing of acidic gas by reversible changes of emission, which may potentially serve as solid-state fluorescent sensors for acidic vapors.

Introduction

Solid-state emissive organic luminophores have been intensively studied because of their potential applications in opto-electronic devices such as organic light-emitting diodes (OLEDs), fluorescent polarizers and sensors.$^1$ Organic difluoride boron complexes (BF$_2$ dyes), with 4,4'-difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY) as an example, are a family of well-known luminescent compounds, which display some excellent properties such as high molar absorption coefficients, outstanding fluorescence quantum yields and tunable emission from visible light to near infrared.$^2$ However, despite their intense fluorescence in solution, BF$_2$ dyes show very weak emission in their aggregated states, and this “aggregation-caused emission quenching (ACQ)” has greatly limited the practical applications of BF$_2$ dyes as electroluminescence materials.$^{2c,3}$ Thus, great efforts have been paid to the design and synthesis of new BF$_2$ luminophores, in particular, based on novel frameworks, with high emission in the solid state.

The ACQ of BF$_2$ dyes is caused by self-absorption resulting from their narrow Stokes shifts and aggregation-induced energy transfer. The narrow Stokes shifts (typically 200–400 cm$^{-1}$) of BF$_2$ dyes are attributed to their rigid symmetrical molecular structures with minimal difference between the ground- and excited-states.$^2$ On the other hand, BF$_2$ dyes with panel-like structure often exhibit strong intermolecular interactions (e.g., π–π stacking, the formation of excimers and exciplexes) in their aggregation states, which quenches the emission efficiency.

Various strategies have been developed to construction of solid-state emissive BF$_2$ dyes via the way of improve the Stokes shift and/or decrease intermolecular interactions of BF$_2$ dyes. Desymmetrization of the N,N-bidentate ligand of BF$_2$ dyes and decorating BF$_2$ dyes with bulky groups have been proved to be effective strategies for decreasing intermolecular aggregation.$^{2,4,5}$ Nevertheless, aggregation-induced emission (AIE) which was discovered by Tang et al can also be a useful strategy for the development of fluorescent luminophores with high emission in the solid state.$^6$ However, only few examples of BF$_2$ luminophores with AIE have been developed due to the lack of appropriate frameworks.$^7$

Recently, we have reported that boron complexes based on pyridyl-enamido-ligands with propeller-shape structure showed interesting fluorescence properties such as large Stokes shift, high solid-state emission and AIE effect.$^7b$ In light of this research, we can rationalized that design of boron complexes with propeller-shaped structure should be useful for the development of new AIE-active BF$_2$ complexes. In the course of our studies on the development of solid-state emissive boron complexes bearing heterocycle-enamido-ligand, we are interested in the synthesis of the BF$_2$ complex based on benzothiazole structure. In this paper, we report the synthesis and fluorescence properties of a series benzothiazole-enamide-based BF$_2$ complex (Fig. 1). Borebt1–6 possess a general propeller-shaped non-planar molecular structure in the solid state and exhibit spectacular luminescence characteristics: AIE and tunable emission profiles in solution and high efficient solid-state emission.
Results and Discussion

Synthesis of Borebt1–6. Borebt1–6 were synthesized from benzothiazole-enamide-based N,N-bidentate ligands (Scheme 1). The reaction of 2-methylbenzothiazole with ethyl benzoate or methyl 4-(dimethylamino)benzonate gave compounds 1 and 2. 1 and 2 were reacted with aniline, 2,6-dimethylaniline and 4-(dimethylamino)aniline in the presence of CF$_3$COOH (cat.) in toluene to afford the benzothiazole-enamide-based N,N-bidentate ligands 3–8. By reacting of 3–8 with boron trifluoride etherate in the presence of DBU in toluene gave Borebt1–6 in high yield. The structures of compounds Borebt1–6 were confirmed by $^1$H, $^13$C NMR, ESI-MS, elementary analysis and X-ray crystallography.

