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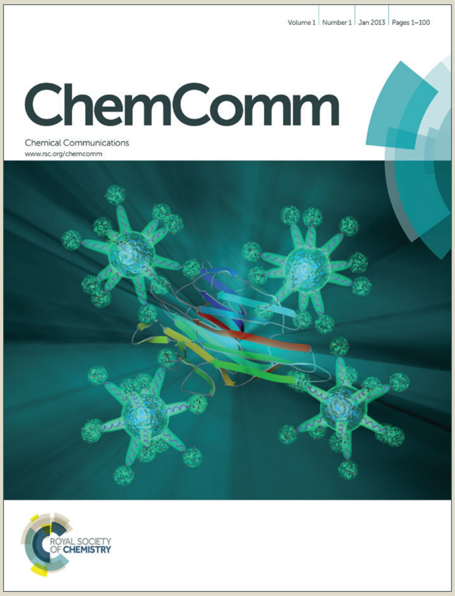

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# Piezochromic Luminescent Behaviors of Two New Benzothiazole-enamido Boron Difluoride Complexes: Intra- and Inter-molecular Effects Induced by Hydrostatic Compression

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**Two new propeller-shaped benzothiazole-enamide boron difluoride complexes exhibiting the piezochromic luminescence upon mechanical grinding or hydrostatic compression were prepared. The two analogues displayed the red shifts in luminescence under high pressure, while compound 2 with ICT effect showed a more sensitive piezochromic response at low pressure (<1.5 GPa). The different piezochromic luminescence behaviors of these compounds were investigated.**

Piezochromic luminescent materials (PLMs) which change their luminescence upon the mechanical grinding/shearing or hydrostatic compression are attracting great interests owing to their promising potential as memory devices, sensors and switches.[1] As the PLMs of novel structures were being developed, the different mechanisms for their piezochromic luminescent behaviours such as phase transformation of aggregation,[2] excimer formation or dissolution,[3] and pressure-induced chemical changes were proposed based on their luminescence alteration stimulated by the mechanical grinding and shearing.[4] Moreover, the piezochromic luminescent response of new PLM systems upon high hydrostatic compression have been reported,[5] and this controllable stimulation is more helpful to understand these PLMs.

The propeller-shaped π-conjugated molecules are among the most frequently adopted structures to devise PLMs.[3d-e, 6] These compounds display high efficient emission in the solid state due to aggregation-induced emission,[6] and the pressure-induced structure or packing alteration was proposed for their piezochromic luminescence. Besides the grinding-induced piezochromic luminescence, both Yamaguchi and Tian have reported the hydrostatic pressure-stimulated piezochromic luminescence of the propeller-shaped π-conjugated molecules, and the tetrathiazolythiophene- and anthracene-derived luminophores upon hydrostatic compression displayed the red-shifted emission.[5a,b] These studies also showed that the hydrostatic compression is a more effective and controllable means to explore piezochromic effect of the propeller-shaped π-conjugated molecules. Herein, two new propeller-shaped benzothiazole-enamido boron difluoride complexes (**1** and **2**, Chart 1) were reported as the new class of PLMs, in which compound 2 bears two additional *N*,*N*-dimethylamino groups. The piezochromic luminescent behavior of the two compounds upon compression/decompression implied that the compression-promoted intramolecular charge transfer (ICT) instead of the intermolecular interaction contributed largely to the PLM nature of compound 2.

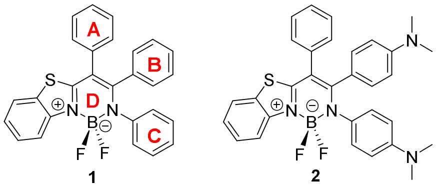

**Chart 1.** Chemical structures of compounds **1** and **2**.

Compounds **1** and **2** were synthesized via a three-step procedure shown in Scheme S1 (See details in SI). Their three-ring-fused π-conjugated skeleton (parent aromatic plane, **D**) was constructed via the boron coordination of the benzothiazole-enamide derived ligand. Three phenyl groups (**A**, **B** and **C**) were tethered to ring **D** to form a propeller-shaped structure. Both **1** and **2** were expected to display high efficient solid-state emission due to the restricted intramolecular rotation of phenyl rings **A**, **B**, and **C** in the solid state. The two *N*,*N*-dimethylamino groups were decorated to phenyl rings **B** and **C** in **2** as the electron-donating group to explore the ICT effect on the piezochromic luminescence, considering the intrinsic electron-withdrawing nature of boron difluoride complexes. The TD-DFT calculations using the crystal structure of compound **2** showed that its HOMOs were mainly delocalized on the **B** and **C** phenyl rings, while its LUMOs were mainly delocalized on the **D** ring, supporting the ICT nature of compound **2** (Figure S11).

