Organic & Biomolecular Chemistry

Dynamic Article Links

Cite this: *Org. Biomol. Chem.*, 2011, **9**, 8141

www.rsc.org/obc

PAPER

Solid-state emissive triarylborane-based BODIPY dyes: Photophysical properties and fluorescent sensing for fluoride and cyanide ions†

Guang-Liang Fu, Hong Pan, Yi-Hong Zhao and Cui-Hua Zhao*

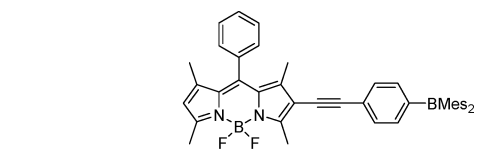
Received 14th June 2011, Accepted 12th September 2011
DOI: 10.1039/c1ob05959a

We disclose two novel BODIPY dyes, which contain the bulky substituent, [(4-dimesitylboryl)phenyl]ethynyl at 2- and 2,6-positions. The steric bulkiness of the boryl group is effective to suppress the intermolecular interaction in the solid state and thus these two compounds display intense fluorescence not only in solution but also in the solid state. In addition, the BODIPY dyes display sensitive fluorescence responses to fluoride and cyanide anions through the complexation with the boron center of the boryl group and the subsequent decomposition of the BODIPY core, illustrating their potential uses for the fluorescence sensing of fluoride and cyanide ions.

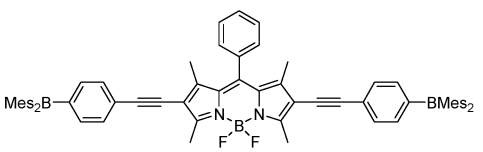
Introduction

The pirromethene–BF_2 complex (BODIPY) is known as an extraordinary class of fluorescent dyes, which has attracted remarkable research interest because of its unusual and excellent properties, such as high fluorescence quantum yields, large molar extinction coefficient, sharp emission spectra, and outstanding chemical, thermal, and photochemical stabilities.[1] To tune its optical properties, a variety of strategies has been achieved by functionalizing the BODIPY core at the *meso*- and/or 3,5-positions, fusing some aromatic rings to the BODIPY core and replacing the 8-carbon atom with a nitrogen atom to form aza-BODIPY dyes.[2–4] However, it may be noted that only very recently the functionalization of the BODIPY core at the 2,6-positions has gained attention and thus has not been fully investigated and utilized.[5–7] In addition, in spite of their high fluorescence quantum yields in dilute solutions, most BODIPY dyes hardly fluoresce in the solid state due to the severe fluorescence quenching arising from their small Stokes shift (5–20 nm, in most cases) and high planarity.[8] As a result, the increased efforts have been devoted to achieve BODIPY dyes that exhibit intense fluorescence even in the solid state. To improve the solid-state fluorescence intensity of BODIPY dyes, one effective strategy is to introduce sterically bulky substituents to inhibit molecular aggregation.[9]

We and others have recently focused our attention on the creation of solid-state fluorescent dyes utilizing boron elements.[10] The incorporation of boron element into π-conjugated framework can lead to the intriguing electronic and photophysical properties owing to the p_π–π* conjugation between the vacant p orbital on the boron center with the π* orbital of the π-conjugated framework.[11] In addition, triarylboranes have shown promising applications as fluoride and cyanide sensors with high selectivity through the complexation with these Lewis basic anions.[10a,12–21] It is more noteworthy that we and others have demonstrated that the steric bulkiness of boryl groups arising from the aryl substituents, such as Mes (2,4,6-trimethylphenyl) and Tip (2,4,6-triisopropylphenyl) on the boron atom to get enough kinetic stability can effectively prevent an intermolecular interaction.[10] Although recent research on tri-coordinate organoboron compounds has described a vast of variety of molecular structures, little has been reported on the boryl functionalized BODIPY dyes.[19] We envisioned that the functionalization of BODIPY core with the bulky dimesitylboryl group might provide a new molecular design method to obtain solid-state emissive BODIPY dyes. With these considerations, we herein designed triarylborane-based BODIPY dyes **1** and **2** (Fig. 1), which contain one and two [(4-dimesitylboryl)phenyl]ethynyls at the 2- and 2,6 positions of the BODIPY core, respectively. We comprehensively studied their photophysical properties, including the solution and solid state photophysical properties. It was found that the introduction of the bulky boryl group is very



1



2

Fig. 1 The structures of compounds **1** and **2**.

School of Chemistry and Chemical Engineering, Shandong University, Shanda Nanlu 27, Jinan, 250100, People's Republic of China. E-mail: chzhao@sdu.edu.cn; Fax: 86 531 88564464; Tel: 86 531 88363756

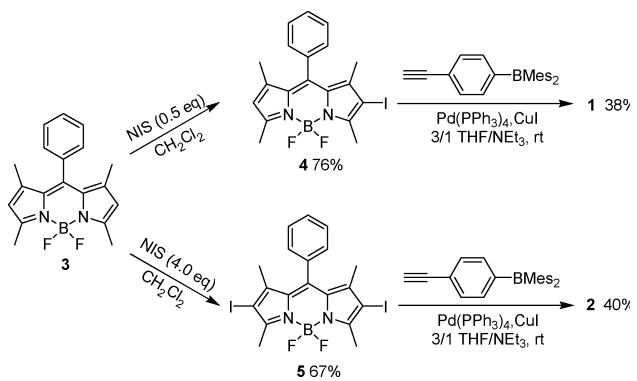
† Electronic supplementary information (ESI) available: NMR spectra for all new compounds, the titration of **1** and **2** with fluoride and cyanide ions. See DOI: 10.1039/c1ob05959a

effective to prevent intermolecular interactions in the solid-state. These two compounds exhibit intense fluorescence not only in solution but also in the solid state. In addition, to demonstrate the utility of these two highly emissive fluorescent BODIPY dyes, we also investigated their application as the fluorescent chemosensor for fluoride and cyanide ions. Both **1** and **2** display sensitive fluorescence responses to fluoride and cyanide anions.

