## Tetrahedron Letters 54 (2013) 4167-4170

Contents lists available at SciVerse ScienceDirect

**Tetrahedron Letters** 

journal homepage: www.elsevier.com/locate/tetlet

# A simple approach to aggregation-induced emission in difluoroboron dibenzoylmethane derivatives



**etrahedro** 

Junyi Hu, Zhen He, Zhi Wang, Xiaoyu Li, Jingsong You, Ge Gao\*

Key Laboratory of Green Chemistry and Technology of Ministry of Education, College of Chemistry, Sichuan University, 29 Wangjiang Road, Chengdu 610064, PR China

### ARTICLE INFO

Article history: Received 28 February 2013 Revised 12 May 2013 Accepted 23 May 2013 Available online 4 June 2013

#### Keywords:

Difluoroboron dibenzoylmethane Twisted intramolecular charge transfer Aggregation-induced emission Sensor

Difluoroboron compounds with intense emission are useful as bioprobes, multifunctional materials, and optoelectronic materials.<sup>1</sup> Of particular interest are boron dipyrromethene (BODIPY) dyes,<sup>2</sup> which have prominent properties such as sharp fluorescence peaks, high quantum yields, and high photostability. These dyes usually exhibit high fluorescence in dilute solutions but the fluorescence diminishes in the solid state due to aggregation-caused quenching (ACQ). In 2001, Tang group discovered that hexaphenylsilole (HPS) is non-luminescent in solution but emissive upon aggregation, which is termed as 'aggregation-induced emission' (AIE).<sup>3</sup> This 'abnormal' phenomenon attracts much attention and a lot of work on new AIE luminogens has been reported.<sup>4</sup> However, only very few difluoroboron dyes such as BODIPY derivatives,<sup>5</sup> BF<sub>2</sub>-hydrazone,<sup>6</sup> and BF<sub>2</sub>-Thiazole<sup>7</sup> have been reported to exhibit AIE effect.

Difluoroboron dibenzoylmethane derivatives (BF<sub>2</sub>dbms), are another type of important difluoroboron dyes structurally related to BODIPYs.<sup>8</sup> These dyes possess large molar extinction coefficients, two-photon absorption cross sections, high emission quantum yields and high sensitivity toward surrounding medium.<sup>9</sup> But AIE effect of these dyes has never been disclosed thus far.

The BF<sub>2</sub>dbm fluorogenic core **1** is a conjugated aromatic system with an electron-accepting center at the difluoroboron moiety. We envisage that connecting a simple electron-donating dimethylamino group with the phenyl ring through a C–N single bond would form a D– $\pi$ –A molecular system with twisted intramolecular charge transfer (TICT) property,<sup>10</sup> which might generate

# ABSTRACT

The first example of an AIE active BF<sub>2</sub>dbm derivative with a single dimethylamino group connecting to the phenyl ring was revealed. It also showed capability of sensing HCl gas both in solution and in the solid state.

© 2013 Elsevier Ltd. All rights reserved.

BF<sub>2</sub>dbms with AIE effect.<sup>4</sup> Herein, we want to report the first example of AIE active BF<sub>2</sub>dbms by this design. In addition, these dyes can be used as the colorimetric and fluorescent sensors for HCl gas both in solution and in the solid state.

All of the boron dibenzoylmethane derivatives **1–6** (Scheme 1) were synthesized in moderate yields by the classic Claisen condensation of the corresponding acetophenones with benzoates followed by the coordination with  $BF_3/Et_2O$  or  $(C_6F_5)_3B$ . The optical properties of **1–6** are summarized in Table 1. The C2 symmetric unsubstituted  $BF_2dbm$  **1**, as the fluorogenic core, showed the absorption at 364 nm and the emission at 414 nm in THF with a weak blue fluorescence of the quantum yield of 0.11, and no significant variation was observed in different solvents. The titration of water into the THF solution of **1** resulted in small variation of the emission (Fig. S1) and invisibility of the Tyndall phenomenon (Fig. S2),<sup>7,11</sup> suggesting no AIE effect.

