



Cite this: *New J. Chem.*, 2014, **38**, 6088

Synthesis and aggregation-induced fluorescence emission properties of boron-containing derivatives that respond to viscous alcohols†

Weibo Yan,* Guankui Long, Xuan Yang and Yongsheng Chen

Received (in Porto Alegre, Brazil)
7th September 2014,
Accepted 25th September 2014

DOI: 10.1039/c4nj01512f

www.rsc.org/njc

A series of boron-complex-type fluorophores, with enhanced fluorescence emission in the solid state, have been synthesized. When introducing electronic-withdrawing fluorine or electronic-donating phenyl/4-methoxy-phenyl groups on the boron atom, the emissions of these dye compounds in the solid state change from yellow to red. Furthermore, these emissions are affected by viscous alcohols due to their inhibition of the fluorophore's intramolecular rotations. The intensity of the emission is enhanced with increasing viscosity of the alcohol fluids. These dyes with aggregation-induced emission effects are thus expected to find application in estimating the viscosity of transparent viscous fluids.

Introduction

Recently, unique fluorescent dyes showing aggregation-induced emission enhancement (AIEE) effects, which are opposite of “aggregation-caused quenching” (ACQ) effects, have attracted much interest.^{1,2} Due to their unique fluorescent properties, such AIEE dyes have a wide range of potential applications, such as in organic electroluminescence devices,^{3,4} in fluorescent sensors,^{5–7} for cell imaging,⁸ and in investigating the micro-structure of aggregate materials.^{9–11}

Many AIEE dyes have been found, and they consist of molecular features and groups such as hexaphenylsiloles, hydrocarbons, heterocycles, supramolecular assemblies, polymers and organo-metallic molecules. Although organoboron complexes are together one of the most important types of fluorescent dyes, little work has been published on their AIEE effects. Boron dipyrromethene (BODIPY) dyes have been extensively studied and are considered important fluorescent dyes because of their advantageous properties such as high quantum yield in dilute solution, sharp spectra, and high photostability.¹⁰ However, BODIPY dyes mostly show a very small Stokes shift and ACQ, which affect their applications in, for example, organic electroluminescence devices. So far, only a few types of AIEE-active boron complexes have been reported.^{12–14} Therefore, novel boron complex dyes that display AIEE effects should be further developed.

In this paper, we report a series of novel phenalene-based boron complexes and their AIEE effects. Also reported, for the first time, are preliminary studies of their use as chemical sensors of viscosity of alcohol fluids.

Experimental section

Materials and methods

Bromobenzene, 2-bromonaphthalene and 3-thiopheneboronic acid were purchased from the Alfa Aesar Company. All solvents were purified by standard methods prior to use. Phenylboronic acid and 2-naphthaleneboronic acid were synthesized according to the literature.¹⁵ The procedures for the synthesis of compounds **A1–A7** are shown in ESI.† The ¹H NMR and ¹³C NMR spectra were acquired using a Bruker AC-300 and a Bruker AC-400 using tetramethylsilane (TMS) as the internal standard. High-resolution mass spectra (HRMS) were recorded on a Fourier transform ion cyclotron resonance mass spectrometer (Bruker, APEX IV FTMS) equipped with an electrospray ionization (ESI) source. Absorption and fluorescence spectra were obtained with JASCO V-570 and FluoroMax-3P spectrophotometers, respectively. Cyclic voltammetry was performed with a computer-controlled CHI600C electrochemical work station using a conventional three-electrode configuration consisting of a one-compartment electrolysis cell with a platinum button as a working electrode, platinum wire as a counter electrode and an Ag/AgCl reference electrode. Cyclic voltammograms were obtained in dichloromethane (1 × 10^{−3} M) using tetrabutylammonium hexafluorophosphate (TBAPF₆) (0.1 M) as the supporting electrolyte at a scan rate of 0.1 V s^{−1} and Fc/Fc⁺ as an internal reference.

State Key Laboratory for Functional Polymer Materials and Center for Nanoscale Science & Technology, Institute of Polymer Chemistry, College of Chemistry, Nankai University, Tianjin 300071, China. E-mail: yanweibo605@mail.nankai.edu.cn; Fax: +86-010-62757156; Tel: +86-010-62754745

† Electronic supplementary information (ESI) available: Experimental procedures with spectral and analytical data for all intermediates; summary of optical and electrochemical data of compound **1a–3c**. See DOI: 10.1039/c4nj01512f

Synthesis

Synthesis of compounds 1a–1c. General procedure:¹⁶ BF₃·Et₂O (1 M) (1.2 mL, 1.2 mmol) was added to a solution of A5–A7 (1.0 mmol) in *o*-xylene (80 mL), and the color of this solution immediately became dark red. After reflux for 5 hours, the solution became light yellow and some solid precipitated. The mixture was then stirred at 130 °C for 12 hours until the starting material completely disappeared according to analysis by thin layer chromatography (TLC). After the mixture was cooled down, saturated aqueous NaHCO₃ was added to remove the excess BF₃ and by-product HF. The mixture was then extracted with CH₂Cl₂. The obtained organic phase was dried using anhydrous Na₂SO₄, and filtrated and concentrated to obtain crude product, which was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 1:1, v/v) to give compounds 1a–1c. (Yields of compounds 1a–1c vary between 70.0 and 80.0%.)