Results and discussion

Synthesis of triarylborane-based BODIPY dyes

The synthetic route to the BODIPY derivatives **1** and **2** is shown in Scheme 1. First the iodination of the precursor BODIPY **3** with different equivalents of *N*-iodosuccinimide (NIS) could afford 2-iodo-BODIPY **4** and 2,6-diiodo-BODIPY **5** selectively. The monoiodide **4** was obtained as the major product in 76% yield for the iodination with only 0.5 equivalent of NIS while the iodination with excess NIS provided diiodide **5** with a high yield (67%). With the monoiodide and diiodide in hand, the following Pd(0)-catalyzed Sonogashira coupling reaction with [(*p*-dimesitylboryl)phenyl]acetylene afforded the target compounds in moderate yields, confirming that Pd(0)-catalyzed Sonogashira coupling reactions were very efficient and versatile methods to develop novel BODIPY dyes with longer conjugation length.[22] The structures of these two BODIPY dyes **1** and **2** were fully characterized by ^{1}H NMR, ^{13}C NMR and HRMS. And they are stable in air and water and can be purified by silica-gel column chromatagrophy.



Scheme 1 Synthesis of triarylborane-containing BODIPY dyes **1** and **2**.

Photophysical properties in solution

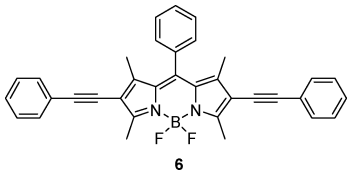
The UV/Vis absorption and emission spectra of compounds **1–2** were first characterized in THF solution, which are shown in Fig. 2 and the related data are summarized in Table 1. To elucidate the effect of the dimesitylboryl group, the photophysical property data of the reference compound **6** were also included for comparison.[23]

In THF solution, the BODIPY dye **1** exhibits an intense absorption at 535 nm (log $\varepsilon = 4.96$). In the fluorescence, it displays a strong orangish yellow emission at 570 nm with a high quantum yield ($\Phi_F = 0.78$). A large red shift *ca.* 40 nm was observed in the absorption and emission from 2-monosubstituted BODIPY **1** to 2,6-disubstituted BODIPY **2**, suggesting the more extended conjugation in **2**. Thus **2** shows intense fluorescence at 611 nm

Table 1 Photophysical properties of **1**,**2** and **6** in THF

	λ_{abs}/nm[a] (log ε)	λ_{em}/nm	Φ_F[b]
1	535 (4.96)	570	0.78
2	576 (5.23)	611	0.54
6	573 (4.86[c])	608	0.60[c]

[a] Only the longest maxima are shown. [b] Calculated using Rhodamine B as a standard. [c] Cited from ref. 21



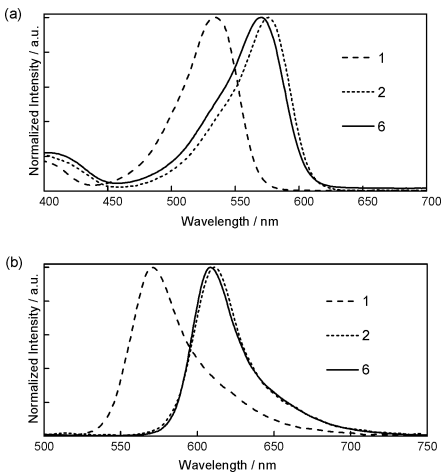


Fig. 2 (a) Absorption and (b) emission spectra of **1**,**2** and **6** in THF.

($\Phi_F = 0.54$), entering the red region. It is out of our expectation that the absorption and emission spectra of **2** are almost same to those of **6**, in contrast to the significant bathochromism of the general tri-coordinate organoboron compounds compared with the parent π-conjugated framework.[11] This presumably suggests trivial contribution of the boryl groups to the frontier orbitals for these borane-based BODIPY dyes.

Theoretical calculations

To further elucidate the effect of the boryl groups on the electronic structures and thus the photophysical properties of the borane-based BODIPY dyes, we conducted theoretical calculations of the compounds **2** and **6**. The optimizations of the molecular geometry and total energy calculation were carried out using density functional theory (DFT) calculations at the B3LYP/6-31G(d) level of theory. We also performed time-dependent density-functional theory (TD-DFT) calculations of these two compounds at the B3LYP/6-31G(d) theory. The pictorial drawing of their molecular orbitals are shown in Fig. 3, and the calculated data are summarized in Table 2.

