

Phenalenyl-based boron–fluorine complexes: Synthesis, crystal structures and solid-state fluorescence properties

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ABSTRACT

A novel series of phenalenyl-based boron–fluorine complex-type fluorophores, with a drastic fluorescence quenching in solution but high fluorescence emission in the solid-state, have been synthesized. The X-ray structure demonstrates that the bulky substituents result in steric hindrance and prevent the fluorophores forming short intermolecular interaction thereby enhancing the solid-state fluorescence emission.

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1. Introduction

Organoboron compounds with high efficiency fluorophores have attracted considerable attention because of their excellent photophysical properties and potential use in molecular sensors [1], biomolecular probes [2], and in the construction of optoelectronic devices such as organic light-emitting devices (OLEDs) [3]. However, most organoboron compounds, like other organic fluorophores, undergo fluorescence quenching when aggregated due to both intermolecular energy and electron transfer, which affects their use in OLEDs [4].

On the other hand, solid-emissive fluorescent compounds have attracted much attention for fundamental research of solid-state photochemistry [5] and their possible applications in optoelectronics [6]. For example, Tang and co-workers have reported a series of molecules such as siloles, pyrans, fulvenes and butadienes which show aggregation-induced emission (AIE) phenomenon [7]. And several dyes have been proved to be excellent light-emitting materials for the device applications [8]. Park and co-workers have prepared several new classes of fluorescent organic molecules which assemble into stable nanoparticles (FONs), which show extremely strong solid-fluorescence emission [9]. Yoshida et al. have synthesized a class of heterocyclic quinol-type fluorophores with intense solid-state fluorescence by introducing bulky substituents to the original fluorophores [10].

2. Experimental

2.1. General

All reagents are commercially available and purified by standard methods prior to use. Absorption spectra were observed with a JASCO V-570 spectrophotometer and fluorescence spectra were measured with a Fluora Max-3P spectrophotometer. Bruker SMART 1000 CCD automatic diffractometer was used for data collection at 113(2)K using graphite monochromated MoK α -radiation ($\lambda = 0.71073 \text{ \AA}$). The fluorescence quantum yields (ϕ) in solution were determined by using quinine sulfate ($\phi = 0.54$, $\lambda_{\text{ex}} = 350 \text{ nm}$) in 0.1 M H₂SO₄ as the standard. The solid-fluorescence quantum yields (ϕ) were determined by using a calibrated integration sphere system ($\lambda_{\text{ex}} = 470 \text{ nm}$). The ¹H NMR spectra were measured on a Bruker AC-300 and a Bruker AC-400 using tetramethylsilane (TMS) as internal standard. HRMS were recorded on a VG ZAB-HS mass spectrometer with ESI resource.

2.2. Synthesis

2.2.1. Synthesis of 2,2-difluoro-3-hydro-2-bora-s-3-aza-1-oxophenylene (**2a**)

To a degassed solution of **1a** (0.195 g, 1 mmol) in 1,2-dichloroethane was added BF₃·Et₂O (0.15 ml, 1.2 mmol), the resulting mixture was stirred at ambient temperature for 2 h and then refluxed for 12 h under an Ar atmosphere. After solvent was removed under reduced pressure, the crude product was purified by column

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chromatography (silica gel, petroleum ether/ethyl acetate 2:1, v/v) to give **2a** (0.206 g, 85%) as a light yellow powder. ^1H NMR (300 MHz, DMSO): δ [ppm] = 7.26 (1H, d, J = 9.3 Hz), 7.50 (1H, d, J = 9.3 Hz), 7.77 (1H, t, J = 7.5 Hz), 8.26 (1H, d, J = 7.5 Hz), 8.30 (1H, d, J = 9.3 Hz), 8.36 (1H, d, J = 7.5 Hz), 8.56 (1H, d, J = 9.3 Hz), 10.26 (1H, s). HRMS (ESI) calcd. for $[\text{C}_{13}\text{H}_8\text{ONBF}_2 + \text{Na}]^+$: 266.0559; found: 266.0564.

2.2.2. Synthesis of compounds **2b–2e**

General procedure: To a degassed solution of **1** (**1b–1e**) (1 mmol) in *o*-xylene was added $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (0.15 ml, 1.2 mmol), the resulting mixture was stirred at ambient temperature for 2 h and then refluxed at 140 °C for 12 h under an Ar atmosphere. After solvent was removed under reduced pressure, the crude product was purified by column chromatography (silica gel, petroleum ether/ethyl acetate 20:1, v/v) to give **2** (**2b–2e**) (yields vary between 80% and 90%).