Synthesis of compound 1a. Yield: 76.0%, ¹H NMR (400 MHz, CDCl₃): δ [ppm] = 8.37 (1H, d, *J* = 4.8 Hz), 8.35 (1H, d, *J* = 2.4 Hz), 8.23 (1H, d, *J* = 2.4 Hz), 7.99 (1H, d, *J* = 10.0 Hz), 7.74 (2H, d, *J* = 7.2 Hz), 7.56–7.52 (5H, m), 7.48–7.43 (4H, m), 6.91 (1H, d, *J* = 9.6 Hz). ¹³C NMR (400 MHz, CDCl₃): δ [ppm] = 165.62, 158.41, 142.80, 140.75, 139.64, 139.48, 138.24, 132.37, 132.21, 129.72, 129.23, 128.26, 128.08, 127.35, 127.14, 126.57, 126.08, 125.04, 124.65, 122.62, 118.52. HRMS (ESI) calculated for [C₂₅H₁₆ONBF₂ + Na]⁺: 418.1189; found: 418.1180.

Synthesis of compound 1b. Yield: 74.5%, ¹H NMR (300 MHz, CDCl₃): δ [ppm] = 8.34 (2H, d, *J* = 9.0 Hz), 8.23 (1H, s), 7.97 (1H, d, *J* = 9.6 Hz), 7.65–7.64 (1H, m), 7.55–7.43 (8H, m), 6.90 (1H, d, *J* = 9.6 Hz). ¹³C NMR (400 MHz, CDCl₃): δ [ppm] = 173.57, 142.67, 140.62, 140.60, 139.64, 132.96, 131.59, 131.26, 129.71, 128.26, 127.18, 127.14, 126.56, 126.20, 126.16, 126.06, 122.73, 122.71, 121.34, 118.69, 118.58. HRMS (ESI) calculated for [C₂₃H₁₄SONBF₂ + Na]⁺: 424.0754; found: 424.0750.

Synthesis of compound 1c. Yield: 71.8%, ¹H NMR (300 MHz, CDCl₃): δ [ppm] = 8.48 (1H, d, *J* = 1.5 Hz), 8.39 (1H, d, *J* = 9.0 Hz), 8.36 (1H, d, *J* = 1.5 Hz), 8.19 (1H, d, *J* = 1.5 Hz), 8.03 (1H, d, *J* = 4.2 Hz), 8.01 (1H, d, *J* = 3.3 Hz), 7.97–7.86 (3H, m), 7.58–7.53 (5H, m), 7.49–7.44 (3H, m), 6.93 (1H, d, *J* = 9.6 Hz). ¹³C NMR (400 MHz, CDCl₃): δ [ppm] = 165.64, 158.42, 142.80, 140.76, 139.65, 138.11, 136.71, 133.71, 132.88, 132.53, 132.41, 129.73, 129.05, 128.27, 128.24, 127.78, 127.14, 126.77, 126.64, 126.54, 126.31, 126.16, 125.22, 124.68, 122.67, 118.56. HRMS (ESI) calculated for [C₂₉H₁₈ONBF₂ + Na]⁺: 468.1347; found: 468.1348.

Synthesis of compounds 2a–2c. General procedure: to a degassed solution of 1a (0.5 mmol) in dry THF (15 mL) was added fresh PhMgBr solution in THF {the PhMgBr Grignard reagent was prepared from PhBr (1.0 mmol) and Mg (2.0 mmol) refluxed in THF (15 mL)}, the resulting mixture was stirred at ambient temperature for 3 hours under an argon atmosphere. The color of the solution turned from light yellow into dark pink. The starting material was completely consumed, as indicated by TLC. Excess solvent was then removed under reduced pressure and the crude product was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 10:1, v/v) to give 2a–2c as a jujube red powder. (Yields of the compounds vary between 50.0 and 60.0%.)

Synthesis of compound 2a. Yield: 51.6%, ¹H NMR (300 MHz, CDCl₃): δ [ppm] = 8.13 (1H, d, *J* = 1.5 Hz), 8.08 (1H, d, *J* = 9.0 Hz), 8.02 (1H, d, *J* = 1.5 Hz), 7.75 (1H, d, *J* = 9.9 Hz), 7.69 (2H, d, *J* = 7.2 Hz), 7.53–7.39 (7H, m), 7.27 (1H, d, *J* = 9.9 Hz), 7.18–7.12 (9H, m), 6.97 (1H, d, *J* = 7.2 Hz), 6.95 (1H, d, *J* = 7.2 Hz), 6.77 (1H, d, *J* = 9.6 Hz). ¹³C NMR (400 MHz, CDCl₃): δ [ppm] = 168.36, 158.54, 142.81, 141.24, 140.02, 139.84, 137.18, 133.79, 131.53, 131.37, 129.10, 128.94, 127.76, 127.54, 127.15, 126.98, 126.71, 126.29, 126.12, 126.06, 125.96, 123.70, 120.04, 109.84. HRMS (ESI) calculated for [C₃₇H₂₆ONB + H]⁺: 512.2186; found: 512.2179.