The 2,6-bis{[(4-dimesitylboryl)phenyl]ethynyl} substituted BODIPY **2** has a HOMO delocalized over the central BODIPY core and the entire phenylethynyl arms, whereas its LUMO is mostly localized on the central BODIPY moiety. The HOMO and LUMO energy levels are –5.52 eV and –3.12 eV, respectively. The

Table 2 Calculated Kohn–Sham molecular orbital energy levels and the first excited-state energies for the BODIPY dyes **2** and **6**

	HOMO [eV]	LUMO [eV]	HOMO–LUMO gap [eV]	Transition energy[a] [eV] (λ [nm])	f[b]
2	−5.52	−3.12	2.40	2.12 (586)	1.003
6	−5.44	−3.02	2.42	2.16 (575)	0.616

[a] The first excited-state transition energy. [b] Oscillator strength.

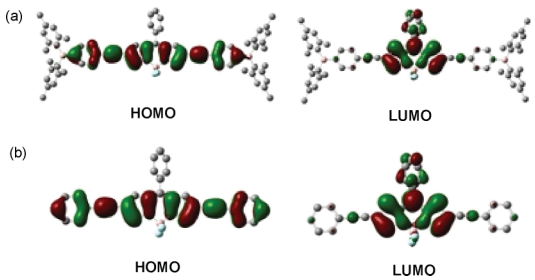


Fig. 3 Pictorial drawings of the HOMO and LUMO for (a) **2** and (b) **6**, calculated at the B3LYP/6-31G (d) level of theory.

calculated first excited state, mainly consisting of a HOMO → LUMO transition, has an excitation energy of 2.12 eV (586 nm) with an oscillator strength of 1.003. It is noteworthy that in sharp contrast to the remarkable contribution of the boryl group to the LUMO for the general tri-coordinate organoboron compound,[11] the boryl groups in compound **2** have almost no contribution to both the HOMO and the LUMO. As a result, the frontier energy levels, the energy gap and the transition energy of **2** are almost same as those of compound **6**, which contains no boryl groups. All the calculated results are in good agreement with the experimental results, confirming the negligible effect of the boryl groups on the electronic structures when they are introduced at 2,6-positions of the BODIPY core.

Photophysical properties in the solid state

It is intriguing to note that compounds **1** and **2** still retain intense fluorescence even in the powder form while the powder of **6** hardly fluoresces. This observation prompted us to investigate their photophysical properties in the solid state in details. Thin films of compounds **1**, **2** and **6** were prepared by spin-coating from their dichloromethane solutions with *ca.* 3 mg mL^{-1} concentration on the quartz plates, and their absorption and fluorescence spectra were directly measured. The corresponding spectra are shown in Fig. 4.

When going from THF solution to the spin-coated film, the triarylborane-containing BODIPY dyes **1** and **2** only exhibit trivial red shifts (7 nm for **1**, 8 nm for **2**) in the absorption spectra. Again no significant red shifts were observed for **1** and **2** in the fluorescence spectra from THF solution to the spin-coated film (22 nm for **1**, 16 nm for **2**), demonstrating the formation of neither the aggregate in the ground state nor the excimer in the excited state. In contrast, the absorption and emission spectra of **6** are significantly red shifted by 48 nm and 44 nm, indicative of the presence of the intense intermolecular interactions in the solid state. It is most noteworthy that the fluorescence intensity of **2** is about 10 times stronger than that of **6** in the spin-coated

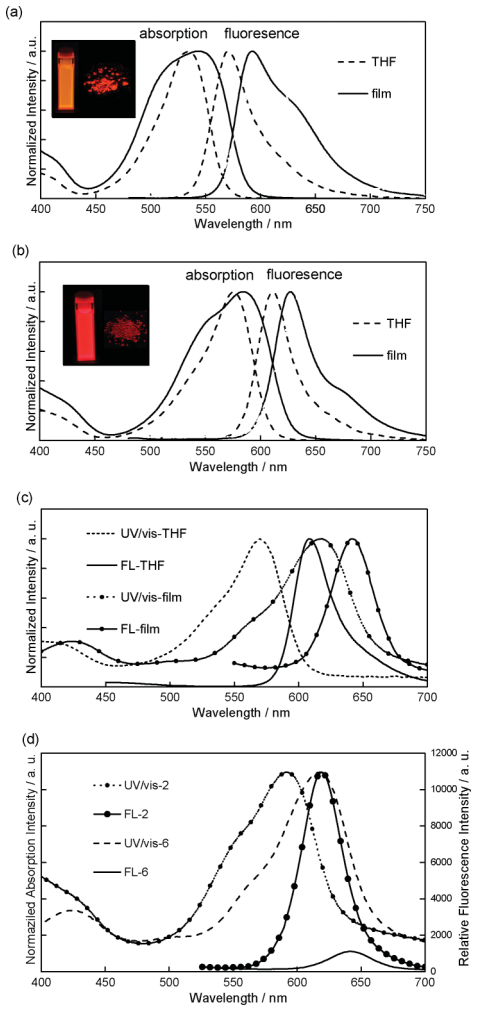


Fig. 4 UV/Vis absorption and emission spectra of (a) **1**, (b) **2**, (c) **6** in THF and the solid state and (d) **2** and **6** in the spin-coated films. The insets show the photographs of THF solution and powders of the compounds under UV irradiation at 360 nm.

film state, suggesting the introduction of the bulky dimesitylboryl group is very effective to enhance the solid state emission efficiency of BODIPY dyes. In addition, it is interesting to note that the emission band of **2** (λ_{em} = 627 nm) in the spin-coated film belongs to the red light region. Our current molecular design provides an efficient strategy to achieve solid-state red emissive materials, which is of great interest for realizing full color display of organic light-emitting devices (OLEDs).