General Optical Properties of Borebt1–6. The photophysical properties of Borebt1–6 were measured in different solvents and in the solid state. The full details can be found in Fig. S1–2 and Table 1. In THF, Borebt1–3 showed absorption maxima at 392 nm ($\varepsilon = 19000$ M$^{-1}$cm$^{-1}$), 386 nm ($\varepsilon = 40200$ M$^{-1}$cm$^{-1}$) and 397 nm ($\varepsilon = 19300$ M$^{-1}$cm$^{-1}$), respectively. Compared with Borebt1–3, Borebt4–6 showed red-shifted absorption bands (~15 nm) with absorption maxima at 409 nm ($\varepsilon = 37700$ M$^{-1}$cm$^{-1}$), 405 nm ($\varepsilon = 39000$ M$^{-1}$cm$^{-1}$) and 408 nm ($\varepsilon = 35500$ M$^{-1}$cm$^{-1}$), respectively. The red shift of absorption band can be explained by the N,N-dimethylamino group at B ring causing charge transfer (CT) enhancement. On the other hand, Borebt1 and Borebt3, and Borebt4 and Borebt6 exhibited almost the same absorption maxima, suggesting that N,N-dimethylamino group in C ring has less electronic effect on the fundamental states of Borebt1–6. The solvent effects on the absorption of Borebt1–6 were examined (Fig. S1). The absorption bands of Borebt1–6 were hardly affected by solvent polarity.

Borebt1, Borebt3, Borebt4 and Borebt6 were found to possess broad fluorescence emission spectra spanning 400–600 nm, associated with very low fluorescence quantum yields in low-viscosity solvents. While in high-viscosity solvents such as glycerol, these compounds showed dramatically enhanced fluorescence intensity (Fig. 2b and S2). This result suggests that the viscous medium inhibits intramolecular rotation, thereby suppressing the nonradiative process which leads to increased $\Phi_f$ (Table 1). It should be noted that, Borebt1 and Borebt4 showed enhanced fluorescence intensity in glycol or glycerol, while the fluorescence intensity enhancement of Borebt3 and Borebt6 was only found in glycerol. This should be ascribed to the additional rotation group (N,N-dimethylamino group) of Borebt3 and Borebt6 induced more nonradiative process than Borebt1 and Borebt4.

With two methyl groups in C ring, Borebt2 and Borebt5 showed relatively strong fluorescence in solution (Fig. 2b and S2), which suggests that the intramolecular rotation induced nonradiative process of Borebt2 and Borebt5 was inhibited efficiently. The maximum fluorescence wavelength ($F_{\text{max}}$) of Borebt2 showed almost no variation with changing solvent polarity, and only an intensity change was observed in different solvents (Fig. 2b). Borebt5 showed a red shift of the emission band and increment of the emission intensity with the increasing of the polarity of solvents. This should be ascribed to the N,N-dimethylamino group at B ring caused CT enhancement. It should be noted that Borebt5 showed slightly red-shifted emission (~6 nm) in glycerol when compared with Borebt1–4, which suggests that the ICT effect of the N,N-dimethylamino group at B ring was inhibited due to the steric effect of the two methyl groups in C ring (Fig. S2e).

In the solid state, Borebt1–6 showed almost the same absorption maxima with $\lambda_{\text{abs}}$ at 393 nm, 388 nm, 410 nm, 392 nm, 405 nm and 414 nm, respectively, compared with those in solution. The emission bands of Borebt1–6 remained narrow and the $F_{\text{max}}$ values (482–555 nm) were more bathochromic than those in THF (438–485 nm) (Fig. 3, S3 and Table 1). The red-shift of emission band should be ascribed to the aggregation-induced CT enhancement.

![Fig. 1. Chemical structures of Borebt1–6.](image1)

![Fig. 2. Absorption (a) and Emission (b) spectra of Borebt1–6 (10 $\mu$M) in THF.](image2)
Importantly, Borebt1–6 showed intense emission in the solid state with high Φ\text{f} of 0.29, 0.37, 0.27, 0.21, 0.30 and 0.23, respectively. This result suggests that the interactions of Borebt1–6 should be very weak in the solid state, and AIE was at play in Borebt1–6.

