Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron Letters 48 (2007) 6633–6636
Tetrahedron Letters

A novel three-coordinate organoboron derivative: synthesis, photophysical property and ion recognization

Zhiguo Zhou, Fuyou Li,* Tao Yi* and Chunhui Huang*

Department of Chemistry and Lab of Advanced Materials, Fudan University, Shanghai, PR China

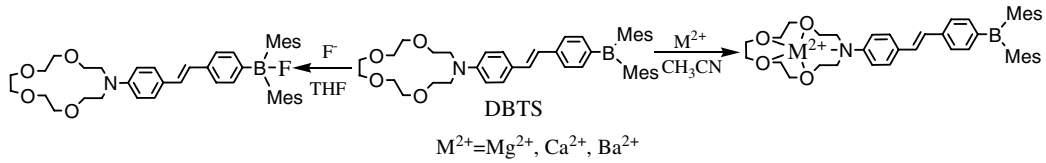
Received 5 June 2007; revised 18 July 2007; accepted 20 July 2007
Available online 27 July 2007

Abstract—A new push–pull type compound *trans*-4-dimesitylboryl-4′-(1,4,7,10-tetraoxa-13-aza-cyclopentadecyl) stilbene (**DBTS**) with aza-15-crown-5 as a donor and a three-coordinate organoboron as an acceptor was designed and synthesized. **DBTS** shows intense fluorescence in a wide spectra range in different solvents. Furthermore, **DBTS** can recognize fluoride anions with a high selectivity for the special Lewis acid–base interaction between a trivalent boron atom and a fluoride anion. As a typical alkaline earth cations receptor, **DBTS** also showed spectral changes upon their addition.
© 2007 Published by Elsevier Ltd.

1. Introduction

Three-coordinate organoborons containing π-conjugate systems have recently received tremendous attention due to their intriguing electronic and photophysical properties as a result of overlap between the vacant p-orbital of the boron atom and the conjugate system.[1] The extensive studies on them have demonstrated their potential uses for various photonic and optoelectronic applications such as nonlinear optical properties,[2] two-photon fluorescence,[3] organic light-emitting diodes (OLEDs).[4] In particular, several research groups have reported that organoborons derivatives could be used as effective fluorogenic, colorimetric and ratiometric chemosensors for fluoride anions.[5–7] Recently, colorimetric sensors are popular due to their capability to detect analytes by the naked eyes without resorting to the use of any expensive instruments.[8] Our group has also reported the colorimetric and two-photon fluorescent sensors for fluoride anions derived from three-coordinate organoborons.[9a] Herein, as an extension of our previous work on organoboron-based chemosensor, we designed and synthesized a new bis-functional derivative **DBTS** (see Scheme 1) to recognize alkaline earth cations and fluoride anions independently by a colorimetric method.

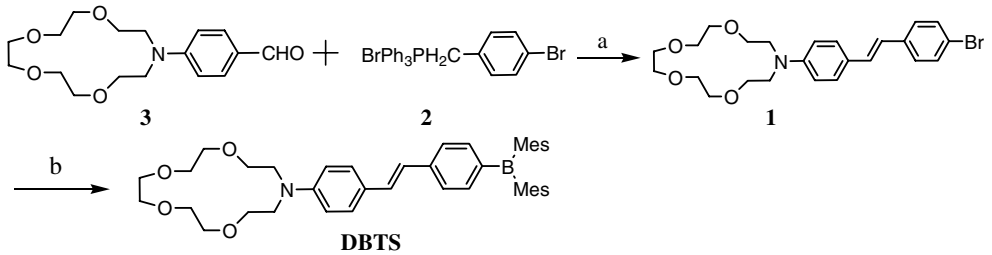
Compound **DBTS** (*trans*-4-dimesitylboryl-4′-(1,4,7,10-tetraoxa-13-aza-cyclopentadecyl)stilbene) was synthesized as described in Scheme 2. The precursor **1** was prepared by Witting reaction. Substitution of the 4′-bromine atom on the precursor **1** by a dimesitylboron group in the presence of *n*-butyllithium at low temperature afforded 40% yields of **DBTS**. The structure of **DBTS** was characterized by ^{1}H NMR, ^{13}C NMR, mass spectroscopy and elemental analysis.[10]



Scheme 1. The concept of a bis-functional chemosensor.