Fluorescent sensing of fluoride and cyanide ions

The selective detection of the fluoride ions has attracted great attention because it is highly relevant to human health and environment issues.[24] Fluorescence sensing is one of the most powerful methods due to its high sensitivity. The organoboron compounds generally possess high selectivity for fluoride binding over other anions, such as chloride, bromide, and iodide, owing to the steric hindrance of bulky substituents on the boron center, which not only ensures stability to water, including atmospheric moisture, but also prevents the complexation of the boron center with other large Lewis bases. Hereby, tri-coordinate conjugated

organoboron compounds have attracted increased attention as efficient fluoride ion sensors. Considering the intense fluorescence of compounds **1** and **2**, we next investigated their fluorescence sensing abilities for fluoride anions.

The titration experiments of **1** and **2** were carried out in THF solutions by using *n*-Bu_4NF (TBAF) as the fluoride source. The fluorescence spectra changes of **1** (4.28 μM) and **2** (2.61 μM) are shown in Fig. 5 and Fig. 6, respectively. A two-step stepwise response to the fluoride ions was observed for compound **1**. Thus upon addition of a TBAF solution, the emission band of **1** at 570 nm decreased gradually. This spectra change became saturated when the concentration of TBAF amounted to 16.5 μM. This is accompanied by a slight red shift (3 nm) in the absorption (see ESI†), confirming the negligible effect of the boryl groups on the electronic structures when they are introduced at 2,6-positions of the BODIPY core. It is noteworthy that the further addition of a large excess of TBAF caused the appearance of a significantly blue-shifted emission band with maxima at 507 nm and 535 nm.

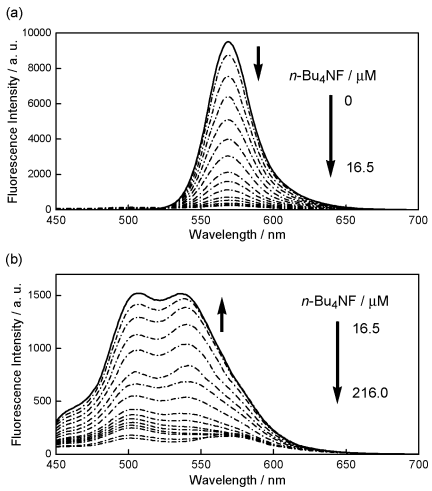


Fig. 5 Fluorescence spectra change of (a) **1** (4.28 μM in THF, λ_{ex} = 370 nm) upon addition of TBAF with the range of (a) 16.5 μM and (b) 216.0 μM.

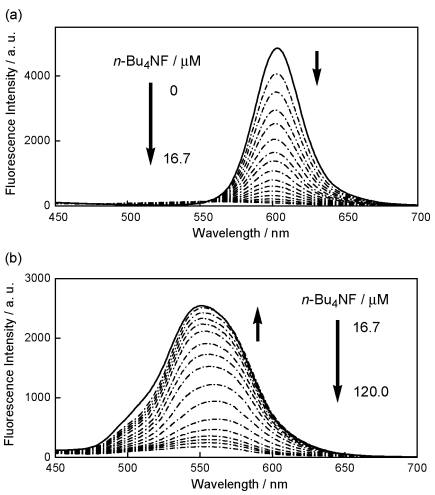


Fig. 6 Fluorescence spectra change of **2** (2.61 μM in THF, λ_{ex} = 370 nm) upon addition of TBAF with the range of (a) 16.7 μM and (b) 120.0 μM.

At the same time, the absorption is remarkably blue-shifted to 448 nm. Similar results were also observed for the fluorescence and absorption spectra of **2** upon addition of fluoride anions (Fig. 6, see ESI†). The changes in the UV-vis and fluorescence spectra in the first step may be ascribed to the complexation of F^- to the boron center of the mesityboryl groups to form electron-donating anionic four-coordinate boranate species groups.[25] BODIPY dyes containing electron-donating (4-subsitutedphenyl)ethynyl groups at 2,6-positions generally display very weak emissions, presumably due to the intramolecular charge transfer (ICT) from the (*p*-boranate-substituted)phenylethynyl residues to the BODIPY core.[6] The further changes in the UV-vis and fluorescence spectra in the second stage may result from the decomposition of BODIPY moiety in the presence of fluoride anions, as evidenced by the titration experimental results of compound **6** with fluoride anions (Fig. 7). The addition of a TBAF solution to THF solution of **6** causes significant blue shift in the absorption and fluorescence spectra. Moreover, the UV-vis and emission spectra of **6** in the presence of excess fluoride anions are almost same to those of **2** in the second state of the titration, in terms of not only the absorption and emission maxima but also in the spectra shape (Fig. 8). The decomposition of the BODIPY cores in the presence of fluoride anions probably arise from a nucleophilic displacement that breaks a B–N bond resulting in a B–F bond.[5b,26] The assignment for the changes in the UV-vis and fluorescence spectra of these BODIPY–borane dyes was further confirmed by the titration experiments with ^{11}B spectroscopy (see ESI†). Both **1** and **2** still exhibit a triplet signal in the ^{11}B NMR spectra in the first step of the titration, suggesting the binding of fluoride to the borane moiety. In contrast, the triplet ^{11}B NMR signal changed into a quartet signal in the second step of the titration, indicative of the decomposition of the BODIPY core through the fluoride attack on the B–N bond to form a B–F bond.