2.2.2.1. Synthesis of 2,2-difluoro-3-*n*-propyl-2-bora-s-3-aza-1-oxophenylene (2b**).** Yield 92%: ^1H NMR (400 MHz, CDCl_3): δ [ppm] = 1.08 (3H, t, J = 7.4 Hz), 1.90 (2H, m), 3.82 (2H, t, J = 5.6) 7.23 (1H, d, J = 9.6 Hz), 7.43 (1H, d, J = 9.2 Hz), 7.63 (1H, t, J = 7.6 Hz), 7.98 (1H, d, J = 9.6 Hz), 8.05 (1H, d, J = 9.6 Hz), 8.10 (1H, d, J = 8.0 Hz), 8.20 (1H, d, J = 9.2 Hz). HRMS (ESI) calcd. for $[\text{C}_{16}\text{H}_{14}\text{ONBF}_2 + \text{Na}]^+$: 308.1065; found: 308.1035.

2.2.2.2. Synthesis of 2,2-difluoro-3-phenyl-2-bora-s-3-aza-1-oxophenylene (2c**).** Yield 91%: ^1H NMR (300 MHz, CDCl_3): δ [ppm] = 6.88 (1H, d, J = 9.6 Hz), 7.42–7.57 (6H, m), 7.68 (1H, t, J = 7.5), 7.94 (1H, d, J = 9.6 Hz), 8.02 (1H, d, J = 7.2 Hz), 8.18 (1H, d, J = 8.1 Hz), 8.32 (1H, d, J = 9.0 Hz). HRMS (ESI) calcd. for $[\text{C}_{19}\text{H}_{12}\text{ONBF}_2 + \text{Na}]^+$: 342.0872; found: 342.0879.

2.2.2.3. Synthesis of 2,2-difluoro-3-(4-methoxyphenyl)-2-bora-s-3-aza-1-oxophenylene (2d**).** Yield 83%: ^1H NMR (400 MHz, CDCl_3): δ [ppm] = 3.88 (3H, s), 6.92 (1H, d, J = 9.6 Hz), 7.04 (2H, d, J = 8.8 Hz), 7.35 (2H, d, J = 8.8 Hz), 7.51 (1H, d, J = 8.8 Hz), 7.67 (1H, t, J = 8.0 Hz), 7.93 (1H, d, J = 9.6 Hz), 8.01 (1H, d, J = 7.2 Hz), 8.16 (1H, d, J = 8.0), 8.30 (1H, d, J = 9.6). HRMS (ESI) calcd. for $[\text{C}_{20}\text{H}_{14}\text{O}_2\text{NBF}_2 + \text{Na}]^+$: 372.0983; found: 372.0982.

2.2.2.4. Synthesis of 2,2-difluoro-3-(4-cyanophenyl)-2-bora-s-3-aza-1-oxophenylene (2e**).** Yield 80%: ^1H NMR (300 MHz, CDCl_3): δ [ppm] = 6.85 (1H, d, J = 9.3 Hz), 7.55 (1H, d, J = 9.0), 7.60 (2H, d, J = 8.4), 7.74 (1H, t, J = 7.5 Hz), 7.85 (2H, d, J = 8.1 Hz), 8.04 (1H, d, J = 9.3 Hz), 8.10 (1H, d, J = 7.2 Hz), 8.24 (1H, d, J = 8.1 Hz), 8.38 (1H, d, J = 9.0 Hz). HRMS (ESI) calcd. for $[\text{C}_{20}\text{H}_{11}\text{ON}_2\text{BF}_2 + \text{Na}]^+$: 367.0825; found: 367.0832.

2.3. X-ray crystallography

The diffraction-quality single crystals of **2b** and **2d** were mounted on glass fibers in random orientation using epoxy-glue. The structures were solved by direct methods, and all non-hydrogen atoms were subjected to anisotropic, full-matrix least squares refinement on F^2 using the SHELXTL package [11]. More details on data collection and structure calculation are summarized in Table 1. Crystallographic data for all structures reported here have been deposited with the Cambridge Crystallographic Data Centre; CCDC numbers are given in Table 1.