Keywords: Organoboron; Fluoride anion; Alkaline earth cation; Aza-15-crown-5.
* Corresponding authors. Tel.: +86 21 55664185 (C.H.); e-mail: chhuang@fudan.edu.cn

0040-4039/$ - see front matter © 2007 Published by Elsevier Ltd.
doi:10.1016/j.tetlet.2007.07.127



Scheme 2. Reagents and conditions: (a) t-Bu_4OK, anhydrous THF, room temperature, 4 h, 60%; (b) $FB(Mes)_2$, n-BuLi, anhydrous THF, −78 °C, 12 h, 40%.

2. Experiment

The photophysical properties of **DBTS** are investigated in detail and the data are shown in Table 1. As shown in Figure 1a, the maximum absorption peak (λ_{abs}) of **DBTS** in acetonitrile is very similar to that in xylene (see Table 1). However, the emission of **DBTS** was sensitive to different solvents. Its maximum emission peak (λ_{em}) showed remarkable bathochromic shifts with increasing polarity of the solvent. For example, λ_{em} was centered at 490 nm in xylene and red-shifted to 577 nm in acetonitrile. Furthermore, the fluorescence quantum yields and fluorescent lifetimes were also increased with increasing polarity of the solvent. These results suggest that **DBTS** has a fairly large excited-state dipole moment, indicating the strong intramolecular charge transfer process (ICT) between the dimesitylboron group (as an electron acceptor) and the aza-crown group (as an electron donor).[9a]

Table 1. Summary of photophysical properties in different solvents

	λ_{abs} (nm)	λ_{em} (nm)	$\Delta\nu_{st}$ (cm^{-1})	φ	τ (ns)
Xylene	408	490	4042	0.48	0.74
THF	410	540	5931	0.61	1.31
Acetone	410	565	6751	0.66	1.52
MeCN	406	577	7300	0.75	4.04

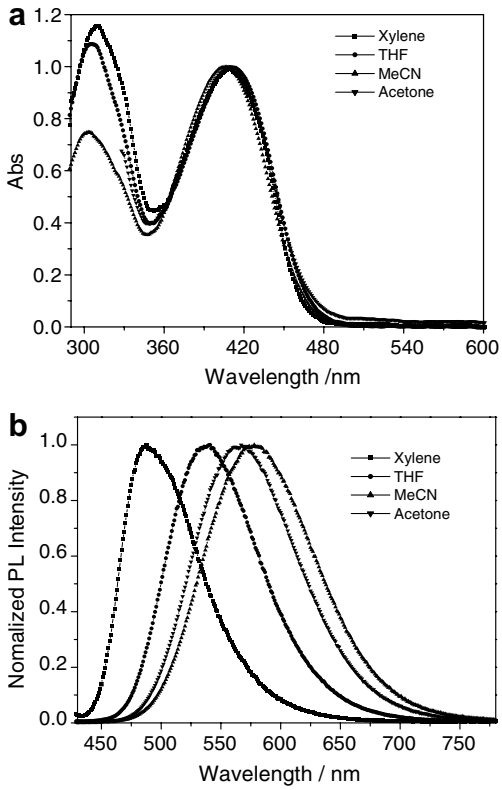


Figure 1. Normalized absorption (a) and fluorescence spectra (b) of **DBTS** in different solvents ($\lambda_{ex} = 410$ nm).

