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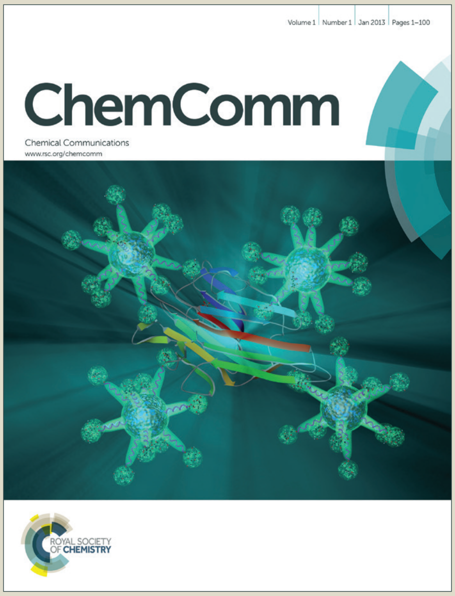

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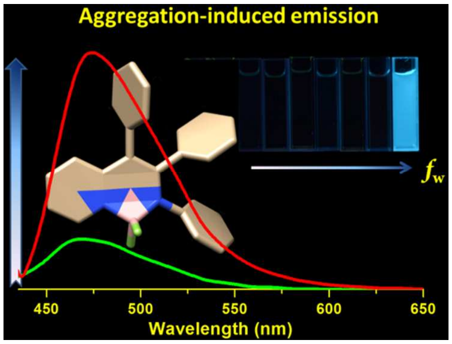
GRAPHIC ABSTRACT

Organoboron complexes having aggregation-induced emission (AIE) properties are presented. The series of pyridyl-enamido-based organoboron complexes (**Borepy1-4**) were synthesized and the AIE behaviors of **Borepy1-4** in solution and in the solid state were investigated.



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COMMUNICATION

Aggregation-induced emission (AIE) of Pyridyl-Enamido-based Organoboron Luminophores

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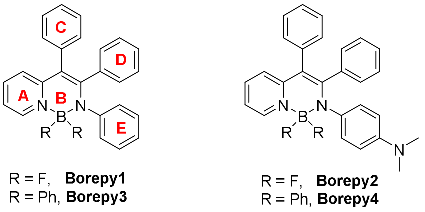
A new family of pyridyl-enamido-based organoboron complexes (Borepy1–4) with aggregation-induced emission (AIE) properties were developed. They show very weak fluorescence in low-viscosity organic solvents and exhibit intense fluorescence in high-viscosity or in their aggregation/solid-state. X–ray crystallographic analysis show that the weak intermolecular interactions by fixing the molecular conformations of Borepy1–4 are responsible for intense fluorescence in the solid state. TD–DFT calculations show that the maximum absorption bands for Borepy1–4 can be easily tuned.

Design of efficient luminescent emitters in the solid and aggregate states are of importance to the development of advanced optical and biomedical devices, such as organic light-emitting diodes (OLEDs) and luminescent biosensors.[1] One of the main challenges in the field is the fact that the emission of conventional luminophores is often weakened or even totally annihilated in the solid or aggregate states as a result of the notorious photophysical effect of “aggregation-induced quenching” (ACQ).[2] The reason behind this is that most luminophores with panel-like structure may exhibit undesirable intermolecular interactions in the solid or aggregate states (e.g., π–π stacking, the formation of excimers and exciplexes), which quenches the emission efficiency. This phenomenon is prominently displayed in borondipyrromethene (**BODIPY**) dyes that have high quantum yields in the solution phase, but barely emit in the solid states.[3] Various strategies have been developed to overcome this obstacle. For example, decorating the luminophores with bulky substituents has been proved to be an effective strategy for decreasing their π–π stacking.[4] Another more successful approach to create emissive luminophores is aggregation-induced emission (AIE).[5] AIE luminophores are nonluminescent in the dilute solutions, but become highly emissive in the aggregate states. No elaborate work needs to be done to interrupt the aggregation process of the luminophores. Instead, one can take advantage of aggregate formation to generate efficient solid emitters. Even with the AIE strategy, the number of luminophores that efficiently emit in the solid states is still rare. Therefore, the development of new AIE luminophores will contribute to a better understanding of the phenomenon and lead to novel applications. In this communication, we report a new family of pyridyl-enamido-based organoboron luminophores (**Borepy1–4**) that display AIE, in high quantum yields in the solid states.