In $CH_2Cl_2$, compound **1** showed the absorption ($\lambda_{abs}$) and luminescence maxima ($\lambda_{em}$) at 395 ($\varepsilon$ = 34200 $M^{-1}cm^{-1}$) and 460 nm, respectively; while those for compound **2** were 409 ($\varepsilon$ = 43800 $M^{-1}cm^{-1}$) and 492 nm (Figure S1-2 and Table S1). The longer $\lambda_{abs}$ and $\lambda_{em}$ of **2** can be attributed to its ICT effect from the *N*,*N*-dimethyl group of phenyl rings **B** and **C** to phenyl ring **D**, in which the boron difluoride coordination endows ring **D** with the electron-withdrawing nature. Both compounds **1** and **2** displayed very weak fluorescence with the quantum yields ($\phi_f$) lower than 0.01 in organic solvents of low viscosity such as hexane, toluene and $CH_2Cl_2$ (Figure

1). However, their $\phi_f$ in solvents of high-viscosity such as glycerol, were significantly enhanced to 0.46 (**1**, $\lambda_{em}$, 458 nm) and 0.10 (**2**, $\lambda_{em}$, 522 nm). This viscosity-dependent fluorescence suggested that the non-radiative relaxation of the excited luminophore via intramolecular rotation of phenyl rings **A**, **B** and **C** was impeded by the higher solvent viscosity, which is the typical luminescence behavior of AIE compounds.[6g,7] Solvent substitution with the viscous solvent did not induce any obvious luminescence shift for compound **1**, while a distinct bathochromic shift from 478 nm (in hexane) to 522 nm (in glycol) was observed for compound **2** (Figure 1b), suggesting compound **2** is an ICT luminophore. Considering the propeller-shaped structure and the additional *N,N*-dimethylamino groups in **2**, the high polarity-induced bathochromic luminescence shift of **2** could be ascribed to the promoted ICT effect in **2** other than the excimer formation.

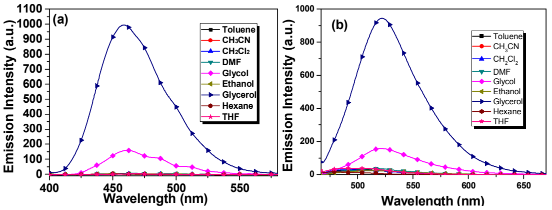

**Figure 1.** Luminescence spectra of compounds **1** (a, $10^{-5}$ M) and **2** (b, $10^{-5}$ M) in hexane, toluene, $CH_2Cl_2$, THF, $CH_3CN$, DMF, ethanol, ethylene glycol and glycerol.

The absorption band of compounds **1** and **2** in the solid state disclosed the $\lambda_{abs}$ of 406 nm (**1**) and 414 nm (**2**), which were slightly bathochromic shifted from those in solutions. The two compounds showed the strong luminescence bands centered at 473 nm (**1**) and 518 nm (**2**), respectively, and the corresponding $\phi_f$ were 0.60 (**1**) and 0.27 (**2**), much higher than those in normal organic solvents (<0.01) (Figure S3 and Table S1). There is no distinct luminescence shift for both **1** and **2** when compared with their luminescence in solvents such as $CH_2Cl_2$ and THF. The blocked intramolecular rotation due to the crystal matrix led to the luminescence enhancement in the solid powder state. [6g,7]

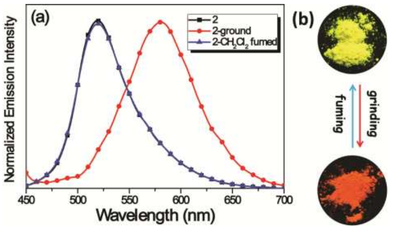

**Figure 2.** (**a**) Normalized luminescence spectra of solid compound **2**, after being ground and $CH_2Cl_2$ fumed, $\lambda_{ex}$, 414 nm. (**b**) Photographs of the ground powder of **2** and the $CH_2Cl_2$-fumed ground powder under UV light (365 nm).