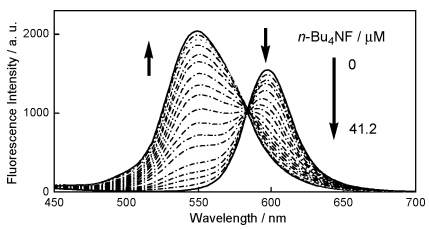


Fig. 7 Fluorescence spectra change of **6** (3.66 μM in THF, λ_{ex} = 370 nm) upon addition of TBAF.

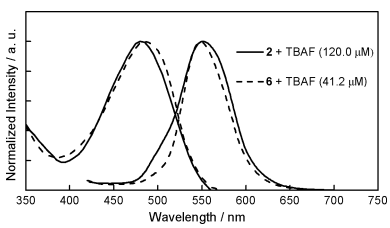


Fig. 8 UV/Vis absorption and fluorescence spectra of **2** (2.61 μM in THF) and **6** (3.66 μM in THF) after addition of excess TBAF.

While the selectivity of dimesitylboranes for fluoride ions over chloride, bromide, iodide and others is well documented, these compounds are also well-known to be responsive to cyanide ions

owing to their small size.[20,21] Compounds **1** and **2** were also evaluated for potential responses to cyanide anions. The addition of tetrabutylammonium cyanide (TBACN) to a solution of **1** in THF also first induced the gradual decrease in fluorescence (see ESI†). The fact that the absorption spectrum is very similar to that of the titration with TBAF when this fluorescence spectra change became saturated, irrespective of the absorption maxima and the absorption efficiency, suggests cyanide is first bound to the dimesityboryl group to form a four-coordinate complex. However, a new blue-shifted band did not appear with the further addition of TBACN. Notably, the absorption became very weak, suggesting the BODIPY moiety is presumably decomposed by the cyanide anions in a different way compared to fluoride anions.[5b] Similar results were obtained for the titration of **2** with TBACN. It has been documented that the addition of TBAF resulted in the decomposition of the BODIPY moiety directly and the addition of TBACN gave rise to the formation of four-coordination borate while the BODIPY core remained intact for a BODIPY–borane dyad,[19] For our BODIPY–borane dyes **1** and **2**, both fluoride and cyanide anions preferably complex with the boron center of the boryl groups and then decompose the BODIPY moiety. Although the reaction mechanism of fluoride and cyanide to decompose BODIPY core might need further investigations, our current results provide new insights into the stabilities of the borane-functionalized BODIPY dye.

Conclusions

Two novel BODIPY dyes were obtained by the introduction of the bulky substitutent, [(4-dimesitylboryl)phenyl]ethyl at the 2, and 2,6-positions. The steric bulkiness of the boryl group is effective to suppress the intermolecular interaction in the solid state and thus makes these two compounds keep intense fluorescence even in the solid state. In addition, the BODIPY–borane dyes exhibit sensitive responses to fluoride and cyanide anions, through the complexation with the boron center of the boryl group and subsequent decomposition of BODIPY core. Our preliminary results will provide a basis for the further design of new BODIPY-borane dyes, which is under way in our group.

Experimental

General

^{1}H and ^{13}C NMR spectra were recorded with a Bruker 300 or 400 spectrometer in $CDCl_3$ with TMS as internal reference. UV-vis absorption spectra and fluorescence spectra measurement were performed with a Hitachi UV-4100 spectrophotometer and a Perkin Elmer LS-55 Luminescence spectrometer, respectively. All reactions were carried out under nitrogen atmosphere. Compounds **3**,[27] **5**[23] and [(*p*-dimesitylboryl)phenyl]acetylene[28] were prepared according to the literature.

Computation methods

All calculations were conducted by using the Gaussian 09 program.[29]

Synthesis

4,4-difluoro-2-iodo-1,3,5,7-tetramethyl-8-phenyl-4-bora-3*a*,4*a*-diaza-*s*-indacene (4). To a solution of 4,4-difluoro-1,3,5,7-tetramethyl-8-phenyl-4-bora-3*a*,4*a*-diaza-*s*-indacene **3** (243 mg, 0.75 mmol) in anhydrous CH_2Cl_2 (30 mL) was added NIS (112 mg, 0.5 mmol). The reaction mixture was stirred at room temperature for 30 min. After addition of a saturated solution of NaCl, the aqueous layer was extracted with CH_2Cl_2 (3 times). The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting crude product was subjected to a silica gel column chromatography (2/1 petroleum ether/CH_2Cl_2, R_f 0.41) to afford 170 mg (0.38 mmol) of **4** in 76% yield as red solids: mp 158–160 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 1.38 (s, 6H), 2.57 (s, 3H), 2.63 (s, 3H), 6.04 (s, 1H), 7.25–7.28 (m, 2H), 7.49–7.51 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 14.5, 14.8, 15.8, 16.6, 84.3, 122.3, 127.9, 129.2, 129.3, 131.0, 131.9, 134.9, 141.6, 143.3, 145.1, 154.6, 157.8.