3. Results and discussion

3.1. Synthesis

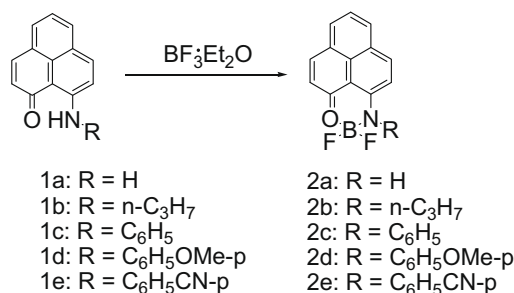
In this paper, we have designed and synthesized a novel phenalenyl-based boron–fluorine complex-type fluorophores (**2a–2e**), which are constructed to have a large rigid planar π -system with different sterical hindered substituents. The compounds **1a–1e** were synthesized using a methodology previously described [12]. The fluorophores **2a–2e** were synthesized in 80–90% yields by treatment **1a–1e** with BF_3 in *o*-xylene (**2a**, in $\text{ClCH}_2\text{CH}_2\text{Cl}$) (Scheme 1).

3.2. Spectroscopic properties of **2a–2e**

The visible absorption and fluorescence spectroscopic data of **2a–2e** in solution and solid-state are summarized in Table 2. In solution, the absorption maxima are at around 359–372 nm and fluorescence maxima are at around 453–471 nm. Alkyl-substituted

Table 1
Experimental data for the X-ray diffraction studies of prepared compounds at 113(2) K.

| Compounds | 2b | 2d |
|--|--|--|
| Numbers in CCDC | 725287 | 725288 |
| Empirical formula | $\text{C}_{32}\text{H}_{28}\text{B}_2\text{F}_4\text{N}_2\text{O}_2$ | $\text{C}_{60}\text{H}_{42}\text{B}_3\text{F}_6\text{N}_3\text{O}_6$ |
| Formula weight | 570.18 | 1047.40 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | $P2(1)/c$ | $P2(1)/c$ |
| <i>a</i> (Å) | 18.541(4) | 10.8705(6) |
| <i>b</i> (Å) | 16.237(3) | 14.9755(7) |
| <i>c</i> (Å) | 8.8182(18) | 29.2018(15) |
| α (°) | 90 | 90 |
| β (°) | 100.28(3) | 93.779(3) |
| γ (°) | 90 | 90 |
| <i>V</i> (Å ³) | 2612.1(9) | 4743.5(4) |
| <i>Z</i> | 4 | 4 |
| <i>D</i> _{calcd.} (mg/m ³) | 1.450 | 1.476 |
| Crystal size (mm) | 0.18 × 0.14 × 0.02 | 0.18 × 0.16 × 0.14 |
| μ (mm ⁻¹) | 0.109 | 0.110 |
| <i>F</i> (0 0 0) | 1184 | 2160 |
| θ Range for data collection (°) | 3.04–25.02 | 1.40–27.89 |
| Index ranges | −19 ≤ <i>h</i> ≤ 22, −19 ≤ <i>k</i> ≤ 19, −10 ≤ <i>l</i> ≤ 9 | −14 ≤ <i>h</i> ≤ 14, −19 ≤ <i>k</i> ≤ 18, −38 ≤ <i>l</i> ≤ 32 |
| Completeness (%) | 99.8 | 99.6 |
| Reflections collected/unique | 17,602/4605 | 34,194/11,296 |
| <i>R</i> _{int} | 0.1760 | 0.0640 |
| Data/restraints/parameters | 4605/0/381 | 11,296/0/706 |
| Goodness-of-fit (GOF) on <i>F</i> ² | 1.125 | 1.048 |
| Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)] | <i>R</i> ₁ = 0.0958, <i>wR</i> ₂ = 0.2822 | <i>R</i> ₁ = 0.0638, <i>wR</i> ₂ = 0.1441 |
| <i>R</i> indices (all data) | <i>R</i> ₁ = 0.1809, <i>wR</i> ₂ = 0.3207 | <i>R</i> ₁ = 0.0984, <i>wR</i> ₂ = 0.1660 |
| Largest difference peak and hole (e Å ⁻³) | 0.380 and −0.376 | 0.298 and −0.384 |



Scheme 1. Synthetic route of **2a–2e**.

Table 2
Spectroscopic properties of **2a–2e** in THF and in the solid-state.

| Compounds | In THF | | | In the solid-state | | |
|-----------|---|--|--------|--|--|--------|
| | $\lambda_{\text{max}}^{\text{abs}}/\text{nm}$ | $\lambda_{\text{max}}^{\text{fl}}/\text{nm}$ | ϕ | $\lambda_{\text{max}}^{\text{ex}}/\text{nm}$ | $\lambda_{\text{max}}^{\text{fl}}/\text{nm}$ | ϕ |
| 2a | 359(15,300) | 456 | 0.344 | 467 | 506 | <<0.01 |
| 2b | 365(28,500) | 471 | 0.399 | 467 | 508 | <0.01 |
| 2c | 366(21,000) | 454 | 0.006 | 499 | 538 | 0.04 |
| 2d | 366(19,700) | 453 | 0.007 | 510 | 550 | 0.08 |
| 2e | 372(26100) | 453 | 0.003 | 500 | 539 | 0.03 |