In order to confirm whether Borebt1–6 have the AIE character, the emission properties of Borebt1–6 were investigated in THF–water mixture of various ratios (Fig. 4 and Table 1). In pure THF, Borebt1, Borebt3, Borebt4 and Borebt6 had very low emission intensity. When water was added to the THF solution, the emission intensity of Borebt1, Borebt3 and Borebt6 kept almost the same until the water fraction (f\text{w}) reached 80%, 80% and 70%, respectively. However, upon addition of 99% (for Borebt1), 99% (for Borebt3) and 80% (for Borebt6) water in THF, the emission intensity of Borebt1, Borebt3 and Borebt6 was significantly enhanced, and the Φ\text{f} value was 0.07 for Borebt1, 0.16 for Borebt3 and 0.20 for Borebt6, which was 7-fold, 5-fold and 10-fold higher than that in pure THF solution. Interestingly, Borebt4 showed gradually increment of the emission intensity with the addition of water into THF solution. In contrast to Borebt1, Borebt3, Borebt4 and Borebt6, Borebt2 and Borebt5 showed intense emission in THF solution with Φ\text{f} of 0.17 and 0.37, respectively. With the addition of water, the emission of Borebt2 slightly quenched with the increment of f\text{w}, while the emission intensity of Borebt5 increased in a small range (Fig. 4b, 4e). With the additional N,N-dimethylamino group in B and/or C phenyl rings, Borebt3–6 showed large red-shifted emission with the increase of f\text{w}, and this should be ascribed to the aggregation-induced CT enhancement (Fig. 4c–f). The aqueous solution of Borebt2 and Borebt4–6 became turbid when the f\text{w} exceeded 80%, 80%, 70% and 90%, respectively, because of the formation of visible aggregates that hindered the acquisition of the emission spectra. As mentioned above, the addition of water into the THF solutions of Borebt1 and Borebt3–6 resulted in aggregation that led to enhanced/red-shifted emission. The restriction of phenyl ring and N,N-dimethylamino group’s free rotation via aggregates formation should be responsible for this AIE.

X-ray crystal structure analysis. In order to better understand the aggregation and solid-state emission properties of Borebt1–6, X-ray crystallographic analysis was performed. The ORTEP drawings and molecular packing structures of Borebt1–6 are shown in Fig. 5. All the boron atoms of Borebt1–6 adopt a typical tetrahedral geometry to form N\text{\textdegree}N–chelate six-membered rings (ring B), which contributes to the construction of the three-ring-fused π-conjugated skeletons. As anticipated, Borebt1–6 adopt propeller-shaped conformations. The dihedral angles of A and B and A and C are 69.86° and 66.16° in Borebt1, 59.48° and 78.06° in Borebt2, 54.40° and 66.59° in Borebt3, 35.43° and 69.73° in Borebt4, 51.06° and 81.38° in Borebt5, 55.69° and 79.40° in Borebt6, respectively.
Intermolecular π–π interactions were not detected in Borebt1–6. However, multiple short interatomic contacts existed within the crystals: F1···H14–C14 (135.98°, 3.34 Å), F2···H15–C15 (166.70°, 3.32 Å), and B1···H21–C21 (158.52°, 4.05 Å) interactions in Borebt1, F2···H22c–C22 (167.38°, 3.58 Å) interactions in Borebt2, F1···H5–C5 (132.72°, 3.25 Å), F1···H13–C13 (142.29°, 3.32 Å), F2···H23c–C23 (110.05°, 3.09 Å), and B1···H13–C13 (127.50°, 3.82 Å) interactions in Borebt3, F2···H1–C1 (127.19°, 3.08 Å) interactions in Borebt4, F2···H12–C12 (135.33°, 3.39 Å) and S1···H16a–C16 (149.92°, 3.75 Å) interactions in Borebt5, F2···H4–C4 (149.47°, 3.45 Å) and F2···H12–C12 (172.61°, 3.54 Å) interactions in Borebt6. Furthermore, C–H···π interactions fix the molecular conformations of Borebt1–6 in the solid state, thus inhibiting the internal rotations and blocking their non-radiative relaxation. These results agree well with the observation that Borebt1–6 show intense emissions in the solid state.