When a dimethylamino group was introduced into the *para* position of one of the phenyl rings, the  $BF_2$ dbm derivative **2** exhibited the absorption at 454 nm and the emission at 530 nm with a large red shifts of 90 nm and 116 nm compared with **1**, respectively,



Scheme 1. The molecular structures of compounds 1-6.

<sup>\*</sup> Corresponding author. Tel.: +86 2885418195. *E-mail address:* gg2b@scu.edu.cn (G. Gao).

<sup>0040-4039/\$ -</sup> see front matter  $\odot$  2013 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.tetlet.2013.05.099

Table 1		
Photophysical properties of $1-6$ in solution	(THF) and	film

Compounds	$\lambda_{ab}^{a,b}$ (nm)	$\lambda_{\rm em}^{\ a}({\rm nm})$	
	Solution ( $\varepsilon$ )	Solution <sup>b,c,d</sup> ( $\Phi_F$ )	$\operatorname{Film}^{c,e}(\varPhi_{\mathrm{F}})$
1	364 nm (16,480)	414 nm (0.11)	439 nm (0.15)
2	454 nm (33,060)	530 nm (0.02)	532 nm (0.75) <sup>f</sup>
3	481 nm (29,680)	512 nm (0.69)	545 nm (0.62)
4	478 nm (36,490)	544 nm (<0.01)	534 nm (0.80)
5	445 nm (35,530)	500 nm (0.05)	518 nm (0.63)
6	363 nm (20,460)	431 nm (0.75)	509 nm (0.36)

<sup>a</sup> ±1 nm.

 $^{\rm b}\,$  Measured at a concentration of 1  $\times$  10  $^{-5}\,{\rm M}.$ 

<sup>c</sup> ±0.03.

<sup>d</sup> Excited at each  $\lambda_{ab}$ .

<sup>e</sup> Excited at each  $\lambda_{ex}$ .

<sup>f</sup> The quantum yield of **2** in the solid state is 0.06.

which suggested a typical D– $\pi$ –A conjugated structure with ICT process from the electron-donating dimethylamino group to the electron-accepting difluoroboron moiety.<sup>12</sup> The quantum yield of **2** in THF dramatically decreased to only 0.02. In addition, the fluorescence behavior of **2** varied in different solvents: Upon excited by UV light, the solution of **2** emitted strong yellow–green fluorescence in a nonpolar solvent such as toluene. Yellow-colored and weakened fluorescence was observed in relatively polar solvents such as chloroform and THF. In highly polar media such as acetone, acetonitrile (MeCN), DMF, and DMSO, the emission became so weak that it could hardly be seen with naked eyes (Fig. S3). This bathochromic shift in color and weakened intensity with the increase of solvent polarity indicated that a twisted intramolecular charge transfer (TICT) process might be involved.

The temperature effect was then investigated to verify the TICT process in the BF<sub>2</sub>dbm derivative **2**. When elevating the temperature of the THF solution of **2** from -10 to 60 °C, the fluorescence intensity gradually increased, accompanied by a small blue-shift of the maximum emission from 536 nm to 526 nm (Fig. S3d). This enhanced fluorescence with mounting temperature was consistent with the typical TICT process.<sup>5</sup> Therefore, the BF<sub>2</sub>dbm derivative **2** is TICT active.

In a nonpolar solvent such as toluene, **2** stayed in the locally excited (LE) state with good conjugation of the donor (D) and the acceptor (A) to emit strong fluorescence. When dissolved in a polar solvent such as MeCN, It rotated to the TICT state, which resulted in elevation of the HOMO level and the narrowed band gap, leading to red shift of the emission. The weakened emission could be interpreted by the increased nonradiative decay processes in the TICT state.<sup>13</sup> The AIE phenomenon was expected when a poor solvent such as water was added to induce the aggregation of **2** because the restriction of intramolecular rotation (RIR) of a TICT active molecule in the aggregates was considered as the main reason for the AIE effect.<sup>4</sup>

The fluorescence properties of **2** were then investigated in the MeCN and water mixtures of various ratios (Fig. 1). The MeCN solution of **2** emitted weak yellow fluorescence under UV irradiation, which was quenched when a small amount of water was added into the solution. In pace with the increasing water fraction (fw), its emission weakened gradually with the fw between 10% and 50%. When the fw exceeded 50%, the original emission peak at 550 nm completely vanished, and a new peak at 622 nm appeared, which was attributed to the solid-state fluorescence of BF<sub>2</sub>dbm derivatives.<sup>14</sup> There was about 16-fold enhancement of the fluorescence.