Borepy1–4 are new analogues of **BODIPY**s with propeller-shaped structure derivate from desymmetrized *N^N*-bidentate ligand. As is known to all, the quenched emission of **BODIPY**s in the solid states is mostly caused by self-absorption resulting from very narrow Stokes shifts inducing a strong overlap of the dye absorption and emission spectra.[6] In the course of our efforts in developing solid-state emissive **BODIPY**s, we realized that the desymmetrization bidentate ligand of **BODIPY**s should be a valuable strategy for construction of **BODIPY**s with large Stokes shift. However, these desymmetrized bidentate ligand based **BODIPY**s still exhibit weak fluorescence quantum yield in the solid state due to the uncurbable deleterious π–π stacking.[7] Propeller-shaped AIE molecules such as tetraphenylethene (TPE) and hexaphenylsilole (HPS) exhibit very weak intermolecular interactions,[5] in light of this, we reasoned that desymmetrized bidentate ligand based **Borepy1–4** with propeller-shaped structure might display large Stokes shifts along with high quantum yield in the solid state.



Scheme 1. The structures of **Borepy1–4**

Borepy1-4 were easily synthesized from pyridyl-enamide-based *N^N*-bidentate ligands (Scheme S1). The reaction of 2-benzylpyridine with ethyl benzoate gave compound **1**. **1** was reacted with aniline and 4-(dimethylamino)aniline in the presence of CF_3COOH in toluene to afford the pyridyl-enamide-based *N^N*-bidentate ligands **2** and **3**. By reacting of **2** and **3** with boron trifluoride etherate or triphenylboron in toluene gave **Borepy1–4** in high yield. The structures of **Borepy1–4** were confirmed by ^{1}H, ^{13}C NMR, ESI–MS, and X–ray crystallography.

The photophysical properties of **Borepy1–4** were measured in several solvents and in the solid state. The full details can be found in the ESI (Fig. S5–7 and Table S1). In CH_2Cl_2, **Borepy1** showed absorption maxima at 407 nm (ε = 20000 $M^{-1}cm^{-1}$) and 330 nm (ε =

10000 $M^{-1}cm^{-1}$), respectively. **Borepy2** showed a similar absorption spectrum with wavelength slightly red-shifted compared to **Borepy1**, with maximum at 416 nm (ε = 21000 $M^{-1}cm^{-1}$) and 330 nm (ε = 15000 $M^{-1}cm^{-1}$). The slightly red shift can be explained by the *N*, *N*-dimethylamino group caused charge transfer (CT) enhancement. Interestingly, **Borepy3** and **Borepy4** exhibited large red-shifted absorption band and lower molar absorption coefficient compared to **Borepy1** and **Borepy2**, with maximum at 353 nm (ε = 6000 $M^{-1}cm^{-1}$) and 448 nm (ε = 11000 $M^{-1}cm^{-1}$) for **Borepy3**, and 353 nm (ε = 8000 $M^{-1}cm^{-1}$) and 461 nm (ε = 14000 $M^{-1}cm^{-1}$) for **Borepy4**, respectively. This red-shift of absorption band and decrease in ε of **Borepy3** and **Borepy4** may be due to the molecular bending of **Borepy3** and **Borepy4** caused by the introduction of bulky phenyl groups at the boron atom. The solvents effects on the absorption of **Borepy1**–**4** were examined (Figure S5). The absorption band and ε values of **Borepy1**–**4** were hardly affected by solvent polarity.

Due to the intramolecular rotation induced nonradiative process, **Borepy1**–**4** were found to possess very weak fluorescence in low-viscosity organic solvents along with very low fluorescence quantum yield.[5,8] In high-viscosity solvents such as glycerol, these compounds showed dramatically enhanced fluorescence intensity (Fig. 1). This result suggests that the viscous medium inhibits intramolecular rotation, thereby suppressing the nonradiative process which leads to increased Φ_f (Table S1). It should be noted that, **Borepy1** (F_{max} = 471 nm) and **Borepy3** (F_{max} = 522 nm) showed enhanced fluorescence intensity in glycol or glycerol, while the fluorescence intensity enhancement of **Borepy2** (F_{max} = 464 nm) and **Borepy4** (F_{max} = 513 nm) was only found in glycerol. This should be ascribed to the additional rotation group (*N*,*N*-dimethylamino) of **Borepy2** and **Borepy4** induced more nonradiative process than **Borepy1** and **Borepy3**. Additionally, the observed Stokes shifts of **Borepy1**–**4** are in the range of 2200–3340 cm^{-1} (Table S1), which are larger than fluorescent boron complexes such as **BODIPY** (400–600 cm^{-1})[6] and pyrido-methene-BF_2 complexes (250–400 cm^{-1}).[9]