Both compounds **1** and **2** displayed the red-shifted luminescence upon being ground with a pestle for 20 min. Compound **2** showed a distinct luminescence shift from 518 to 582 nm, and the green yellow emitting powder turned into orange (Figure 2). However, the bathochromic shift of **1** was only 8 nm (Figure S4). In addition, the luminescence decrease was also observed for both compounds. Fuming the ground powder with $CH_2Cl_2$ vapor led to the luminescence recovery for both **1** and **2**. All these indicated that both compounds were piezochromic compounds. In addition, the grinding led to distinct changes in their powder X-ray diffraction (XRD) patterns (Figure S5). All the diffraction peaks of compound **1** were weakened, while the peaks for **2** displayed the more significant weakening and broadening. Grinding-induced higher amorphization of compound **2** probably lead to changes in packing, allowing a more planar structure and perhaps better dipole-dipole intermolecular interactions which lead to a large red shift of the fluorescence.[6]

The piezochromic luminescence of the two compounds was further investigated by compression with the hydrostatic pressure created by a diamond anvil cell (DAC) up to ~11 GPa. For compound **1**, as shown in Figure 3a, no distinct change in the luminescence can be observed in the pressure range from 1 atmospheric pressure to 1.13 GPa. The distinct luminescence decrease was observed only after pressure above 1.47 GPa, and the luminescence band became asymmetric due to the emergence of a shoulder on its right side. Further increment of pressure led to a gradual red shift and intensity decrease of the luminescence. The luminescence spectrum recorded at 8.3 GPa showed one broad and significantly weakened band centered at 554 nm. The luminescence maximum of the band was shifted to 571 nm at 10.84 GPa. In the following decompression process, the distinct splitted luminescence band appeared again in the pressure range from 4.23 to 0.07 GPa (Figure 3b). The dual bands observed in the luminescence spectra implied an additional excited species besides the excited **1**, and the excimer formed upon hydrostatic compression might be the origin for the additional luminescence band. Compared with the symmetric single-banded luminescence spectrum at 1.13 GPa in the compression process, the dual-banded luminescence spectrum at 0.07 GPa in the decompression process suggested that the luminescence recovery upon decompression was distinctly delayed due to the dimer formed at high hydrostatic pressure. On the other hand, the more obvious dual band luminescence spectra found in the decompression process than those found upon compression suggested the delayed recovery of the compound in the decompression process.

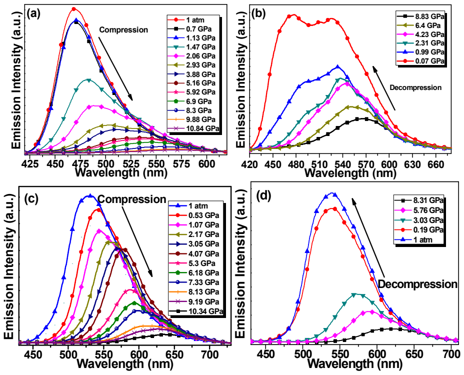

**Figure 3.** Luminescence spectra of compounds **1** (**a** and **b**) and **2** (**c** and **d**) recorded in the compression (**a** and **c**) and the following decompression processes (**b** and **d**).

As to compound **2**, the gradual bathochromic shift of its luminescence band was observed with the concomitant intensity decrease upon hydrostatic compression (Figure 3c). The luminescence maximum was gradually red-shifted from 520 nm at ambient pressure to 645 nm at 10.34 GPa. All the changes in the compression process were reversible upon decompression, and the luminescence spectra of **2** recovered back to the original one when the pressure turned back to the ambient pressure (Figure 3d). Different from compound **1**, all the luminescence spectra of compound **2** determined in the compression/decompression cycle showed only one luminescence band, suggesting no new excited species was formed in this process.