Figure 1. The fluorescent emission spectra of 2 in the MeCN/water mixtures. Measured at a concentration of  $1\times 10^{-4}\,M.$ 

cence intensity of **2** in MeCN with the maximum 70% fw than without water, indicating the AIE occurred. After the fw continuously increased over 70%, the fluorescence intensity just decreased. AIEs were also observed in other polar solvents such as THF, acetone, and DMSO (Fig. S4). The photographs of **2** in the MeCN/water and DMSO/water mixtures taken under the UV irradiation were shown in Figures S5 and S6. The Tyndall phenomenon of **2** in the DMSO/water solutions demonstrated the nano-sized aggregates of **2** were formed (Fig. S7).<sup>7.11</sup>

The BF<sub>2</sub>dbm derivative 2 in the solid state emitted weak red fluorescence ( $\lambda_{em}$  = 641 nm and  $\Phi_{F}$  = 0.06), indicating the existence of nonradiative decay caused by the intermolecular interactions in the solid state. In order to better understand the molecular packing of 2 in the solid state, the single crystals were obtained by slow evaporation of the THF solution of 2 and subjected to the X-ray diffraction analysis (Fig. 2). It showed that the molecule is almost planar but the BF<sub>2</sub> moiety bends off the skeleton plane 26.4° (the dihedral angle between the B1-O1-O2 plane and the O1-C10-C4–O2 plane). Two molecules pack head-to-tail each other to form a dimer by two hydrogen bonds. Each one is 2.639 Å and formed between a F atom of one molecule and a methyl hydrogen atom of the other molecule. The two dimethylaminophenyl rings are partially overlapped with a centroid distance of 3.647 Å, indicating the  $\pi$ - $\pi$  stacking between these two molecules. The dimers pack into columns by another two hydrogen bonds of 2.495 Å, formed between the other F atom and the other methyl hydrogen atom. Notably, this F atom also forms three hydrogen bonds with two phenyl hydrogen atoms (2.430 and 2.432 Å) and a methylene hydrogen atom (2.517 Å) of another molecule in the adjacent column, which makes packing columns staggered (Fig. S12). These multiple hydrogen bonding and  $\pi$ - $\pi$  stacking may be responsible for the red shift and weakened emission of 2 in the solid state.

As we mentioned before, **2** is a TICT active molecule and its weak emission in THF is due to the nonradiative de-excitation caused by the free rotation of the phenyl ring and the dimethyl-amino group. Restricting its free rotation and preventing the multiple intermolecular interactions at the same time could regenerate its emission in the solid state. So we prepared a poly(methylmeth-acrylate) (PMMA) film doped with 0.1% **2**. The film exhibited strong yellow-colored fluorescence with a quantum yield of 0.75, demonstrating the effects of both RIR and the isolation of the molecules.<sup>15</sup>

Interestingly, BF<sub>2</sub>dbm derivatives **3**, which has two electrondonating dimethylamino groups on both sides of the phenyl rings to recover the C2 symmetry, showed much higher quantum yield than **2** in THF solution ( $\Phi_F$  = 0.69). The enhanced emission of **2** was attributed to the ICT process compared with **1**. The solvent ef-



**Figure 2.** (a) The crystal structure of **2**; (b) a wire drawing of the crystal packing of **2** (the  $\pi$ - $\pi$  interactions and H–F bonds are shown as dashed lines).

fect experiment showed that with an increasing solvent polarity, the fluorescence of **3** was just red-shifted without much change of the intensity. This indicated that **3** does not have a TICT state, which was confirmed by the gradual increase of the emission when lowering the temperature (Fig. S8). The AIE phenomenon was therefore not observed.