Synthesis of compound 2b. Yield: 53.0%, ¹H NMR (400 MHz, CDCl₃): δ [ppm] = 8.01 (1H, d, *J* = 1.6 Hz), 7.93 (1H, d, *J* = 9.6 Hz), 7.91 (1H, d, *J* = 1.6 Hz), 7.64 (1H, d, *J* = 9.6 Hz), 7.49–7.46 (5H, m), 7.43 (2H, d, *J* = 1.6 Hz), 7.21 (1H, d, *J* = 8.8 Hz), 7.18–7.11 (9H, m), 6.97 (2H, d, *J* = 1.6 Hz), 6.73 (1H, d, *J* = 9.6 Hz). ¹³C NMR (400 MHz, CDCl₃): δ [ppm] = 168.24, 158.49, 142.82, 141.16, 140.87, 139.90, 133.92, 133.84, 131.82, 130.59, 130.56, 128.96, 127.54, 127.01, 126.90, 126.76, 126.19, 126.12, 126.03, 126.01, 125.81, 123.67, 120.74, 120.06, 109.93. HRMS (ESI) calculated for [C₃₅H₂₄SONB + H]⁺: 518.1750; found: 518.1751.

Synthesis of compound 2c. Yield: 54.5%, ¹H NMR (300 MHz, CDCl₃): δ [ppm] = 8.26 (1H, s), 8.15 (2H, s), 8.11 (1H, d, *J* = 6.9 Hz), 7.98 (1H, d, *J* = 6.9 Hz), 7.94 (1H, d, *J* = 5.4 Hz), 7.90 (1H, d, *J* = 5.4 Hz), 7.84 (1H, d, *J* = 7.2 Hz), 7.79 (1H, d, *J* = 7.2 Hz), 7.54–7.47 (6H, m), 7.29 (1H, d, *J* = 7.2 Hz), 7.20–7.11 (9H, m), 6.97 (2H, d, *J* = 5.4 Hz), 6.79 (1H, d, *J* = 6.9 Hz). ¹³C NMR (400 MHz, CDCl₃): δ [ppm] = 168.38, 158.54, 142.79, 141.26, 140.04, 137.10, 137.04, 133.79, 133.13, 132.77, 131.76, 131.54, 128.95, 128.88, 128.19, 127.74, 127.54, 126.99, 126.72, 126.65, 126.37, 126.31, 126.22, 126.07, 125.93, 125.24, 123.77, 120.10, 109.86. HRMS (ESI) calculated for [C₄₁H₂₈ONB + H]⁺: 562.2344; found: 562.2337.

Synthesis of compounds 3a–3c. General procedure: to a degassed solution of 1a (0.5 mmol) in dry THF (15 mL) was added a fresh *p*-CH₃OPhMgBr solution in THF. {The *p*-CH₃OPhMgBr Grignard reagent was prepared from *p*-CH₃OPhBr (1.0 mmol) and Mg (2.0 mmol) refluxed in THF (15 mL)}, the resulting mixture was stirred at ambient temperature for 3 hours under an argon atmosphere. The color of the solution turned from light yellow to dark pink, and the starting material was completely consumed according to TLC. Then, excess solvent was removed under reduced pressure, and the crude product was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 10:1, v/v) to give 3a–3c as a jujube red powder. (Yields of compounds 3a–3c vary between 50.0 and 60.0%.)

Synthesis of compound 3a. Yield: 56.8%, ¹H NMR (400 MHz, CDCl₃): δ [ppm] = 8.12 (1H, d, *J* = 1.6 Hz), 8.06 (1H, d, *J* = 9.2 Hz), 8.00 (1H, d, *J* = 1.6 Hz), 7.73 (1H, d, *J* = 9.6 Hz), 7.69 (1H, d, *J* = 7.2 Hz), 7.52–7.48 (2H, m), 7.40–7.36 (4H, m), 7.34 (1H, d, *J* = 8.4 Hz), 7.26 (1H, d, *J* = 9.2 Hz), 7.20–7.14 (4H, m), 6.93 (1H, d, *J* = 8.4 Hz), 6.91 (1H, d, *J* = 7.2 Hz), 6.74–6.71 (5H, m), 3.74 (6H, s). ¹³C NMR (400 MHz, CDCl₃): δ [ppm] = 168.24, 158.31, 158.16, 142.81, 141.11, 139.86, 137.07, 134.97, 134.85, 131.44, 131.25, 129.10, 128.94, 127.74, 127.54, 127.15, 126.94, 126.24, 126.10, 126.01, 123.76, 120.05, 112.34, 112.30, 109.62, 54.91. HRMS (ESI) calculated for [C₃₉H₃₀O₃NB + H]⁺: 572.2398; found: 572.2390.