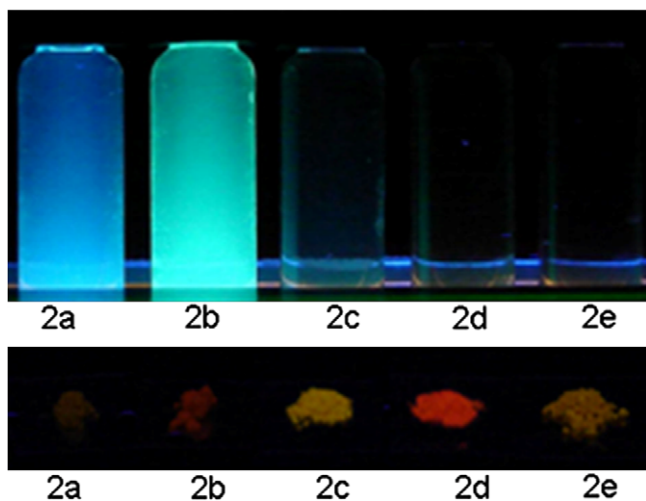


Fig. 1. Top: compounds **2a–2e** dissolved in THF ($1 \times 10^{-5} \text{ mol L}^{-1}$) and bottom: in solid-state under 365 nm UV light.

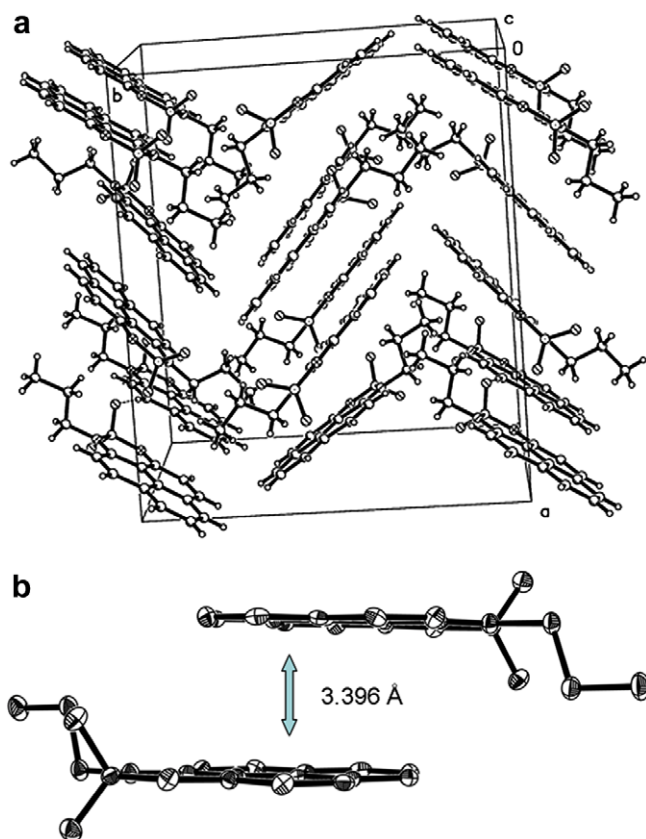


Fig. 2. Crystal packing of **2b**: (a) a stereo view of the molecular packing structure and (b) a side view of a face-to-face overlap between the fluorophores.

2b and the parent compound **2a** show strong fluorescence emission, while the aryl-substituted **2c–2e** exhibit very weak fluorescence emission in solution in comparison with **2a–2b**. It is believed that the active intramolecular rotations in compound **2c–2e** of the peripheral phenyl ring around the axes of the single bonds linked to the central ring effectively annihilate the excitons, thus making the molecular fluorescence weakly emissive [7a] (Fig. 1).