4,4-difluoro-2-{[(4-dimesitylboryl)phenyl]ethynyl}-1,3,5,7-tetramethyl-8-phenyl-4-bora-3*a*,4*a*-diaza-*s*-indacene (1). To a mixture of 4-difluoro-2-iodo-1,3,5,7-tetramethyl-8-phenyl-4-bora-3*a*,4*a*-diaza-*s*-indacene **4** (170 mg, 0.38 mmol), [(4-dimesitylboryl)-phenyl]acetylene (160 mg, 0.46 mmol), $Pd(PPh_3)_4$ (22 mg, 0.019 mmol) and CuI (7.2 mg, 0.038 mmol) was added a degassed mixed solvent of THF/NEt_3 (3 : 1) (20 mL) under a stream of nitrogen. The reaction mixture was stirred at room temperature overnight and then quenched with saturated solution of NH_4Cl. The aqueous layer was extracted with CH_2Cl_2 (3 times). The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting mixture was purified by a silica gel column chromatography (2/1 petroleum ether/CH_2Cl_2, R_f 0.35) to afford 98 mg (0.15 mmol) of **1** in 38% yield as orange solids: mp > 300 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 1.40 (s, 3H), 1.50 (s, 3H), 1.99 (s, 12H), 2.30 (s, 6H), 2.58 (s, 3H), 2.70 (s, 3H), 6.04 (s, 1H), 6.81 (s, 4H), 7.26–7.3 (m, 2H), 7.39(d, J = 8.1 Hz, 2H), 7.45 (d, J = 8.1 Hz, 2H), 7.50–7.52 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 13.2, 13.6, 14.5, 14.8, 21.2, 23.4, 84.4, 96.4, 115.9, 122.2, 127.0, 127.9, 128.2, 129., 129.3, 130.3, 130.7, 132.6, 134.7, 136.2, 138.8, 140.9, 141.6, 142.2, 142.8, 144.9, 156.6, 157.9; HRMS (MALDI/DHB): 670.3749 (M^+); Calcd for $C_{45}H_{44}B_2N_2F_2$: 670.3726.

4,4-difluoro-2,6-bis{[(4-dimesitylboryl)phenyl]ethynyl}-1,3,5,7-tetramethyl-8-phenyl-4-bora-3*a*,4*a*-diaza-*s*-indacene (2). This compound was prepared essentially in the same manner as described for **1** using 4-difluoro-2,6-diiodo-1,3,5,7-tetramethyl-8-phenyl-4-bora-3*a*,4*a*-diaza-*s*-indacene **4** (140 mg, 0.24 mmol), [(4-dimesitylboryl)phenyl]acetylene (252 mg, 0.72 mmol), $Pd(PPh_3)_4$ (14 mg, 0.012 mmol) and CuI (0.024 mmol, 4.6 mg) in 20 mL THF/NEt_3 (3 : 1) at room temperature. The purification by a silica gel column chromatography (3/1 petroleum ether/CH_2Cl_2, R_f 0.48) afforded 90 mg (0.09 mmol) of **2** in 40% yield as dark red solids: mp > 300 °C;^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 1.53 (s, 6H), 1.99 (s, 24H), 2.3 (s, 12H), 2.72 (s, 6H), 6.81 (s, 8H), 7.28–7.31 (m, 2H), 7.40 (d, J = 8.4 Hz, 4H), 7.46 (d, J = 8.4 Hz, 4H), 7.52–7.54 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 13.4, 13.7, 21.2, 23.4, 83.9, 97.1, 126.7, 127.9, 128.2, 129.3, 129.5, 130.7, 131.4, 134.4, 136.2, 138.9, 140.9, 141.6, 142.7, 144.3,

145.8, 158.7; HRMS (MALDI/DHB): 1017.5811 (M^+); Calcd for $C_{71}H_{69}B_3N_2F_2$: 1017.5811.

Acknowledgements

The authors gratefully acknowledge the financial support from the National Nature Science Foundation of China (Grant Nos. 21072117, 20802041), Nature Science Foundation of Shandong Province (No Q2008B02), Science Foundation of Ministry of Education of China (No 200804221009), and 973 Program (2010CB933504).