Synthesis of compound 3b. Yield: 51.0%, ¹H NMR (400 MHz, CDCl₃): δ [ppm] = 8.06 (1H, d, *J* = 1.6 Hz), 7.98 (1H, d, *J* = 9.2 Hz),

7.95 (1H, d, $J = 1.6$ Hz), 7.66 (1H, d, $J = 9.6$ Hz), 7.53–7.52 (1H, m), 7.46–7.44 (2H, m), 7.37 (4H, d, $J = 8.8$ Hz), 7.24 (1H, d, $J = 3.6$ Hz), 7.21–7.16 (3H, m), 6.93 (1H, d, $J = 1.6$ Hz), 6.91 (1H, d, $J = 1.6$ Hz), 6.72 (4H, d, $J = 8.8$ Hz), 6.69 (1H, d, $J = 9.6$ Hz), 3.73 (6H, s). ^{13}C NMR (400 MHz, CDCl_3): δ [ppm] = 168.15, 158.26, 158.18, 142.81, 141.01, 140.96, 139.72, 134.87, 131.77, 130.50, 128.94, 127.54, 126.95, 126.88, 126.17, 126.14, 126.04, 125.90, 123.76, 120.69, 120.08, 112.31, 109.69, 54.92. HRMS (ESI) calculated for $[\text{C}_{37}\text{H}_{28}\text{SO}_3\text{NB} + \text{H}]^+$: 578.1962; found: 578.1969.

Synthesis of compound 3c. Yield: 53.5%, ^1H NMR (300 MHz, CDCl_3): δ [ppm] = 8.24 (1H, d, $J = 1.6$ Hz), 8.14–8.13 (2H, m), 8.09 (1H, d, $J = 9.2$ Hz), 7.97 (1H, d, $J = 8.4$ Hz), 7.95–7.88 (2H, m), 7.83 (1H, dd, $J_1 = 1.6$ Hz, $J_2 = 8.4$ Hz), 7.76 (1H, d, $J = 9.6$ Hz), 7.56–7.48 (2H, m), 7.39 (4H, d, $J = 8.8$ Hz), 7.27 (1H, d, $J = 9.2$ Hz), 7.18 (2H, d, $J = 7.2$ Hz), 6.94 (1H, d, $J = 1.6$ Hz), 6.92 (1H, d, $J = 1.6$ Hz), 6.75 (4H, d, $J = 8.8$ Hz), 6.74 (1H, d, $J = 7.2$ Hz), 3.74 (6H, s). ^{13}C NMR (400 MHz, CDCl_3): δ [ppm] = 168.29, 158.32, 158.18, 142.81, 141.12, 139.87, 137.13, 136.92, 134.98, 134.86, 133.73, 132.76, 131.65, 131.41, 128.94, 128.86, 128.19, 127.74, 127.54, 126.95, 126.64, 126.32, 126.30, 126.19, 126.06, 125.90, 125.24, 123.81, 120.10, 112.31, 109.64, 54.91. HRMS (ESI) calculated for $[\text{C}_{43}\text{H}_{32}\text{O}_3\text{NB} + \text{H}]^+$: 622.2555; found: 622.2542.

Results and discussion

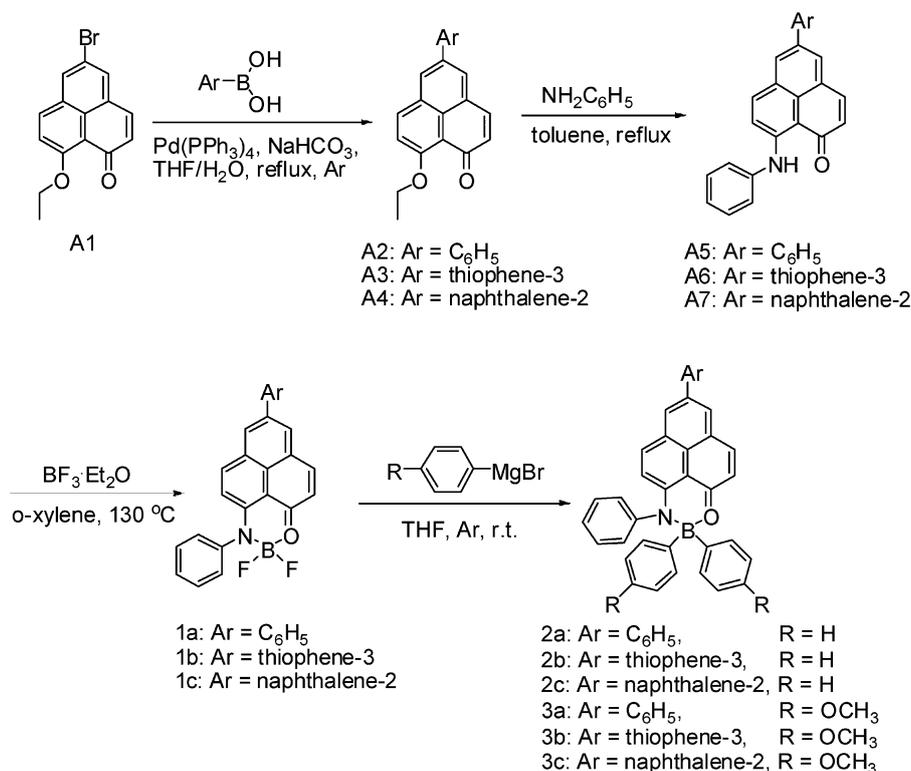
Synthesis

The chemical structures of compounds **1(a,b,c)**, **2(a,b,c)** and **3(a,b,c)**, and the synthetic routes used to produce them, are depicted in Scheme 1.