Electrochemical studies. The electrochemical behaviors of Borebt1–6 were investigated by cyclic voltammetry (CV) (Fig. 6). Borebt1–6 have similar two couple of irreversible reduction peaks. The calculated LUMO levels of Borebt1–6 are around -2.36 to -2.67 eV (Fig. 6 and Table 2). Borebt1 and Borebt2 display one irreversible oxidation peak originated from the benzothiazole moiety, with high potential of 0.96 eV and 1.01 eV, respectively. For Borebt4–5, except for the oxidation peaks originated from the benzothiazole moiety, the irreversible peaks at 0.51 eV and 0.59 eV are attributed to the N,N-dimethylamino group in B phenyl ring. Borebt3 and Borebt6 with the N,N-dimethylamino group in C phenyl ring display three and four irreversible oxidation peaks, respectively. The HOMO energy levels for Borebt1–6 are calculated to be -5.98 eV for Borebt1, -5.75 eV for Borebt2, -5.55 eV for Borebt3, -5.55 eV for Borebt4, -5.58 eV for Borebt5, and -5.60 eV for Borebt6, respectively (Fig. 6 and Table 2). Based on these results, we can conclude that the introduction of the electron-donating N,N-dimethylamino group only raises HOMO levels of Borebt1–6, while has less effect on LUMO levels, leading to a red shift in the absorption spectra.

Theoretical Calculations. To further illustrate the effect of the structure modification on the electronic structures which related to the photophysical properties of Borebt1–6, time-dependent density functions theory (TD-DFT) calculation was carried out using the crystal structures as model structures. The pictorial drawings of HOMOs and LUMOs and energy levels are shown in Fig. 7, S6 and Table 2. Borebt1 and Borebt2 have HOMOs delocalized over the benzathiazole unit and the BF4 core (A ring), whereas their LUMOs are mostly localized on the benzothiazole unit, A and B rings. The calculated first excited state, mainly consisting of HOMO→LUMO transition, have excitation energies of 3.64 eV (340 nm, f = 0.6729) for Borebt1 and 3.58 eV (346 nm, f = 0.6343) for Borebt2, respectively. The incorporation of N,N-dimethyl group in Borebt3 is predicated to greatly increase the HOMO energy level by 0.8 eV, but to have little effect on the LUMO, thus decreasing the HOMO-LUMO gap, and resulting in red shift of the main absorption band relative to those of Borebt1 and Borebt2. The lowest-energy absorption band of Borebt3 is dominated by excited state corresponding to the HOMO-1→LUMO transition (3.58 eV, 346 nm, f = 0.6135), but also contains a excited state with minor oscillation strength corresponding to the HOMO→LUMO transition (2.73 eV, 451 nm, f = 0.1130). The energy levels of HOMOs and LUMOs of Borebt4–5 are both increased relative to those of Borebt1–2, due to the introduction of the electron donating amino substituent. The decreased HOMO-LUMO gaps of Borebt4–5 should be responsible for the red-shifted main absorption band relative to those of Borebt1 and Borebt2. Borebt4–5 have HOMOs delocalized over the benzathiazole unit, A, B rings and the N,N-dimethyl group in B ring, whereas their LUMOs are mostly localized on the benzothiazole unit and A ring. The calculated first excited state of Borebt4–5, mainly consisting of...
HOMO→LUMO transition, have excitation energies of 3.30 eV (375 nm, \( f = 0.9230 \)) for Borebt4 and 3.32 eV (372 nm, \( f = 0.7317 \)) for Borebt5, respectively. Borebt3 and Borebt6, which also have \( N,N \)-dimethyl group in C ring, show higher HOMO levels than Borebt4 and Borebt5. Borebt6 has HOMO delocalized over the benzothiazole unit, A, B rings and the \( N,N \)-dimethyl group in B ring, and HOMO-1 delocalized over the C ring. Its LUMO is mostly localized on the benzothiazole unit and A ring. The maximum absorption band of Borebt6 is dominated by the excited state corresponding to the HOMO-1→LUMO transition (3.39 eV, 365 nm, \( f = 0.6676 \)), and the first excited state dominated by HOMO→LUMO component has a relative weak oscillation strength (3.01 eV, 410 nm, \( f = 0.0183 \)).

