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ARTICLE

Synthesis of a borylated boron-dibenzopyrromethene dye enabling the visual detection of H₂O₂ vapor

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Given our interest in the development of reaction-based chemosensors, we developed a novel boron-dibenzopyrromethene dye with a pinacolboryl group (**1**), blue in color ($\lambda_{\text{max}} = 621 \text{ nm}$, $\epsilon = 8.74 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) with red emission ($\lambda_{\text{max}} = 643 \text{ nm}$, $\lambda_{\text{ex}} = 550 \text{ nm}$) in THF. H₂O₂-mediated oxidation of the pinacolboryl group was found to induce a significant fluorescence decrease at 642 nm ($\lambda_{\text{ex}} = 550 \text{ nm}$) in EtOH/H₂O (1:1 v/v) at 25 °C, enabling us to detect trace levels of H₂O₂ visually. The time-dependent response was investigated to evaluate the pseudo-first-order rate constant of 1.69 min^{-1} under basic conditions, meaning that its fluorescence was decreased by 80% in 2 min. Such a remarkable response capability motivated us to test the suitability of **1** for the detection of H₂O₂ vapor. For these experiments, a **1**-coated TLC plate was fabricated by a spin-coating method and then placed in sealed bottles with H₂O₂ vapor. It was found that the increasing vapor concentration of H₂O₂ could be visually monitored by a change in red emission (ΔR value). Based on this, we estimated the detection limit of this method to be 8.43 ppb. We also found that **1**-coated TLC plate could selectively detect H₂O₂ vapor over common solvents tested.

1. Introduction

There has been growing interest in the development of boronic acid or boronate-based chemosensors because of their versatile reactivity toward analytes.¹ For instance, these boron-based functional groups can bind to *cis*-diols (e.g. saccharides),² catechols,³ fluoride,⁴ cyanide,⁵ and reactive oxygen species such as superoxide, hypochlorous acid or nitrating species.⁶ A H₂O₂-triggered response, based on the oxidative conversion of boronates to phenols, is one of the distinctive features of those systems that have been widely used as noninvasive detection tools in biological systems.⁷ In addition, trace detection of peroxide-based explosives is of significant current importance for security purposes.⁸ This is because, compared to aromatic explosives such as 2,4,6-trinitrotoluene (TNT), it is difficult to detect explosives that do not contain a nitro group, such as triacetone triperoxide (TATP) and hexamethylene triperoxide diamine (HMTD).⁹ Therefore, boronate-appended dyes would be highly valuable for use as indicators to monitor H₂O₂ produced by UV or the acid-catalyzed decomposition of TATP or HMTD.¹⁰ Given the demand for real-time detection,¹¹ we decided to develop a visual H₂O₂-detection system with outstanding optical properties.

4,4-Difluoro-4-bora-3a,4a-diaza-*s*-indacene (BODIPY) dyes composed of boron-dipyrrin complexes have emerged as promising candidates because of their excellent optical properties, which include high molecular extinction coefficients

of absorption, high fluorescence quantum yield, and excellent photostability.¹² As such, they have been applied in a wide range of research areas, including chemosensors,¹³ biological labels,¹⁴ bio-imaging,¹⁵ organic light-emitting diodes,¹⁶ photodynamic therapy,¹⁷ light-harvesting arrays,¹⁸ and solar-cell devices.¹⁹ For their use as reaction-based chemosensors, several BODIPY derivatives have been proposed.²⁰ However, to the best of our knowledge, BODIPY and its congeners capable of detecting vapor peroxides involving H₂O₂ have not been reported as yet. Therefore, the direct introduction of a boronate reactive group into the chromophore is a novel approach. We have currently focused on modification of the structure of BODIPY by extending π -conjugation to provide new types of boron-dibenzopyrromethene dyes.²¹ Synthetic acceptability of the dye skeleton led us to prepare a pinacolborylated probe (**1**). In this study, the synthesis and characteristics are described from the standpoint of preparing an H₂O₂-detection system; the addition of H₂O₂ in an EtOH/H₂O (1:1 v/v) solution of **1** induced a bathochromic shift in the absorption band, accompanied by a remarkable decrease in its fluorescence intensity through deboronation. Its fast response was observed when tetrabutylammonium hydroxide (TBAOH)^{10d, 22} was added to the solution under the conditions. A test strip composed of a TLC plate coated with **1** was applied for the visual detection of H₂O₂ vapor.

2. Experimental section

2.1 General

NMR spectra were taken by a Bruker Avance 500 (^1H : 500 MHz, ^{13}C : 125 MHz) spectrometer. In ^1H and ^{13}C NMR measurements, chemical shifts (δ) are reported downfield from the internal standard Me_4Si . Fast atom bombardment (FAB) mass spectra were obtained on a JEOL JMS-700 spectrometer where *m*-nitrobenzylalcohol was used as a matrix. The absorption and fluorescence spectra were measured using a Shimadzu UV-3600 and a JASCO FP-6300 spectrophotometers, respectively. Elemental analyses were performed on an Exeter Analytical, Inc. CE-440F Elemental Analyzer. Photographic images were recorded using a NIKON D3200 digital single-lens reflex camera.