Briefly, these compounds consist of a large rigid planar π -system with different sterically hindered substituents on the exterior edges of the phenalene plane or coordinated to boron in the center. The compounds **1a**, **1b** and **1c** were synthesized with 70–80% yields by treatment of **A5–A7** with BF_3 in *o*-xylene. Substitution of the fluorines of compounds **1a**, **1b** and **1c** upon reaction of these compounds with PhMgBr or with *p*- CH_3OPhBr yielded diphenyl-boron-based coordination compounds **2a–c** and di-4-methoxyphenyl-boron-based **3a–c**, respectively. The reaction proceeded with a moderate yield between 50% and 60% at room temperature under argon. These compounds, when in a THF solution or in a solid powder state, were very stable to the light and to ambient conditions for more than two years, and no degradation occurred even when they were irradiated by strong light during the acquisition of their UV-Vis and fluorescence spectra.

Calculation analysis

Theoretical calculations carried out using the B3LYP/6-31G* basis set reveal that, for each compound, there is a conjugated orbital through the complex that includes the boron, the different substituents on the boron, and the phenyl substituent on the nitrogen. These aryl substituents provide significant contributions to the highest occupied molecular orbitals (HOMOs) with electronic clouds located near the boron. For the compounds **1a–1c** (Fig. 1A) and **2a–2c** (Fig. 1B), the HOMOs are delocalized over the whole molecule, while the LUMO orbitals are mostly located on the rigid phenalene plane. The phenyl substituent on



Scheme 1 Synthesis of phenalenylyl-based boron complex-type compounds **1(a,b,c)**, **2(a,b,c)** and **3(a,b,c)**.

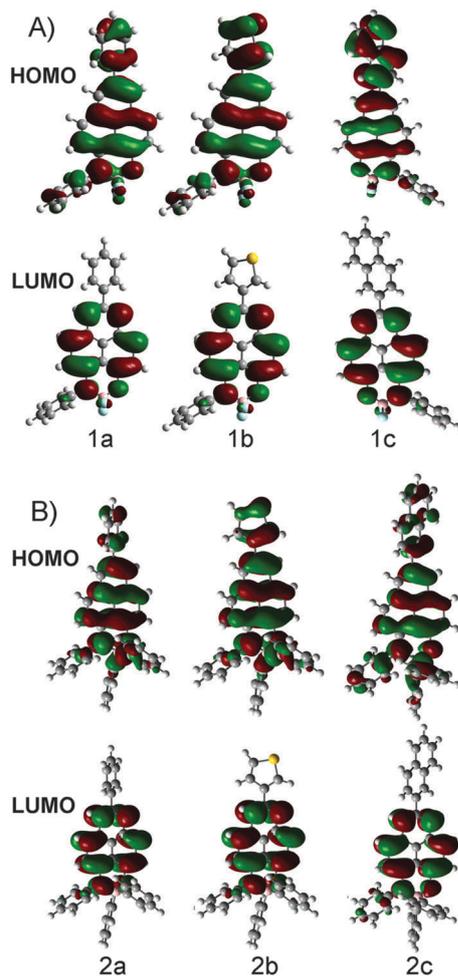


Fig. 1 Optimized molecular structures, and molecular orbital amplitude plots of HOMOs and LUMOs of (A) compounds **1(a,b,c)** and (B) **2(a,b,c)** calculated using B3LYP/6-31G*.

the nitrogen and the substituents on the boron form a conjugated orbital with the phenalene plane through the lone-pair electrons on the nitrogen and the vacant p-orbital of the boron, respectively. For compounds **1a–1c**, the electron cloud located on fluorine indicates the formation of an intramolecular push-pull effect from the aryl groups on the tip carbon atom of the phenalene plane and from the nitrogen atom to the BF₂ moiety, which is favorable for enhancing the fluorescence of the compounds. Calculated molecular orbital amplitude plots of compounds **3(a,b,c)** are given in ESI.†

Spectroscopic properties

Analysis of UV-Vis spectra. The visible absorption spectroscopic data of **1(a,b,c)** and **2(a,b,c)** in solution and in a solid-state film are shown in Fig. 2, and are summarized in Table S1 of ESI.† In the THF solution, compounds **1a**, **1b** and **1c** show similar absorption spectra with two regions of enhanced absorbance, at wavelengths of about 380 nm and 490 nm. Upon substitution of the fluorine with the phenyl group, the maximum absorbance in the latter region is at about 520 nm for