The profiles for the hydrostatic compression/decompression cycle based on the luminescence wavenumber at different pressures were investigated. For compound **1**, its wavenumber remained unchanged in the pressure range from ambient to 1.13 GPa, and the small red shifts of 11 and 21 nm at 1.47 GPa and 2.06 GPa, were observed respectively (Figure 4a). Its wavenumber was decreased in the subsequent compression to 10.84 GPa. The initial following decompression from 10.84 to 2.31 GPa displayed a slightly lower increasing rate of wavenumber than the decreasing rate at the same pressure. The enhanced increasing rate was observed after decompression to 2.31GPa. The distinct hysteresis loop observed in the compression/decompression cycle suggested a delayed recovery of luminescence upon decompression and the poor reversibility of the compression-induced piezochromic effect. The pressure-dependent intermolecular interaction, probably the enhanced π–π intermolecular interaction by high pressure might be the origin. In contrast, an almost linear decrease of wavenumber with the pressure was disclosed for compound **2**, and the following decompression procedure from 10.34 GPa disclosed an inverse process with a similar rate, implying the piezochromic effect of **2** was of excellent reversibility in the studied pressure range (Figure 4b). No hysteresis was observed for the compression/decompression cycle, suggesting the weak intermolecular interaction in compound **2** even upon compression, which favored the quick relaxation of wavenumber upon decompression. Such a reversibility of piezochromic effect even upon compression at 10 GPa is worthy to be noted in the chemistry of piezochromism. Compared with the negligible piezochromic effect of compound **1** at low pressure, compound **2** showed more distinct $\lambda_{em}$ shift in the pressure range from ambient pressure to 2.17 GPa (Figure S6). The red shifts of $\lambda_{em}$ at 0.53 GPa, 1.07 GPa and 2.17 GPa are 21, 26 and 42 nm, respectively. The higher piezochromism sensitivity of **2** than **1** at low compression pressure indicated that compound **2** was more desirable for practical applications.

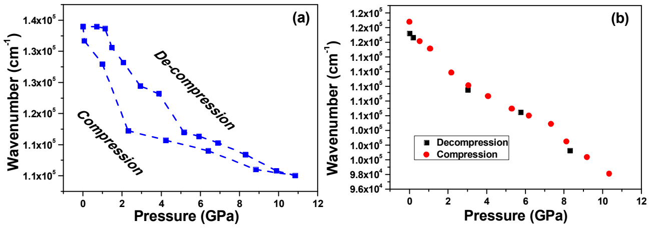

**Figure 4.** Hydrostatic compression/decompression profiles of compounds **1** (**a**) and **2** (**b**) based on the luminescence wavenumber at different hydrostatic pressures according to Figure 3

The crystal structures of compounds **1** and **2** determined by X-ray diffraction showed that both compounds took the similar propeller conformation (Figure S7 and S9), and boron coordination adopted a typical tetrahedral geometry to form *N*^*N*-chelating six-membered ring **D**. In this propeller conformation, the phenyl rings **A**, **B** and **C** act as three blades, while the benzothiozole motif and ring **D** form a large aromatic system as the parent plane. The dihedral angles of this parent plane with the neighboring **A**, **B** and **C** rings are 72.03°, 65.60° and 61.00° in **1**, and 73.63°, 73.56° and 83.16° in **2**, respectively. Multiple weak intermolecular hydrogen bonds such as F1···H21–C21 (3.36 Å), F3···H2–C2 (3.55 Å), F4···H2–C2 (3.18 Å), F3···H48–C48 (3.35 Å) in **1**, and F1···H30–C30 (3.42 Å), F2···H17–C17 (3.41 Å) in **2**, were found (Figure S8 and S10). Although weak intermolecular C–H···π interactions were detected in **1** and **2** (~3.6 Å), the π–π interaction between the aromatic systems was not observed due to the steric hindrance of the three blades. The hydrogen bonding system and intermolecular C–H···π interaction constructed the 3D network, which fixed their propeller conformation and blocked the non-radiative relaxation via blade rotation and excimer formation, favoring their AIE in solid state.