By replacing the BF<sub>2</sub> group in the derivative **2** into the  $B(C_6F_5)_2$  group, the derivative **4** gave the quantum yields of less than 0.01 and 0.8 in THF and in the PMMA film, respectively. Meanwhile, a 22-fold increase of the fluorescent intensity of **4** was observed in the MeCN solution when the water fraction reached 50% (Figs. S9 and S10). The enhanced AIE effect was due to the reinforced TICT in the molecule **4** caused by the larger electron-accepting ability of the  $B(C_6F_5)_2$  group and the rotation of the  $C_6F_5$  rings.<sup>16</sup>

To further address the role of the dimethylamino group in **2** for AIE, analogues **5** and **6** with the methylamino group and the ethoxy group were synthesized, respectively. Compared with **2**, **5** has a N–H as the hydrogen bond donor. The water titration induced quenching of the fluorescence of **5** in the THF solution. When fw reached 50%, a small increase with red shift was observed. The fluorescence quenched again when fw kept going higher (Fig. S11a). This fluorescence variation suggested that the aggregation of **5** caused by water addition was different from that of **2** and the N–H was probably involved in multiple hydrogen bonding interactions to open the nonradiative pathway. On the other hand, **6** has an oxygen atom as the hydrogen bond acceptor. The water titration resulted in constant quenching of the fluorescence of **6** in the THF solution (Fig. S11b). Both **5** and **6** have no AIE effect.

The boron dibenzoylmethane derivatives **2–4** containing amino group are capable of sensing HCl gas both in solution and in the so-



**Figure 3.** The pictures of **2** (left) and  $2-H^+$  (right) on a silica support under ambient light (top) and UV light (bottom).

lid state. For example, a TLC plate dipped with **2** exhibited a red color under ambient light and emitted red fluorescence under UV light. When exposed to HCl gas, the red color of the plate faded and emitted a blue fluorescence, which was attributed to the shut-down of the ICT pathway. The plate regained its original state quickly after exposed to NH<sub>3</sub> gas (Fig. 3).<sup>17</sup> The derivatives **3** and **4** showed the same ability as **2** in sensing HCl gas in the solid state (Fig. S14). This simple acid and base sensing experiment demonstrated the potential applications of the BF<sub>2</sub>dbm derivatives as solid-state sensors.<sup>18</sup>

It is worth noting, that the fluorescent sensing behavior of **2** toward HCl gas in solution was dichotomous depending on the polarity of the solvents used. The fluorescence of **2** was quenched in the nonpolar solvents such as toluene and chloroform while it was turned on in the polar solvents such as THF, acetone, and MeCN with addition of HCl gas (Figs. S15 and S17a–e). This difference could be interpreted using LE and TICT mechanism: In nonpolar solvents, **2** stays in the LE state and emits strong fluorescence through ICT. The protonation of the amino group interrupts the ICT process and quenches the fluorescence. In polar solvents, **2** stays in the TICT state and emits weak fluorescence. The protonation of the amino group blocks the TICT process and recovers the fluorescence. Unlike **2**, derivative **3** has no TICT state, therefore fluorescence quenching and blue shifts were always observed in different solvents (Figs. S16 and S17f–h).

In conclusion, a series of boron dibenzoylmethane derivatives **1–6** were synthesized and their photophysical properties were investigated. It showed that the BF<sub>2</sub>dbm **2** with a single dimethylamino group connecting to the phenyl ring is AIE active, which represents the first AIE active BF<sub>2</sub>dbm dye, while the BF<sub>2</sub>dbm **3** with two dimethylamino groups connecting to the two phenyl rings is not. The X-ray diffraction analysis revealed that multiple hydrogen bonding and  $\pi$ – $\pi$  stacking in **2** are responsible for its red but weak fluorescence in the solid state. Finally, the dyes **2–4** are capable of sensing HCl gas by reversible changes of color and fluorescente acid sensors both in solution and in the solid state.