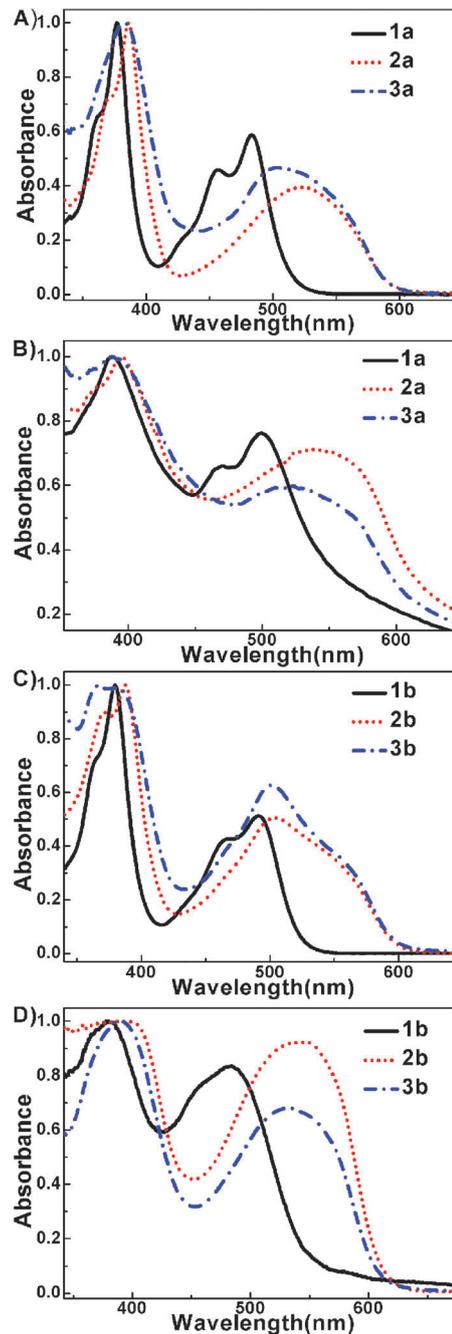


Fig. 2 Absorption spectra of (A) **1(a,b,c)** in THF solutions, (B) **1(a,b,c)** in solid film, (C) **2(a,b,c)** in THF solutions, and (D) **2(a,b,c)** in solid film.

compound **2a**, which is an approximately 40 nm red-shift compared with that of **1a**, while there is an approximately 10 nm red shift of this absorbance for compounds **2b** and **2c** compared, respectively, with their absorbance peaks in **1b** and **1c**. After substituting the fluorine with the 4-methoxyphenyl group, compound **3a** shows a 20 nm red-shift of the maximum absorption to 506 nm, while for compounds **3b** and **3c**, these red shifts are ~10 nm and ~30 nm compared with **1b** and **1c**, respectively.

In the solid film, after substituting the fluorine with the phenyl group, the resulting compound **2a** shows a maximum

absorption at 538 nm, which is an approximately 40 nm red shift compared with that of **1a**, while for compound **2b** and **2c**, there are ~60 nm and ~30 nm red shifts compared with **1b** and **1c**, respectively. After substituting the fluorine with the *p*-methoxyphenyl group, the resulting compound **3a** shows a maximum absorption at 500 nm, which is an approximately 20 nm red shift of the absorbance peak from that of **1a**, while for compounds **3b** and **3c**, the red shifts are ~50 nm and ~20 nm from the absorbance peaks of **1b** and **1c**, respectively. In general, substituting fluorine with aryl groups on boron produces red shifts of the entire absorption and emission spectra, which is probably due to the effects that aryl groups have on the conjugation of the orbitals.

Fluorescence spectra analysis

The fluorescence spectroscopic data of compounds **1a–3a** and **1b–3b** exhibit very weak emission in dilute THF solutions. However, their fluorescence emission intensities are greatly enhanced in the solid state compared with those in THF solution, which indicates an obvious aggregation-induced emission effect. As shown in Fig. 3A, the emission maximum of **1a** is at 579 nm; after substituting the fluorine with the phenyl group, the emission maximum is red-shifted by about 65 nm to 645 nm as seen for **2a**. Comparing the emission maxima of **1a** and **3a** shows that substituting the fluorine with the *p*-methoxyphenyl group causes a similar red shift.

In Fig. 3B, the emission maxima of compounds **2b** and **3b** show red shifts of 42 nm and 43 nm, respectively, compared to

those of **1b**. After substituting the fluorine atom with aryl-groups, the compounds show similar results with those discussed above. Surprisingly, the emissions of compounds **3a** and **3b**, which have *p*-methoxyphenyl groups on the boron, are similar to those of compounds **2a**, and **2b**, which have phenyl groups on the boron. This observation is consistent with the trends in the absorption spectra, and can be explained by considering that although the aryl groups on boron can conjugate with the planar phenalene through the boron, these aryl groups cannot be coplanar with the parent phenalene, resulting in that the different groups have little effect on the electronic structure of the whole molecule.