Acidchromic properties in the solid state. Since the \( N,N \)-dimethylamino group in Borebt3–6 can be easily protonated by acid, the applications of Borebt3–6 as solid-state fluorescent sensors for acidic vapors were examined (Fig. 8 and S13–15). Borebt3–6 emitted intense fluorescence in the powder solid state. When exposed to HCl vapors for a few seconds, Borebt3 and Borebt6 exhibited a blue-shift of emission with colour changing from yellow to cyan (547 nm to 518 nm) for Borebt3, and orange to yellowish green (555 nm to 504 nm) for Borebt6. In contrast, the fluorescence of Borebt4–5 was effectively quenched after exposing to HCl vapors without the shift of emission. The blue-shift of the emission is due to the diminished CT. And the quenched emission is probably because of the changed molecular conformation and packing structure.\(^9\) The protonated powder samples gradually recovered their original colour and fluorescence when they were treated with \( NH_3 \) vapor for few minutes. The switching between emission red-shift/turn-on and emission blue-shift/quenching states by HCl/\( NH_3 \) vapor fuming can be carried out repeatedly without obvious intensity decaying.

![Emission spectra of initial, HCl (g) and NH\(_3\) (g) fumed powders of Borebt3; (b) Reversible switching of the emission of Borebt3 by HCl/NH\(_3\) fuming cycle; (c) Fluorescent pictures of HCl (g) and NH\(_3\) (g) fumed powders of Borebt3.](image)

It is obvious that the lowest-energy excited state for all dyes corresponds to a charge transfer from the benzothiazole fragment and \( N,N \)-dimethyl group in the B and C rings to the A ring. The features of charge transfer make the ground and excited states more energetically distinct, leading to large Stokes shifts. These results indicate that the main absorption bands of Borebt1–6 can be tuned by benzothiazole units and B and C rings with different substitute groups, and that the extent of shift of the absorption can be predicted by theoretical calculations.

<table>
<thead>
<tr>
<th>Compound</th>
<th>HOMO-1 (eV)(^{[a]})</th>
<th>HOMO (eV)(^{[a]})</th>
<th>LUMO (eV)(^{[a]})</th>
<th>LUMO+1 (eV)(^{[b]})</th>
<th>( E_g ) (eV)(^{[b]})</th>
<th>HOMO (eV)(^{[b]})</th>
<th>LUMO (eV)(^{[b]})</th>
<th>( E_g ) (eV)(^{[b]})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Borebt1</td>
<td>-6.89</td>
<td>-5.82</td>
<td>-1.84</td>
<td>-0.73</td>
<td>3.98</td>
<td>-5.98</td>
<td>-2.67</td>
<td>3.31</td>
</tr>
<tr>
<td>Borebt2</td>
<td>-6.53</td>
<td>-5.81</td>
<td>-1.88</td>
<td>-0.69</td>
<td>3.93</td>
<td>-5.99</td>
<td>-2.56</td>
<td>3.43</td>
</tr>
<tr>
<td>Borebt3</td>
<td>-5.69</td>
<td>-4.98</td>
<td>-1.73</td>
<td>-0.54</td>
<td>3.24</td>
<td>-5.75</td>
<td>-2.64</td>
<td>3.11</td>
</tr>
<tr>
<td>Borebt4</td>
<td>-5.69</td>
<td>-5.31</td>
<td>-1.65</td>
<td>-0.42</td>
<td>3.65</td>
<td>-5.55</td>
<td>-2.63</td>
<td>2.92</td>
</tr>
<tr>
<td>Borebt5</td>
<td>-5.71</td>
<td>-5.33</td>
<td>-1.49</td>
<td>-0.51</td>
<td>3.83</td>
<td>-5.58</td>
<td>-2.36</td>
<td>3.22</td>
</tr>
<tr>
<td>Borebt6</td>
<td>-5.38</td>
<td>-4.95</td>
<td>-1.39</td>
<td>-0.41</td>
<td>3.55</td>
<td>-5.60</td>
<td>-2.48</td>
<td>3.12</td>
</tr>
</tbody>
</table>