### Acknowledgments

We thank the financial support from the NSFC (Nos. 21172159, 21025205 and 21021001) and the SRF for ROCS, SEM (No 3520111568-8-2). We also thank the Centre of Testing & Analysis, Sichuan University for NMR measurements and X-ray analysis.

# Supplementary data

Supplementary data (these data include copies of <sup>1</sup>H and <sup>13</sup>C NMR spectra, photophysical data and crystallographic data of compounds described in this Letter. The crystallographic data for the compound **2** have been deposited with the Cambridge Crystallo-

graphic Data Centre as entry CCDC 921254.) associated with this article can be found, in the online version, at http://dx.doi.org/ 10.1016/j.tetlet.2013.05.099.

### **References and notes**

- (a) Zhang, H.; Huo, C.; Zhang, J.; Zhang, P.; Tian, W.; Wang, Y. Chem. Commun. 2006, 281; (b) Maeda, H.; Haketa, Y.; Nakanishi, T. J. Am. Chem. Soc. 2007, 129, 13661; (c) Ran, C.; Xu, X.; Raymond, S. B.; Ferrara, B. J.; Neal, K.; Bacskai, B. J.; Medarova, Z.; Moore, A. J. Am. Chem. Soc. 2009, 131, 15257; (d) Ono, K.; Nakashima, A.; Tsuji, Y.; Kinoshita, T.; Tomura, M.; Nishida, J.; Yamashita, Y. Chem. -Eur. J. 2010, 16, 13539; (e) Kowada, T.; Kikuta, J.; Kubo, A.; Ishii, M.; Maeda, H.; Mizukami, S.; Kikuchi, K. J. Am. Chem. Soc. 2011, 133, 17772; (f) Florian, A.; Mayoral, M. J.; Stepanenko, V.; Fernandez, G. Chem. -Eur. J. 2012, 18, 14957; (g) Nagura, K.; Saito, S.; Fröhlich, R.; Glorius, F.; Yamaguchi, S. Angew. Chem., Int. Ed. 2012, 51, 7762.
- (a) Loudet, A.; Burgess, K. Chem. Rev. 2007, 107, 4891; (b) Ulrich, G.; Ziessel, R.; Harriman, A. Angew. Chem., Int. Ed. 2008, 47, 1184; (c) Benstead, M.; Mehl, G. H.; Boyle, R. W. Tetrahedron 2011, 67, 3573; (d) Xiao, S.; Cao, Q.; Dan, F. Curr. Org. Chem. 2012, 16, 2970.
- Luo, J.; Xie, Z.; Lam, J. W. Y.; Cheng, L.; Chen, H.; Qiu, C.; Kwok, H. S.; Zhan, X.; Liu, Y.; Zhu, D.; Tang, B. Z. Chem. Commun. 2001, 1740.
- (a) Hong, Y.; Lam, J. W. Y.; Tang, B. Z. Chem. Commun. 2009, 4332; (b) Hong, Y.; Lam, J. W. Y.; Tang, B. Z. Chem. Soc. Rev. 2011, 40, 5361.
- Hu, R.; Lager, E.; Aguilar-Aguilar, A.; Liu, J.; Lam, J. W. Y.; Sung, H. H. Y.; Williams, I. D.; Zhong, Y.; Wong, K. S.; Peña-Cabrera, E.; Tang, B. Z. J. Phys. Chem. C 2009, 113, 15845.
- 6. Yang, Y.; Su, X.; Carroll, C. N.; Aprahamian, I. Chem. Sci. 2012, 3, 610.
- 7. Kubota, Y.; Tanaka, S.; Funabiki, K.; Matsui, M. Org. Lett. 2012, 14, 4682.
- (a) Zhang, G.; Palmer, G. M.; Dewhirst, M. W.; Fraser, C. L. Nat. Mater. 2009, 8, 747; (b) Zhang, G.; Lu, J.; Sabat, M.; Fraser, C. L. J. Am. Chem. Soc. 2010, 132, 2160; (c) Maeda, H.; Naritani, K.; Honsho, Y.; Seki, S. J. Am. Chem. Soc. 2011, 133,

8896; (d) Maeda, H.; Bando, Y.; Shimomura, K.; Yamada, I.; Naito, M.; Nobusawa, K.; Tsumatori, H.; Kawai, T. *J. Am. Chem. Soc.* **2011**, *133*, 9266.