Electrochemical analysis

Cyclic voltammetry (CV) was used to investigate the electrochemical properties of the obtained fluorescent compounds. As shown in Fig. 4A, the energy levels of HOMOs and LUMOs, which are -6.05 and -3.52 eV for **1a**, -5.26 and -3.27 eV for **2a**, and -5.35 and -3.34 eV for **3a**, were calculated from the onset oxidation and reduction potential. The electrochemical band gaps of **1a**, **2a** and **3a** are estimated to be 2.53, 1.99 and 2.01 eV, respectively, which is consistent with the optical band gaps. So after substituting the fluorine with the phenyl group, the band gap of compound **2a** is ~0.5 eV lower than that of compound **1a**; while compound **3a**, with the fluorine substituted with the 4-methoxyphenyl group, also shows a band gap that is ~0.5 eV lower than that of compound **1a**. Although the *p*-methoxyphenyl group possesses a stronger electron-donating

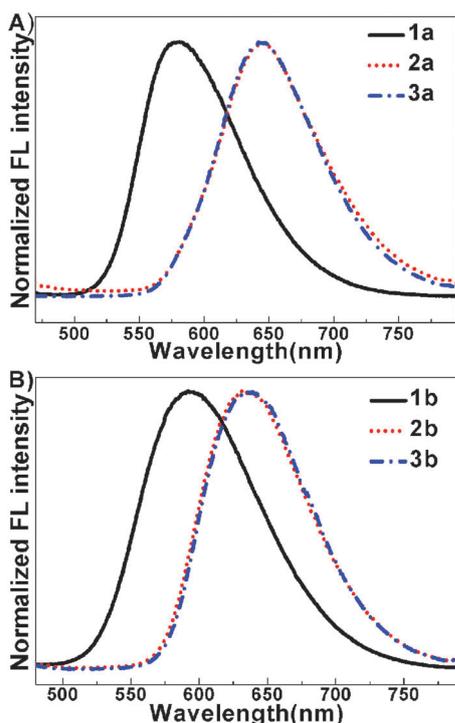


Fig. 3 (A) PL spectra of **1a–3a** in solid film, excited at maximum excitation wavelength of 395 nm; (B) PL spectra of **1b–3b** in solid film, excited at maximum excitation wavelength of 395 nm.

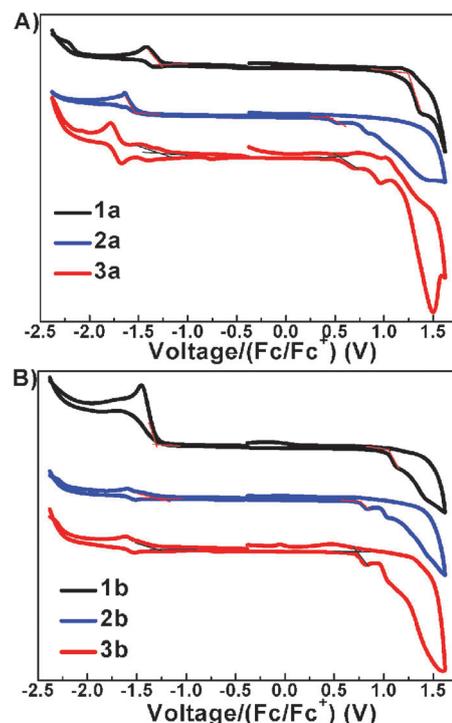


Fig. 4 Cyclic voltammograms of (A) **1a–3a** and (B) **1b–3b** in dichloromethane solutions of $0.1 \text{ mol L}^{-1} \text{ Bu}_4\text{NPF}_6$ with a scan rate of 0.1 V s^{-1} and Fc/Fc^+ as the internal reference.

effect than that of the phenyl group, the band gaps of compounds **2a** and **3a** show no significant change, despite small changes of their HOMOs and LUMOs.

As shown in Fig. 4B, the bandgaps, HOMOs and LUMOs of compounds **1b**, **2b** and **3b** show similar changes as those between compounds **1a**, **2a** and **3a**.

It may be speculated that the aryl substituents are conjugated with the parent phenalene through the coordinating boron atom and hence cause a considerable increase in the HOMO energy level and resulting lowering of the bandgap. Nevertheless, the aryl substituents on the boron cannot be coplanar with the parent phenalene, so the *p*-methoxyphenyl group shows a similar effect as does the phenyl group on the electronic structure of the whole molecule.

Aggregation-induced emission in aqueous solution

We also further checked the AIEE effect of these organoboron compounds by adding water into their THF solutions and analyzing the change of the PL spectra between different THF–water mixtures (illustrated in Fig. 5 using **1b** and **2b** as examples, and in Fig. S3B in ESI† using **3b**). It can be seen that an emission band appears clearly and is markedly enhanced when a large amount of water is added. Since water is a poor solvent for these compounds, the molecules are aggregated in aqueous solutions. In addition, the emission maxima show small red shifts with the volume of water increasing, due to aggregation-induced conjugation of the molecules. It is believed that these molecules cannot

pack through a p–p stacking process due to its propeller shape, similar to that for the hexaphenylsiloles reported by Tang *et al.*, while the intramolecular rotations of its aryl rotors in compounds **1b** and **2b** are greatly restricted owing to the physical constraints. Also, the large substituent groups sterically block the molecules from approaching and interacting with one another. The restriction of intramolecular rotations blocks the non-radiative pathway and opens up the radiative channel. As a result, these molecules become strongly emissive in the aggregate state.