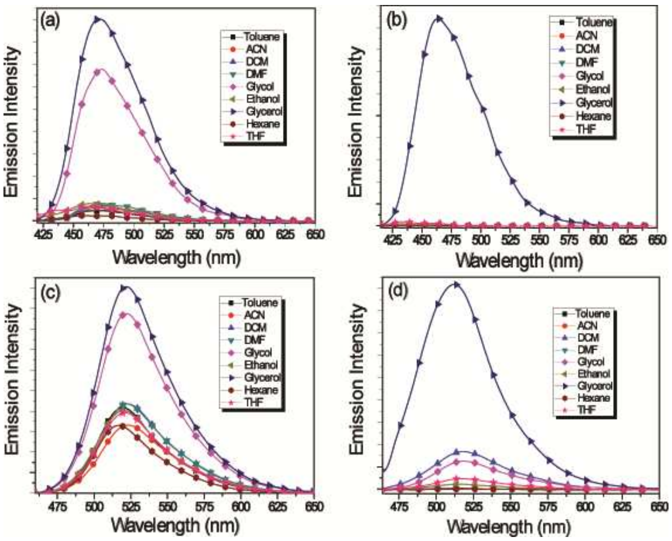


Figure 1. Emission spectra of **Borepy1**–**4** (10 μM) in various solvents such as hexane, toluene, dichloromethane (DCM), tetrahydrofuran (THF), acetonitrile (ACN), dimethylformamide (DMF), ethanol, ethylene glycol (glycol) and glycerol, respectively.

The solid-state absorption and emission spectra of **Borepy1**–**4** are shown in Figure S7 and the main photophysical properties are summarized in Table S1. Dyes with strong intermolecular interactions usually display broad absorption and emission bands in the solid state, which makes it impossible to identify the main electronic bands. Interestingly, the absorption spectra of **Borepy1**–**4** in the solid state were slight broader, and only the red-shift of CT band was found when compared to those in solution. The emission band of **Borepy1**–**4** remained narrow and the F_{max} values (481–577 nm) in the solid state were more bathochromic than those in CH_2Cl_2 (464–513 nm). Importantly, **Borepy1**–**4** showed intense emission in the solid state, with Φ_f of 0.12 for **Borepy1**, 0.20 for **Borepy2**, 0.26 for **Borepy3** and 0.10 for **Borepy4**, respectively. These results suggest that the existence of very weak intermolecular interactions of **Borepy1**–**4** in the solid state. Moreover, the applications of **Borepy1**–**4** as solid- state acid and base fluorescent sensor were examined (Fig. S8–9 and Fig.2). A LCU-shaped filter paper coated with **Borepy4** emitted orange fluorescence under UV light and exhibited yellow color under ambient light. When exposed to HCl vapors for a few seconds, the color changed from dark yellow to bright yellow and the photoluminescence color changed from orange to green as a result of the protonation of the amino group. The protonated **Borepy4** can be quickly switched back to **Borepy4** by exposing the paper to NH_3 vapors. **Borepy2** showed the same ability as **Borepy4** in sensing HCl gas in the solid state (Fig. S9).

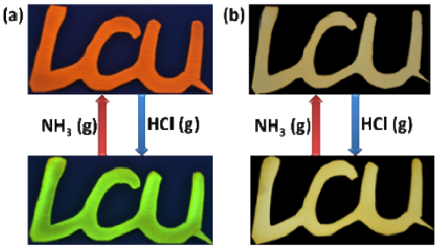


Figure 2. The pictures of **Borepy1**–**4** on a filter paper support under ambient (b) and UV light (a).