Notes and references

1 For recent reviews, see: (*a*) G. Ulrich, R. Ziessel and A. Harriman, *Angew. Chem., Int. Ed.*, 2008, **47**, 1184–1201; (*b*) A. Loudet and K. Burgess, *Chem. Rev.*, 2007, **107**, 4891–4932; (*c*) R. Ziessel, G. Ulrich and A. Harriman,, *New J. Chem.*, 2007, **31**, 496–501.
2 (*a*) M. Baruah, W. Qin, R. A. L. Vallée, D. Beljonne, T. Rohand, W. Dehaen and N. Boens, *Org. Lett.*, 2005, **7**, 4377–4380; (*b*) T. Rohand, M. Baruah, W. Qin, N. Boens and W. Dehaen, *Chem. Commun.*, 2006, 266–268; (*c*) Y.-H. Yu, A. B. Descalzo, Z. Shen, H. Röhr, Q. Liu, Y.-W. Wang, M. Spieles, Y.-Z. Li, K. Rurack and X.-Z. You, *Chem.–Asian J.*, 2006, **1–2**, 176–187.
3 (*a*) C. Jiao, K.-W. Huang and J. Wu, *Org. Lett.*, 2011, **13**, 632–635; (*b*) L. Jiao, C. Yu, M. Liu, Y. Wu, K. Cong, T. Meng, Y. Wang and E. Hao, *J. Org. Chem.*, 2010, **75**, 6035–6038; (*c*) Z. Shen, H. Röhr, K. Rurack, H. Uno, M. Spieles, B. Schulz, G. Reck and N. Ono, *Chem.–Eur. J.*, 2004, **10**, 4853–4871.
4 (*a*) W. Zhao and E. M. Carreira, *Angew. Chem., Int. Ed.*, 2005, **44**, 1677–1679; (*b*) W. Zhao and E. M. Carreira, *Chem.–Eur. J.*, 2006, **12**, 7254–7263; (*c*) S. O. McDonnell and D. F. O'Shea, *Org. Lett.*, 2006, **8**, 3493–3496.
5 (*a*) S. Zhu, J. Zhang, G. Vegesna, F.-T. Luo, S. A. Green and H. Liu, *Org. Lett.*, 2011, **13**, 438–441; (*b*) G. Meng, S. Velayudham, A. Smith, R. Luck and H. Liu, *Macromolecules*, 2009, **42**, 1995–2001; (*c*) V. R. Donuru, G. K. Vegesna, S. Velayudham, S. Green and H. Liu, *Chem. Mater.*, 2009, **21**, 2130–2138.
6 L. Bonardi, G. Ulrich and R. Ziessel, *Org. Lett.*, 2008, **10**, 2183–2186.
7 Y. Cakmak and E. U. Akkaya, *Org. Lett.*, 2009, **11**, 85–88.
8 (*a*) D. Zhang, Y. Wen, Y. Xiao, G. Yu, Y. Liu and X. Qian, *Chem. Commun.*, 2008, 4777–4779; (*b*) A. Hepp, G. Ulrich, R. Schmechel, H. von Seggern and R. Ziessel, *Synth. Met.*, 2004, **146**, 11–15.
9 (*a*) Y. Kubota, J. Uehara, K. Funabiki, M. Ebihara and M. Matsui, *Tetrahedron Lett.*, 2010, **51**, 6195–6198; (*b*) T. Ozdemir, S. Atilgan, I. Kutuk, L. T. Yildirim, A. Tulek, M. Bayindir and E. U. Akkaya, *Org. Lett.*, 2009, **11**, 2105–2107; (*c*) T. T. Vu, S. Badré, C. Dumas-Verdes, J.-J. Vachon, C. Julien, P. Audebert, E. Y. Senotrusova, E. Y. Schmidt, B. A. Trofimov, R. B. Pansu, G. Clavier and R. Méallet-Renault, *J. Phys. Chem. C*, 2009, **113**, 11844–11855; (*d*) S. Badré, V. Monnier, R. Méallet-Renault, C. Dumas-Verdes, E. Y. Schmidt, A. I. Mikhaleva, G. Laurent, G. Levi, A. Ibanez, B. A. Trofimov and R. B. Pansu, *J. Photochem. Photobiol., A*, 2006, **183**, 238–246.
10 (*a*) C.-H. Zhao, E. Sakuda, A. Wakamiya and S. Yamaguchi, *Chem.–Eur. J.*, 2009, **15**, 10603–10612; (*b*) C.-H. Zhao, A. Wakamiya and S. Yamaguchi, *Macromolecules*, 2007, **40**, 3898–3900; (*c*) A. Wakamiya, K. Mori and S. Yamaguchi, *Angew. Chem., Int. Ed.*, 2007, **46**, 4273–4276; (*d*) C.-H. Zhao, A. Wkamiya, Y. Inukai and S. Yamaguchi, *J. Am. Chem. Soc.*, 2006, **128**, 15934–15935.
11 For recent reviews, see: (*a*) C. R. Wade, A. E. J. Broomsgrove, S. Aldridge and F. P. Gabbaï, *Chem. Rev.*, 2010, **110**, 3958–3984; (*b*) T. W. Hudnall, C.-W. Chiu and F. P. Gabbaï, *Acc. Chem. Res.*, 2009, **42**, 388–397; (*c*) Z. M. Hudson and S. Wang, *Acc. Chem. Res.*, 2009, **42**, 1584–1596; (*d*) S. Yamaguchi and A. Wakamiya, *Pure Appl. Chem.*, 2006, **78**, 1413–1424; (*e*) C. D. Entwistle and T. B. Marder, *Chem. Mater.*, 2004, **16**, 4574–4585; (*f*) F. Jäkle, *Chem. Rev.*, 2010, **110**, 3985–4022.