Sensors for viscous alcohols

As shown in Fig. 6A, alcohols with different viscosities, from 2-propanol to glycerol, were chosen to check the effect of viscosity on the fluorescence emissions of compound **1b**. By adding compound **1b** in THF (0.2 mL, 5×10^{-3} M) to the different alcohols (1.8 mL), 5×10^{-4} M solutions of **1b** were obtained. The PL spectra of **1b** were measured in such mixtures and the results show that the emission became stronger upon increasing the viscosity of the alcohols. As shown in Fig. 6B, the peak intensity of the PL spectrum of **1b** almost linearly increased with the increase of the viscosity of the solvents from 2-propanol to tetraglycol. The PL intensity of compound **1b** in glycerol is 100-fold higher than that in the 2-propanol. This phenomenon has been explained by the restriction of intramolecular rotation (RIR) in the aggregates as a main cause for the AIEE effect. Herein, the RIR process is expected to be affected by the viscosity of the medium: the more viscous the medium, the slower the intramolecular rotation and hence the stronger the emission of compound **1b**. Conventional methods used to measure viscosity, such as capillary tube method,

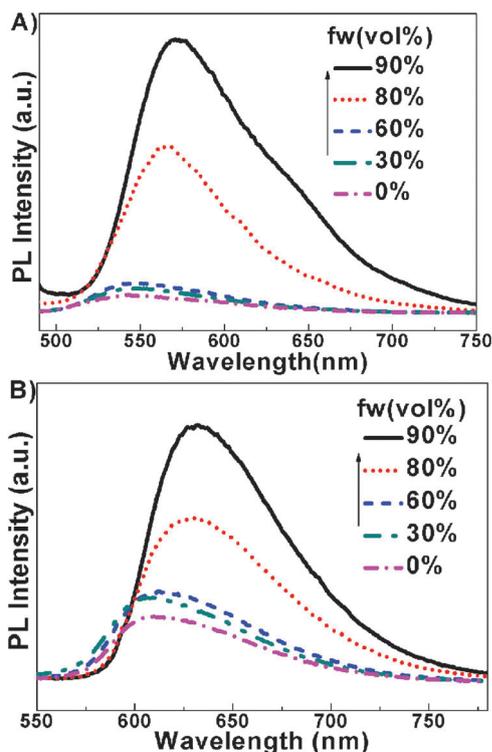


Fig. 5 PL spectra of organoboron compounds in THF–water mixtures with different water fractions (fw), excited at 468 nm. (A) Spectra of compound **1b** and (B) of **2b**.

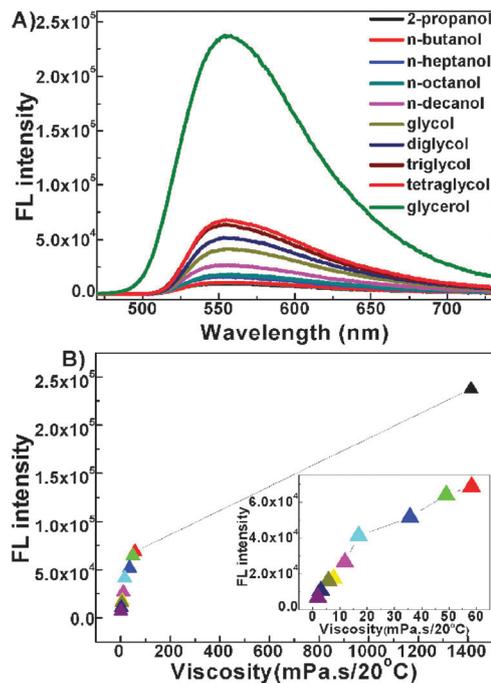


Fig. 6 PL spectra of **1b** in mixtures of different viscous alcohols and THF (5×10^{-4} M), excited at 468 nm.

rotation method, vibration measurements and the newly developed method using micro-measurement technology all need special instruments and are complex. So if precision is not required, the viscosity of transparent viscous fluids can be simply estimated by measuring the change of the intensity of emission of these AIEE dyes with the standard curve prepared in advance.

Conclusions

We have synthesized a novel series of boron-complex-type fluorophores with enhanced fluorescence emission in the solid state, and have investigated how different substituents bonded to the boron atom affect the photophysical properties of these compounds. When introducing electronic-withdrawing fluorine or electronic-donating phenyl/4-methoxy-phenyl groups onto the boron atom, the fluorescence emissions of these compounds in the solid state change from yellow to red. These compounds show aggregation-induced enhancement of the emission. It appears that the large substituent groups in compounds **1a–3c** both inhibit intramolecular rotations and sterically block intermolecular contact. The energy loss of the non-radiative transition is thus reduced and the radiative transition is enhanced in the solid state. Furthermore, the fluorescence of these molecules is affected by viscous alcohols, with the intensity of the emission being enhanced as the viscosity of the alcohol is increased. These aggregation-induced emission enhanced dyes may provide a simple way to estimate the viscosity of transparent viscous fluids.

Acknowledgements

The authors gratefully acknowledge financial support from the NSFC (Grants 50902073, 50933003 and 50903044), MOST (Grants 2011CB932602 and 2011DFB50300).

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