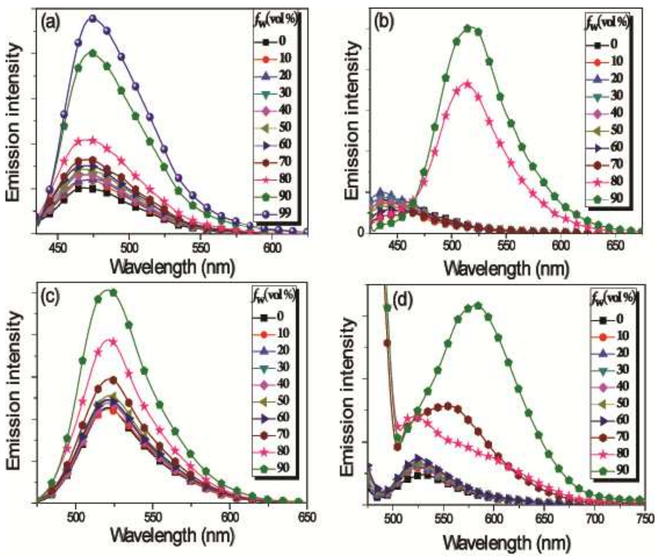


Figure 3. Fluorescence spectra of **Borepy1**–**4** in THF/water mixtures (10 μM) with varied volumetric fractions of water (f_w).

To determine whether **Borepy1**–**4** have the AIE character, the emission properties of **Borepy1**–**4** were investigated in THF-water mixture of various ratios (Fig. 3 and Fig. S6). **Borepy1**–**4** are soluble in THF but not in water. In pure THF solution, **Borepy1** and **Borepy3** have very low emission intensity. The emission properties of **Borepy1** and **Borepy3** almost kept unchanged until the water fraction (f_w) reached to 60%, because **Borepy1** and **Borepy3** were soluble in the THF-water mixtures with lower water content. The Φ_f

was around 0.015 for **Borepy1** and 0.13 for **Borepy3**, respectively. The lifetimes of **Borepy1** and **Borepy3** were too low to be determined accurately (τ<0.2 ns). When the f_w was increased to 99% for **Borepy1** and 90% for **Borepy3**, the Φ_f value was 0.14 for **Borepy1** and 0.35 for **Borepy3**, which was more than 9-fold and 2.6-fold higher than that in pure THF solution. The lifetimes were also increased distinctly to 0.91 ns for **Borepy1** and 5.9 ns for **Borepy3**, respectively. The aqueous solution of **Borepy3** became turbid when the f_w exceeded 90% because of the formation of visible aggregates which hindered the acquisition of the emission spectra (Fig. 3a and 3c). The emission properties of **Borepy2** and **Borepy4** remained unchanged until the f_w reached to 70% and 80%, respectively. Upon addition of 90% water into THF, the F_max of **Borepy2** and **Borepy4** changed dramatically from 464 to 518 nm and 513 to 583 nm, respectively, due to the aggregation-induced CT enhancement (Fig. 3b and 3d). Clearly, the addition of water results in aggregation which leads to enhanced/red-shifted emission. The restriction of phenyl ring and *N*,*N*-dimethylamino group's free rotation via aggregate formation should be responsible for this AIE. Different from **Borepy1** and **Borepy3**, **Borepy2** and **Borepy4** showed very low Φ_f (<0.01) and short lifetimes (τ <0.2 ns) even in their aggregate state, which should be ascribed to the rotation of their *N*,*N*-dimethylamino groups induced more nonradiative process than **Borepy1** and **Borepy3**.

In order to better understand the solid-state emission properties of each compound, X–ray crystallographic analysis was performed. Their ORTEP drawings and molecular packing structures are shown in Fig. 4 and S1–4. **Borepy1**, **Borepy2**, **Borepy3** and **Borepy4** belong to the orthorhombic space group P212121, the triclinic space group P-1, the mononclinic space group P2(1)/n and the orthorhombic space group P212121, respectively. All the boron atoms of **Borepy1–4** adopt a typical tetrahedral geometry to form *N^N*–chelate six-membered rings (ring B). The B–N (pyridyl nitrogen) bond lengths are around 0.04 Å (**Borepy1** and **Borepy2**) and 0.06 Å (**Borepy3** and **Borepy4**) longer than the B–N (enamido nitrogen), due to the asymmetry of these molecules. Similar trends have been reported for the B–N bonds of other unsymmetrical BF_2 complexes.[7,10] As anticipated, **Borepy1–4** adopt twisted conformations and the phenyl rings are not coplanar. For example, the dihedral angles of A and C, C and D, D and E in **Borepy1** are 58.91°, 58.77° and 54.08°, respectively. Intermolecular π–π interactions are not detected in **Borepy1–4**; However, multiple short interatomic contacts exist within the crystals: F2⋯H24–C24 (3.38 Å), F2⋯H18–C18 (3.25 Å), and F1⋯H22–C22 (3.30 Å) interactions in **Borepy1**, F1⋯H31–C31 (3.27 Å), F1⋯H51–C51 (3.13 Å), F2⋯H15–C15 (3.15 Å), F3⋯H3–C3 (3.14 Å), F3⋯H4–C4 (2.97 Å) and F4⋯H43–C43 (3.25 Å) interactions in **Borepy2**. Furthermore, C–H⋯π interactions are detected in **Borepy1** (3.52 Å), **Borepy2** (3.49 Å), **Borepy3** (3.75 Å) and **Borepy4** (3.67 Å). These weak intermolecular interactions fix the molecular conformations of **Borepy1–4** in the solid state, which inhibits the internal rotations and their non-radiative relaxation. This result agrees well with the observation that **Borepy1–4** show intense emissions in the solid state.