A great deal of efforts has been devoted to the design and synthesis of fluoride anion chemosensors which are highly relevant to health and environmental issues.[11] To explore the application of **DBTS** in sensing fluoride anions, the UV–vis absorption and fluorescence spectra were investigated in the presence of anions. When n-Bu_4NF (TBAF, a fluoride source) was added to the THF solution of **DBTS**, an obvious color change from green-yellow to colorless occurred under ambient light. The characteristic absorption band of **DBTS** centered at 410 nm completely disappeared, and a new band centered at 330 nm arose (see Fig. 2a), corresponding to a greater than 90 nm blue-shift. The binding constant (K_a) was determined from the absorption–titration curves to be 3.1×10^5 M^{-1} in THF solution, which is comparable to that of analogous compounds previously reported.[9a] As shown in Figure 2b, the intense emission band of **DBTS** at 540 nm ($\lambda_{ex} = 410$ nm) progressively quenched, when fluoride anions were added. These findings indicate that the strong B–F interaction results in sp^3 hybridization of the boron atom and subsequently interrupts the extended p–π conjugation, thereby causes a dramatic change in the photophysical property.[12]

For an excellent chemosensor, high selectivity is a matter of necessity. Using the ratio of absorbance at 330 and 410 nm ($A_{330\,nm}/A_{410\,nm}$) as an output signal, the responses of **DBTS** to 5.0 equiv of different anions are shown in Figure 3. Compared with the special blue-shift of **DBTS** with fluoride anions, no obvious special change was observed upon addition of other halide anions, AcO^-, NO_2^- and $H_2PO_4^-$. Similar selectivity was also confirmed in the corresponding fluorescence spectra (see Supplementary data). These results imply that **DBTS** can detect fluoride anions with very high selectivity. The highly selective recognition of **DBTS** for fluoride anions can be probably attrib-

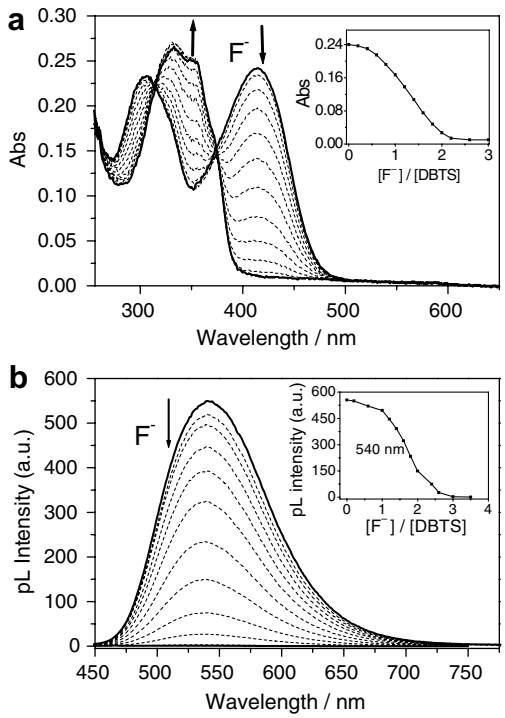


Figure 2. Absorption (a) and emission (b) spectra ($\lambda_{ex} = 410$ nm) of **DBTS** (1.0×10^{-5} M) in THF solution upon addition of different equivalents of fluoride anions.

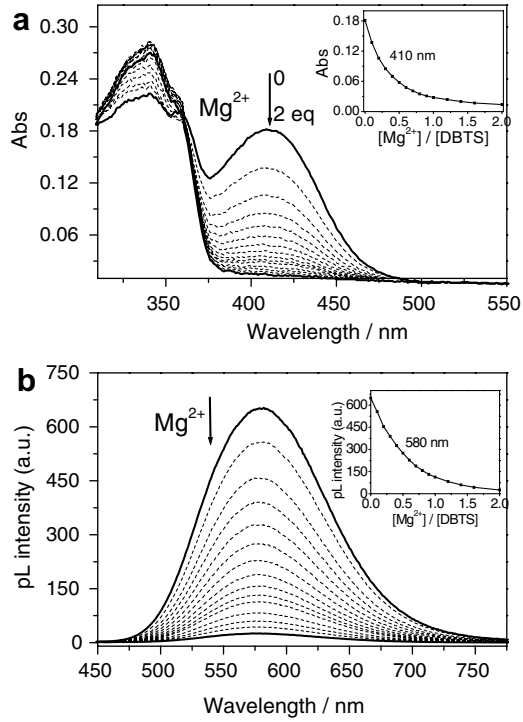


Figure 4. Absorption and emission spectra ($\lambda_{ex} = 410$ nm) of **DBTS** (1.0×10^{-5} M) in CH_3CN solution upon addition of different equivalent of Mg^{2+} ions.