\(^{[a]}\) HOMO, LUMO and band-gap \( (E_g) \) levels were calculated from the TD-DFT calculations.\(^{[b]}\) HOMO and LUMO levels were determined from the onset of the first oxidation and reduction with reference to the HOMO of ferrocene (-4.8 eV), which was used as an internal standard;\(^{[c]}\) \( E_g \) were obtained from the CV.

Conclusions

In this article, a new series of BF\(_2\) luminophores (Borebt1–6) were developed by reacting of benzothiazole-enamide-based desymmetrized \( N,N \)-bidentate ligands with boron trifluoride etherate. The complexes were characterized by X-ray crystallography and NMR spectroscopy and their photophysical properties were investigated. Due to the intramolecular rotation induced nonradiative process, Borebt1, Borebt3–4 and Borebt6 exhibited AIE characteristics and fluorescence efficiently in the aggregate state. Borebt2 and Borebt5, which have two methyl groups in C ring, showed relatively strong...
fluorescence both in low- and high-viscosity organic solvents, suggesting the intramolecular rotation induced nonradiative process of Borebt2 and Borebt5 was inhibited efficiently. Borebt1–6 exhibited intense emission in the solid state with high quantum yield of 0.21-0.37. X-ray crystallographic analysis demonstrated that the weak intermolecular interactions such as F···H–C and C–H···π by fixing the molecular conformations of Borebt1–6 were responsible for intense fluorescence in the solid state. The theoretical calculation and electrochemical studies suggested that the incorporation of N,N-dimethylamino group into the phenyl rings raised HOMO levels of Borebt3–6, while had less effect on LUMO levels.

Furthermore, due to the Lewis-base nature of N,N-dimethylamino group, Borebt3–6 were capable of sensing of acidic gas by reversible changes of emission, which may potentially serve as solid-state fluorescent sensors for acidic vapors.

**Experimental Section**

**Spectroscopic measurements**

UV-vis absorption spectra were recorded on a Shimadzu UV-3600 spectrometer with a resolution of 1.0 nm. A solution of the sample (ca. 10⁻³ M) in a 1 cm square quartz cell was used for the measurement. Fluorescence spectra were recorded on a Hitachi F-7000 spectrometer. The fluorescence lifetimes and the absolute quantum yields (Φ) of the samples were determined with a Horiba Jobin Yvon Fluorolog-3 spectrophotometer. Fluorescence quantum yield of Borebt1–6 in solution were determined by using 4-methylamino-7-nitro-2,1,3-benzoxadiazole (Φf = 0.38 in acetonitrile) as reference.¹⁰

**X-ray structure determination**

The X-ray diffraction data were collected at 298 K on a Gemini A Single Crystal CCD X-ray diffractometer with MoKα radiation (λ = 0.71073 Å) and graphite monochromator. The structure was solved by direct methods (SHELX-97)¹¹ and refined by the full-matrix least-squares on F² (SHELX-97). All the non-hydrogen atoms were refined anisotrOpically and all the hydrogen atoms were placed by using AFIX instructions.

**Borebt1**: C₂₃H₂₅BF₂N₂S; Triclinic, P-1, a = 9.1766(9) Å, b = 9.2490(10) Å, c = 11.8304(13) Å, α = 109.989(10)°, β = 96.898(9)°, γ = 99.154(9)°, V = 914.97(17) Å³, Z = 2, F(000) = 388, ρ = 1.366 mg/m³, R₁ = 0.0443, wR₂ = 0.1113, GOF = 1.077, residual electron density between 0.161 and -0.246 e Å⁻³. CCDC-1029825.