In the solid-state, compounds **2a–2e** all show red-shift of absorption compared with that in solution with compounds **2c–2e** exhibiting a greater red-shift (45–60 nm). Surprisingly, in the solid-state, the fluorescence of **2a–2b** is almost completely quenched while **2c–2e** show much stronger fluorescence emission when excited at their maximum absorption, as indicated by the quantum yields listed in Table 2. The solid-fluorescence quenching of compounds **2a** and **2b** may be due to the following: (1) smaller substituent groups on the nitrogen atom cannot prevent close packing of the molecules in the solid-state as discussed in the single-crystal structure analysis below; (2) the existence of hydrogen on nitrogen in **2a** could induce intermolecular hydrogen bonding. On the other hand, for compound **2c–2e**, the large aryl groups frustrate intermolecular ordered π -stacking between the phenalenyl

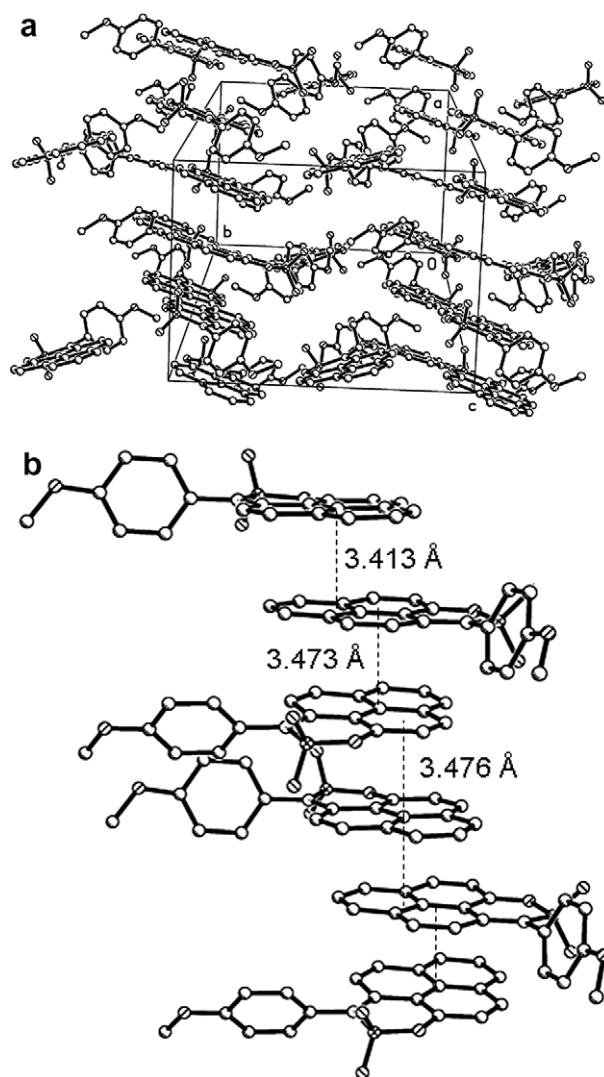


Fig. 3. Crystal packing of **2d**: (a) a stereo view of the molecular packing structure and (b) a side view of a face-to-face overlap between the fluorophores. The interplanar distance between the rings is ca. 3.413, 3.473 and 3.476 Å.

rings in the molecules and thus give efficient solid-fluorescence emission [7a]. Also, compound **2d** with electron-donating effect of the peripheral phenyl ring has stronger solid-state fluorescence emission with red-shift compared with that of compound **2c**, while **2e** with electron-drawing effect shows no obvious change compared with **2c** (Table 2 and Fig. 1). The possible reasons are yet to be understood.

3.3. Crystal structures

Suitable crystals of **2b** and **2d** have been obtained by slow evaporation of dichloromethane and hexane. To better understand the differences in fluorescence of compounds **2a–2e**, we have compared the single-crystal structures of **2b** and **2d**. As shown in Figs. 2 and 3, the molecules of **2b** stack in a sandwich herringbone motif of face-to-face π -dimers and neighbouring planes are parallel with a distance of 3.396 Å. In the crystal of **2d**, the neighbouring phenalenyl planes are not parallel as in **2b**, but tilted with angles of 2.4°, 4.0° and 6.1° for the three molecules in a unit cell and the distance (>3.4 Å) between two neighbouring molecules is significantly longer than that in **2b**. As described in other work reported earlier [10], we suggest that attaching more sterically hindered substituents, such as in **2d**, to the nitrogen atom could prevent the fluorophores from forming short π - π contacts and intermolecular hydrogen bonding in compound **2a**. While we did not get the X-ray crystal structure for compound **2c** and **2e**, we believe similar cases should be true for them.

4. Conclusions

In conclusion, phenalenyl-based boron–fluorine complexes have been synthesized. Single-crystal structure analysis indicates that introduction of bulky substituents could somewhat prevent planar fluorophore molecules from forming π - π stacking and thus enhance their solid-state fluorescence emission.

Supplementary data

Crystallographic data (excluding structure factors) for the structure of **2b** and **2d** in this paper have been deposited with Cambridge Crystallographic Data Centre as Supplementary publication Nos. CCDC 725287 and 725288. Copy of data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 0 1223336033 or e-mail: deposit@ccdc.cam.ac.uk].

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