12 (*a*) Y. Kubo, M. Yamamoto, M. Ikeda, M. Tkeuchi, S. Shinkai, S. Yamaguchi and K. Tamao, *Angew. Chem., Int. Ed.*, 2003, **42**, 2036–2040; (*b*) S. Yamaguchi, T. Shirasaka, S. Akiyama and K. Tamao, *J. Am. Chem. Soc.*, 2002, **124**, 8816–8817; (*c*) S. Yamaguchi, S. Akiyama and K. Tamao, *J. Am. Chem. Soc.*, 2001, **123**, 11372–11375; (*d*) S. Yamaguchi, S. Akiyama and K. Tamao, *J. Am. Chem. Soc.*, 2000, **122**, 6335–6336.
13 (*a*) T. W. Hudnall and F. P. Gabbaï, *J. Am. Chem. Soc.*, 2007, **129**, 11978–11986; (*b*) M. H. Lee, T. Agou, J. Kobayashi, T. Kawashima and F. P. Gabbaï, *Chem. Commun.*, 2007, 1133–1135; (*c*) C.-W. Chiu and F. P. Gabbaï, *J. Am. Chem. Soc.*, 2006, **128**, 14248–14249; (*d*) T. W. Hudnall, M. Melaïmi and F. P. Gabbaï, *Org. Lett.*, 2006, **8**, 2747–2749; (*e*) M. Melaimi and F. P. Gabbaï, *J. Am. Chem. Soc.*, 2005, **127**, 9680–9681; (*f*) S. Solé and F. P. Gabbaï, *Chem. Commun.*, 2004, 1284–1285.
14 M Miyata and Y. Chujo, *Polym. J.*, 2002, **34**, 967–969.
15 (*a*) A. Sundararaman, K. Venkatasubbaiah, M. Victor, L. N. Zakharov, A. L. Rheingold and F. Jäkle, *J. Am. Chem. Soc.*, 2006, **128**, 16554–16565; (*b*) A. Sundararaman, M. Victor, R. Varughese and F. Jäkle, *J. Am. Chem. Soc.*, 2005, **127**, 13748–13749.
16 (*a*) Y. Deng, Y. Chen, D. Cao, Z. Liu and G. Li, *Sens. Actuators, B*, 2010, **149**, 165–169; (*b*) Z.-Q. Liu, M. Shi, F.-Y. Li, Q. Fang, Z.-H. Chen, T. Yi and C.-H. Huang, *Org. Lett.*, 2005, **7**, 5481–5484.
17 (*a*) D.-R. Bai, X.-Y. Liu and S. Wang, *Chem.–Eur. J.*, 2007, **13**, 5713–5723; (*b*) S.-B. Zhao, T. McCormick and S. Wang, *Inorg. Chem.*, 2007, **46**, 10965–10967; (*c*) X. Y. Liu, D. R. Bai and S. Wang, *Angew. Chem., Int. Ed.*, 2006, **45**, 5475–5478.
18 Y.-H. Zhao, H. Pan, G.-L. Fu, J.-M. Lin and C.-H. Zhao, *Tetrahedron Lett.*, 2011, **52**, 3832–3835.
19 J. O. Huh, Y. Do and M. H. Lee, *Organometallics*, 2008, **27**, 1022–1025.
20 (*a*) C. R. Wade and F. P. Gabbaï, *Inorg. Chem.*, 2010, **49**, 714–720; (*b*) C.-W. Chiu and F. P. Gabbaï, *Dalton Trans.*, 2008, 814–817.
21 A. E. J. Broomsgrove, D. A. Addy, C. Bresner, I. A. Fallis, A. L. Thompson and S. Aldridge, *Chem.–Eur. J.*, 2008, **14**, 7525–7529.
22 (*a*) T. Rohand, W. Qin, N. Boens and W. Dehaen, *Eur. J. Org. Chem.*, 2006, 4658–4663; (*b*) C.-W. Wan, A. Burghart, J. Chen, F. Bergström, L. B-, A. Johansson, M. F. Wolford, T. G. Kim, M. R. Topp, R. M. Hochstrasser and K. Burgess, *Chem.–Eur. J.*, 2003, **9**, 4430–4441.
23 D. Zhang, Y. Wang, Y. Xiao, S. Qian and X. Qian, *Tetrahedron*, 2009, **65**, 8099–8103.
24 (*a*) P. E. Rakita,, *J. Chem. Educ.*, 2004, **81**, 677–680; (*b*) K. L. Kirk, *Biochemistry of the Halogens and Inorganic Halides*, Plenum Press, New York, 1991, p. 58; (*c*) M. Kleerekoper, *Endocrinol. Metab. Clin. North Am.*, 1998, **27**, 441–452; (*d*) E. Kissa, *Clin. Chem.*, 1987, **33**, 253–255; (*e*) R. H. Dreisbuch, *Handbook of Poisoning*, Lange Medical Publishers, Los Altos, CA, 1980; (*f*) S.-W. Zhang and T. M. Swager, *J. Am. Chem. Soc.*, 2003, **125**, 3420–3421; (*g*) H. Sohn, S. Létant, M. J. Sailor and W. C. Trogler, *J. Am. Chem. Soc.*, 2000, **122**, 5399–5400.
25 G. Zhou, M. Baumgarten and K. Müllen, *J. Am. Chem. Soc.*, 2008, **130**, 12477–12484.
26 A. Coskun and E. U. Akkaya, *Tetrahedron Lett.*, 2004, **45**, 4947–4949.
27 L. Jiao, C. Yu, J. Li, Z. Wang, M. Wu and E. Hao, *J. Org. Chem.*, 2009, **74**, 7525–7528.
28 Z. An, S. A. Odom, R. F. Kelley, C. Huang, X. Zhang, S. Barlow, L. A. Padilha, J. Fu, S. Webster, D. J. Hagan, E. W. V. Stryland, M. R. Wasielewski and S. R. Marder, *J. Phys. Chem. A*, 2009, **113**, 5585–5593.
29 *Gaussian 09*, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