**Borebt2**: C₂₃H₂₅BF₂N₂S; Monoclinic, P21/c, a = 11.3993(10) Å, b = 12.7664(9) Å, c = 15.0077(17) Å, α = 90°, β = 117.220(7)°, γ = 90°, V = 1942.1(3) Å³, Z = 4, F(000) = 840, ρ = 1.383 mg/m³, R₁ = 0.0520, wR₂ = 0.1249, GOF = 1.025, residual electron density between 0.217 and -0.257 e Å⁻³. CCDC-1029826.

**Borebt3**: C₂₃H₂₅BF₂N₂S; Orthorhombic, Pbc a = 15.8955(3) Å, b = 9.83109(15) Å, c = 26.4038(6) Å, α = 90°, β = 90°, γ = 90°, V = 4126.12(14) Å³, Z = 8, F(000) = 1744, ρ = 1.350 mg/m³, R₁ = 0.0407, wR₂ = 0.1076, GOF = 1.023, residual electron density between 0.186 and -0.232 e Å⁻³. CCDC-1029827.

**Borebt4**: C₂₃H₂₅BF₂N₂S; Monoclinic, P2(1)/c, a = 12.1191(13) Å, b = 14.1236(14) Å, c = 11.9314(11) Å, α = 90°, β = 100.907(2)°, γ = 90°, V = 2002.3(3) Å³, Z = 4, F(000) = 872, ρ = 1.391 mg/m³, R₁ = 0.0480, wR₂ = 0.1341, GOF = 0.948, residual electron density between 0.255 and -0.247 e Å⁻³. CCDC-1029828.

**Borebt5**: C₂₃H₂₅BF₂N₂S; Monoclinic, P2(1)/c, a = 13.0949(9) Å, b = 12.1529(6) Å, c = 14.5043(9) Å, α = 90°, β = 104.475(7)°, γ = 90°, V = 2235.0(2) Å³, Z = 4, F(000) = 936, ρ = 1.329 mg/m³, R₁ = 0.0542, wR₂ = 0.1351, GOF = 1.022, residual electron density between 0.171 and -0.222 e Å⁻³. CCDC-1029829.

**Borebt6**: C₂₃H₂₅BF₂N₂S; Monoclinic, C2/c, a = 20.6963(13) Å, b = 8.5511(6) Å, c = 27.3182(2) Å, α = 90°, β = 106.475(7)°, γ = 90°, V = 4636.1(6) Å³, Z = 8, F(000) = 1936, ρ = 1.325 mg/m³, R₁ = 0.0530, wR₂ = 0.1254, GOF = 1.016, residual electron density between 0.181 and -0.228 e Å⁻³. CCDC-1029830.

**Computational details**

TD-DFT calculations were performed at the hybrid density functional theory level (B3LYP) with the 6-31G(d,p) basis set, using the Gaussian03 software package. The calculations were made in the gas phase.³

**Electrochemical Properties.**

Cyclic voltammetry were recorded with a CHI 660B electrochemical analyzer using degassed and dried CH₂Cl₂ under an argon atmosphere. The CV cell consisted of a glassy carbon electrode, a Pt wire counter electrode, and a Ag/AgCl reference electrode. All measurements were performed using CH₂Cl₂ solutions of samples with a concentration of 1 mM and 0.1 M Bu₄NBF₄ as a supporting electrolyte with a scan rate of 50 mVs⁻¹. Potentials were determined against a ferrocene/ferrocenyl ion couple (Fc/Fc⁺). The frontier orbital energy levels were calculated with the following equation¹²:

\[ E_{\text{HOMO}} = -E_{\text{onset set}} - 4.8 \text{ eV} \]

\[ E_{\text{LUMO}} = -E_{\text{Red set}} - 4.8 \text{ eV} \]

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**Notes and references**

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A series of benzothiazole-enamide-based boron difluoride complexes were demonstrated to possess aggregation-induced emission, tunable, substituent-dependent emission profiles, large Stokes shift and high quantum yield in the solid-state, which were rationalized through X-ray crystal analysis, and electronic structure calculations.