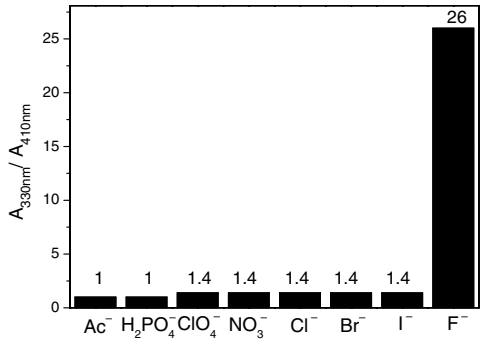


Figure 3. A comparison of the ratio of absorbance at 330 nm and 410 nm of **DBTS** in THF solution (10 μM) in the presence of 5 equiv of anions.

uted to two factors. The specific Lewis acid–base interaction is strong between trivalent boron atom and fluoride anions. Furthermore, the special steric structure of dimesityl group may make some unique contributions.

Alkaline earth cations are the most abundant divalent cations in living cells and play vital roles in many cellular processes. With the presence of aza-15-crown-5, **DBTS** may also recognize alkaline earth cations. Herein, the binding events of **DBTS** were carried out using the absorption and fluorescent technology. The spectra were slightly or not at all affected by alkali metal ions, whereas the great spectral changes for **DBTS** were observed upon addition of alkaline earth ions. As shown in Figure 4a, when magnesium ions were added into the CH_3CN solutions of **DBTS**, the characteristic absorption band of **DBTS** centered at 410 nm completely disappeared, and the band centered at 330 nm arose. The blue-shift of the absorption spectrum of **DBTS** in the presence of alkaline earth cations was due to the interaction of the nitrogen atom of aza-crown with alkaline earth cations which weaken the electron-donating ability of the aza-crown group in the chromophoric π-system.[12] Furthermore, a quenching change in the fluorescent emission was also observed at 540 nm for **DBTS** upon addition of magnesium ions ($\lambda_{ex} = 410$ nm). Similar phenomena were observed upon addition of calcium and barium ions (see Supplementary data). The facts indicate that these alkaline earth cations may be attributed to the reduced intramolecular charge transfer process (ICT) upon complexation. The binding constants (K_a) of **DBTS** in CH_3CN solution for Mg^{2+}, Ca^{2+} and Ba^{2+} are determined from the absorption–titration curves to be 3.5×10^5, 8.6×10^5 and 9.1×10^5 M^{-1}, respectively.

3. Conclusion

In summary, we have demonstrated a bisfunctional organic borane **DBTS** by introducing both aza-15-crown-5 and dimesitylboryl groups. Its absorption property was blue-shifted and its fluorescence was suppressed upon complexation with fluoride anions and alkaline earth cations individually. The result provides a useful design strategy for the synthesis of new chemosensors for further applications.

Acknowledgements

The authors thank NSFC of China (20490210, 20501006 and 20571016), National High Technology Program of China (2006AAZ318), Huo Yingdong Education Foundation (104012) and Shanghai Sci. Tech. Comm. (05DJ14004 and 06QH14002) for financial support.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.07.127.