- (a) Chow, Y. L.; Johansson, C. I.; Zhang, Y.-H.; Gautron, R.; Yang, L.; Rassat, A.; Yang, S.-Z. J. Phys. Org. Chem. **1996**, *9*, *7*; (b) Cogné-Laage, E.; Allemand, J.-F.; Ruel, O.; Baudin, J.-B.; Croquette, V.; Blanchard-Desce, M.; Jullien, L. Chem. -Eur. J. **2004**, *10*, 1445.
- (a) Rettig, W. Angew. Chem., Int. Ed. Engl. 1986, 25, 971; (b) Utard, J.-F.; Lapouyade, R.; Rettig, W. J. Am. Chem. Soc. 1993, 115, 2441; (c) Herbich, J.; Brutschy, B. TICT Molecules. In Electron Transfer in Chemistry; Balzani, V., Ed.; Wiley-VCH: Weinheim, 2001; p 697.
- (a) Li, D.; Sheng, X.; Zhao, B. J. Am. Chem. Soc. 2005, 127, 6248; (b) Tölle, F. J.; Fabritius, M.; Mülhaupt, R. Adv. Funct. Mater. 2012, 22, 1136.
- 12. Wu, Y.-Y.; Chen, Y.; Gou, G.-Z.; Mu, W.-H.; Lv, X.-J.; Du, M.-L.; Fu, W.-F. Org. Lett. 2012, 14, 5226.
- (a) Serrano-Andrés, L.; Merchán, M.; Roos, B. O.; Lindh, R. J. Am. Chem. Soc. 1995, 117, 3189; (b) Cogan, S.; Zilberg, S.; Haas, Y. J. Am. Chem. Soc. 2006, 128, 3335; (c) Palayangoda, S. S.; Cai, X.; Adhikari, R. M.; Neckers, D. C. Org. Lett. 2008, 10, 281.
- (a) Mirochnik, A. G.; Fedorenko, E. V.; Karpenko, A. A.; Gizzatulina, D. A.; Karasev, V. E. Luminescence 2007, 22, 195; (b) Zhang, G.; Chen, J.; Payne, S. J.; Kooi, S. E.; Demas, J. N.; Fraser, C. L. J. Am. Chem. Soc. 2007, 129, 8942; (c) Sazhnikov, V. A.; Aristarkhov, V. P.; Safonov, A. A.; Bagatur'yants, A. A.; Mirochnik, A. G.; Fedorenko, E. V.; Alfimov, M. V. High Energ. Chem. 2011, 45, 315; (d) Sakai, A.; Tanaka, M.; Ohta, E.; Yoshimoto, Y.; Mizuno, K.; Ikeda, H. Tetrahedron Lett. 2012, 53, 4138.
- Tong, H.; Dong, Y.; Haussler, M.; Hong, Y.; Lam, J. W. Y.; Sung, H. H. Y.; Williams, I. D.; Kwok, H. S.; Tang, B. Z. Chem. Phys. Lett. 2006, 428, 326.
- Nagai, A.; Kokado, K.; Nagata, Y.; Arita, M.; Chujo, Y. J. Org. Chem. 2008, 73, 8605.
- 17. The powder of  ${\bf 2}$  exhibited the same color and fluorescence changes upon exposed to HCl and NH<sub>3</sub> gas, see Figure S13.
- (a) Ziessel, R.; Ulrich, G.; Harriman, A.; Alamiry, M. A. H.; Stewart, B.; Retailleau, P. Chem. -Eur. J. 2009, 15, 1359; (b) Li, K.; Chen, Y.; Lu, W.; Zhu, N.; Che, C.-M. Chem. -Eur. J. 2011, 17, 4109.