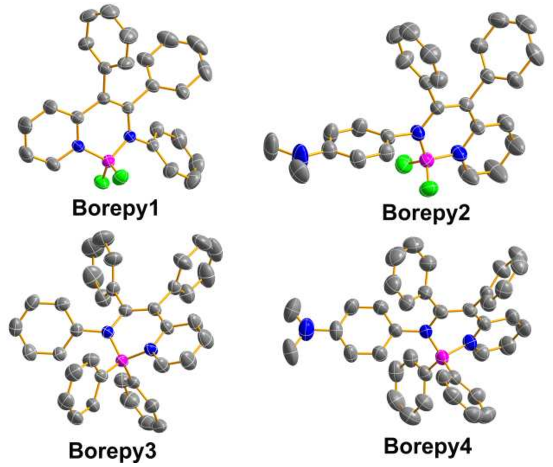


Figure 4. Molecular structures of **Borepy1–4** (50% probability for thermal ellipsoids). H atoms are omitted for clarity.

To understand the photophysical properties of **Borepy1–4**, time dependent density functional theory (TD-DFT) calculations were performed with the Gaussian 03 package.[10] The pictorial drawings of the HOMOs and LUMOs and energy levels are shown in Fig. S10. Based on the TD-DFT calculations, the calculated absorption wavelengths are 3.13 eV/395 nm and 3.66 eV/338 nm for **Borepy1**, 2.78 eV/445 nm and 3.45 eV/358 nm for **Borepy2**, 2.93 eV/422 nm and 3.46 eV/357 nm for **Borepy3**, 2.66 eV/465 nm and 3.27 eV/378 nm for **Borepy4**, respectively, which are slightly higher in energy but in good agreement with the experimental results (Fig. S11). For **Borepy1–4**, the first and the second absorption bands can be attributed to the transitions from the HOMO to the LUMO and the HOMO-1 to the LUMO of the π–systems, respectively.

The LUMOs of **Borepy2** and **Borepy4** are slightly stabilized compared with those of **Borepy1** and **Borepy3**, while the HOMOs are destabilized due to the incorporation of a *N*,*N*-dimethylamino group onto the 4–positions of the phenyl ring. This results in a decrease in the HOMO–LUMO gap, which leads to a red shift of the main absorption band relative to that of **Borepy1** and **Borepy3**. These results indicate that the main absorption bands of **Borepy1–4** can be easily tuned, and that the extent of the shift of the absorption can be predicted by theoretical calculations.

Conclusions

In conclusion, we have designed and synthesized a series of pyridyl-enamido-based organoboron complexes (**Borepy1–4**) with AIE properties. **Borepy1–4** exhibit very weak fluorescence in low-viscosity organic solvents due to the intramolecular rotation induced non-radiative process. In high-viscosity solvents such as glycerol, or in their aggregation/solid- state, **Borepy1–4** show intense fluorescence because of the inhibited internal rotations. X–ray analysis indicates that the weak intermolecular interactions such as F⋯H–C and C–H⋯π interactions fix the molecular conformations of **Borepy1–4** in the solid state. TD–DFT calculations reveal that the maximum absorption bands for **Borepy1–4** are attributed to the HOMO→LUMO transitions, and the maximum absorption bands of **Borepy1–4** can be easily tuned.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [Experimental details, emission spectra of **Borepy1-4**, and computational details]. See DOI: 10.1039/c000000x/

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