References and notes

1. (a) Entwistle, C. D.; Marder, T. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 2927; (b) Entwistle, C. D.; Marder, T. B. *Chem. Mater.* **2004**, *16*, 4574.
2. Yuan, Z.; Entwistle, C. D.; Collings, J. C.; Albesa-Jov, D.; batsanov, A. S.; Howard, J. A. K.; Taylor, N. J.; Kaiser, H. M.; Kaufmann, D.; Poon, S. Y.; Wong, W. Y.; Jardin, C.; Fathallah, S.; Bouoekkine, A.; Halet, J. F.; Marder, T. B. *Chem. Eur. J.* **2006**, *12*, 2758.
3. (a) Liu, Z. Q.; Fang, Q.; Wang, D.; Xue, G.; Yu, W. T.; Shao, Z. S.; Jiang, M. H. *Chem. Commun.* **2002**, 2900; (b) Liu, Z. Q.; Cao, D. X.; Wang, D.; Xu, G. B. *Org. Lett.* **2004**, *6*, 2933.
4. Jia, W. L.; Bai, D. R.; Cormick, T. M.; Liu, Q. D.; Motala, M.; Wang, R. Y.; Seward, C.; Tao, Y.; Wang, S. N. *Chem. Eur. J.* **2004**, *10*, 994.
5. (a) Yamaguchi, S.; Akiyama, S.; Tamao, K. *J. Am. Chem. Soc.* **2001**, *123*, 11372; (b) Kubo, Y.; Yamamoto, M.; Ikeda, M.; Takeuchi, M.; Shinkai, S.; Yamaguchi, S.; Tamao, K. *Angew. Chem., Int. Ed.* **2003**, *42*, 2036.
6. (a) Melaimi, M.; Gabbäi, F. P. *J. Am. Chem. Soc.* **2005**, *127*, 9680; (b) Chiu, C. W.; Gabbäi, F. P. *J. Am. Chem. Soc.* **2006**, *128*, 14248.
7. Parab, K.; Venkatasubbaiah, K.; Jäkle, F. *J. Am. Chem. Soc.* **2006**, *128*, 12879.
8. (a) Zhang, M.; Li, M. Y.; Zhao, Q.; Li, F. Y.; Zhang, D. Q.; Zhang, J. P.; Yi, T.; Huang, C. H. *Tetrahedron Lett.* **2007**, *48*, 2329; (b) Zhao, Q.; Cao, T. Y.; Li, F. Y.; Li, X. H.; Jing, H.; Yi, T.; Huang, C. H. *Organometallics* **2007**, *26*, 2077; (c) Zhang, D. Q.; Zhang, M.; Liu, Z. Q.; Yu, M. X.; Li, F. Y.; Yi, T.; Huang, C. H. *Tetrahedron* **2006**, *47*, 7093–7096.
9. (a) Liu, Z. Q.; Shi, M.; Li, F. Y.; Chen, Z. H.; Yi, T.; Huang, C. H. *Org. Lett.* **2005**, *7*, 5481; (b) Zhou, Z. G.; Xiao, S. Z.; Liu, Z. Q.; Shi, M.; Li, F. Y.; Huang, C. H. *Org. Lett.* **2006**, *8*, 3911; (c) Zhou, Z. G.; Yang, H.; Shi, M.; Xiao, S. Z.; Li, F. Y.; Yi, T.; Huang, C. H. *ChemPhysChem* **2007**, *8*, 1289.
10. Mp: 130–132 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): 2.04 (s, 12H), 2.28 (s, 6H), 3.63–3.68 (m, 16H), 3.78 (t, 4H, $J = 6.0$ Hz), 6.83 (s, 4H), 6.94–7.50 (m, 10H), ^{13}C NMR (100 MHz, $CDCl_3$, TMS): 21.5, 22.7, 23.7, 52.8, 68.7, 70.4, 70.5, 71.6, 111.8, 124.0, 125.7, 128.3, 128.6, 130.8, 137.5, 138.6, 139.1, 141.1, 142.1, 147.7, MS (LDI-TOF): 646.0. Anal. Calcd for $C_{42}H_{52}BNO_4$: C, 78.13; H, 8.12; N, 2.17. Found: C, 77.90; H, 8.47; N, 1.78.
11. Li, Y.; Cao, L. F.; Tian, H. *J. Org. Chem.* **2006**, *71*, 8279.
12. (a) Nicolas, M.; Fabre, B.; Simonet, J. *Chem. Commun.* **1999**, 881; (b) Kubo, Y.; Yamamoto, M.; Ikeda, M.; Takeuchi, M.; Shinkai, S.; Yamaguchi, S.; Tamao, K. *Angew. Chem., Int. Ed.* **2003**, *42*, 2036.