With the crystal structures of compounds **1** and **2**, their molecular packing modes were optimized preliminary by the density functional theory (DFT) simulation at 1.5 and 4.0 GPa using CASTEP program and GGA-PBE function.[5a,8] The results demonstrated that both compounds **1** and **2** adopted two conformations, **I** and **II** upon compression (Figure S13–S20). In conformation **I**, the dihedral angles of phenyl rings **A**, **B** and **C** with ring **D** decreased obviously upon compression (Table S2–5), displaying the tendency of co-planation of rings **A**, **B**, **C** and **D**, and the higher pressure led to more planar structure. Similar tendency was also observed for conformation **II**. At 1.5 GPa, the packing mode showed that both compounds took the more planar structures than those at ambient pressure, favoring the weak intermolecular C–H···F and C–H···π interactions, while no π–π interaction was observed (Figure S14 and S16). At 4.0 GPa, the two luminophores became more planar than those at 1.5 GPa, and π–π intermolecular interaction was observed in the simulated packing modes. In addition, the π–π interaction in compound **1** was much stronger than that in compound **2** (Figure S18 and Figure S20), which is consistent with the observation of the distinct hysteresis loop of compound **1**.

With the piezochromic behaviors and simulated molecular packing modes, it is proposed that the co-planation of the propeller structures upon compression is essential for the piezochromic luminescent behaviors of both compounds. Considering the donor-acceptor structure of **2**, it is expected that the compression-induced molecule co-planation promotes the intramolecular CT effect from *N,N*-dimethyl amino group to ring **D**, resulting in the luminescence bathochromic shift and intensity decrease (Figure 5b). [6g,9] Since no more excited species was induced in the compression/decompression cycle, only one luminescence band was observed. For compound **1**, the compression-induced co-planation leads to the strong π-π intermolecular interaction, which favors not only the excimer formation but also the luminescence quenching. [10] Therefore the dual band luminescence (excimer and monomer bands) was observed accompanying with the intensity decrease. The negligible luminescence change of compound **1** upon compression at low pressure should be originated from the absence of π-π intermolecular interaction at low pressure. For compound **2**, the contribution of intermolecular π–π interaction for the piezochromic response at very high pressure cannot be excluded currently, yet the absence of hysteresis loop suggests the intermolecular interaction is limited.

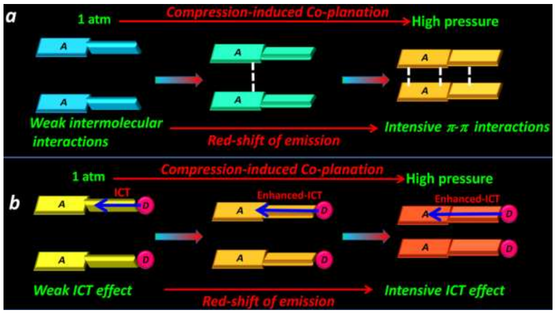

**Figure** 5. Proposed mechanism of the piezochromic behaviors for **1** (a) and **2** (b). ***A***, the electron-withdrawing motif; ***D***, the electron-donating group.

## Conclusions

In summary, two new propeller-shaped benzothiazole-enamide boron difluoride complexes have been synthesized, which demonstrated the piezochromic luminescence upon mechanical grinding or hydrostatic compression but behaved differently due to their structures. Both **1** and **2** exhibited the distinct red-shifted luminescence at high pressure, while compound **2** bearing two *N*,*N*-dimethyl amino groups showed more sensitive piezochromic response at low pressure ($<1.5$ GPa) compared with compound **1**. Compound **1** showed the dual band luminescence and the distinct hysteresis loop during the compression/decompression process, while compound **2** always showed a single band luminescence and no hysteresis. The compression-induced luminophore co-planation led to the distinct enhancement of $\pi$-$\pi$ intermolecular interaction in compound **1** or intramolecular CT effect in compound **2**, which were proposed to be responsible for their different piezochromic luminescence. The enhanced $\pi$-$\pi$ intermolecular interaction favored the excimer formation, resulting in the dual band luminescence (excimer and monomer luminescence) of compound **1**. This study implied that the pressure-dependent $\pi$-$\pi$ intermolecular interaction and intramolecular CT effect were efficient to induce the piezochromic luminescence. The distinct piezochromic effect of **2** at low compression pressure implied that the propeller-shaped AIE luminophore with ICT effect should be a valuable strategy to design PLMs of high sensitivity.

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## Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details, structures, absorption, luminescence, DFT calculations and NMR spectra. See DOI: 10.1039/c000000x/

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