2.2 Materials

Unless otherwise indicated, reagents used for the synthesis were commercially available and were used as supplied. 1-(2-(2-Methoxybenzoyl)phenyl)ethanone **2**²³ was prepared through two steps from 2-hydroxyacetophenone. Synthesis of 1-(4-bromo-2-(2-methoxybenzoyl)phenyl)ethanone **3** was conducted according to our previous paper.^{21b}

2.3 Synthesis

5-BROMO-1-((3-(2-METHOXYPHENYL)-2H-ISOINDOL-1-YL)-METHYLENE)-3-(2-METHOXYPHENYL)-1H-ISOINDOLE (4). Compounds **2** (1.190 g, 4.680 mmol) and **3** (1.559 g, 4.680 mmol) were dissolved in MeOH (47 mL) and AcOH (27 mL). To the solution was added NH_4OH (21 mL) under an icy condition. The resulting mixture was stirred for overnight at 45 °C. After treating with NaHCO_3 aqueous solution (150 mL), the precipitation was then collected. It was chromatographed on silica gel (Wacogel C-300) using hexane/benzene (3:2 v/v) as an eluent to give 314.7 mg of **4** as a deep-blue solid in 25% yield. ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ (ppm) 3.75 (s, 6H), 7.18 (t, 2H, $J = 7.45$ Hz), 7.25 (d, 1H, $J = 6.25$ Hz), 7.26 (d, 1H, $J = 6.30$ Hz), 7.30 (td, 1H, $J = 7.53$ and 0.93 Hz), 7.43 (td, 1H, $J = 7.60$ and 0.60 Hz), 7.47 (dd, 1H, $J = 8.00$ and 1.58 Hz), 7.49–7.52 (m, 2H), 7.83 (d, 1H, $J = 8.20$ Hz), 7.90 (dd, 1H, $J = 7.55$ and 1.60 Hz), 7.92 (dd, 1H, $J = 7.60$ and 1.60 Hz), 7.96 (d, 1H, $J = 1.35$ Hz), 8.14 (s, 1H), 8.16 (t, 2H, $J = 8.80$ Hz); FAB MS: m/z 534 $[\text{M}]^+$, 536 $[\text{M}+2]^+$.

DIFLUORO[5-BROMO-1-[[3-(2-METHOXYPHENYL)-2H-ISOINDOLE-1-YL]METHYLENE]-3-(2-METHOXYPHENYL)-1H-ISOINDOLATO- N^1,N^2]-BORON (5). Et_3N (0.8 mL, 5.771 mmol) was added to a solution of **4** (1.179 g, 2.201 mmol) in dry toluene (83 mL), followed by the addition of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (3 mL, 23.99 mmol) at 80 °C. The mixture was stirred overnight at 100 °C. The solution was poured into water (40 mL) and extracted with AcOEt (120 mL), the organic layer being washed with H_2O (300 mL) and dried with Na_2SO_4 . After removal of the solvent *in vacuo*, the residue was chromatographed on silica gel (Wacogel C-300) using a gradient of hexane (50% $\rightarrow$ 0% v/v) in benzene as an eluent to give **5** (1.147 g) in 89% yield. Dye **5** is present as a mixture of

conformation isomers at room temperature. As such, integration values for the ^1H NMR data were based on that (3H) of OMe signal of the anisole unit. ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ (ppm) 3.67(s, 3H), 3.68 (s, 3H), 3.72 (s, 3H), 3.73 (s, 3H), 7.00 (t, 1H, $J = 6.63$ Hz), 7.02 (t, 1H, $J = 6.82$ Hz), 7.07 (t, 1H, $J = 7.12$ Hz), 7.08 (t, 1H, $J = 6.93$ Hz), 7.17 (d, 1H, $J = 8.20$ Hz), 7.18 (d, 1H, $J = 8.70$ Hz), 7.20 (d, 1H, $J = 8.60$ Hz), 7.22 (d, 1H, $J = 7.95$ Hz), 7.31 (t, 2H, $J = 7.80$ Hz), 7.33 (d, 2H, $J = 8.45$ Hz), 7.37 (d, 2H, $J = 7.80$ Hz), 7.39 (s, 2H), 7.44 (d, 1H, $J = 8.00$ Hz), 7.45 (d, 1H, $J = 8.00$ Hz), 7.49 (t, 2H, $J = 7.93$ Hz), 7.50 (t, 2H, $J = 7.60$ Hz), 7.60 (t, 2H, $J = 8.10$ Hz), 7.63 (d, 2H, $J = 9.25$ Hz), 8.12 (d, 2H, $J = 8.70$ Hz), 8.16 (d, 2H, $J = 8.05$ Hz), 8.71 (s, 2H); FAB MS: m/z 582 $[\text{M}]^+$, 584 $[\text{M}+2]^+$.

DIFLUORO[5-PINACOLBORYL-1-[[3-(2-METHOXYPHENYL)-2H-ISOINDOLE-1-YL]METHYLENE]-3-(2-METHOXYPHENYL)-1H-ISOINDOLATO- N^1,N^2]-BORON (1). Compound **5** (1.120 g, 1.923 mmol) and KOAc (1.953 g, 19.90 mmol) were dissolved in dry 1,2-dimethoxyethane (DME) (33.5 mL). The solution was degassed by three freeze-pump-thaw cycles. After adding bis(pinacolate)diboron (1.330 g, 5.237 mmol) and a degassed solution of $\text{PdCl}_2(\text{dppf})_2$ (0.3800 g, 0.4569 mmol) in dry DME (33.5 mL) to the solution, the resulting solution was stirred at 80 °C for 10 h under a N_2 atmosphere, poured into water (10 mL), and then extracted with AcOEt. The organic layer was washed with water (200 mL) and dried with Na_2SO_4 . After the removal of solvent *in vacuo*, the material was chromatographed on silica gel (Wacogel C-300) using a gradient of hexane (50% $\rightarrow$ 66.7%) in CH_2Cl_2 as an eluent. In this way, 1.005 g of **1** was obtained in 83% yield. Because **1** is present as a mixture of conformation isomers at room temperature (Fig. S3 in ESI †), integration values for the ^1H NMR data were based on that (3H) of OMe signal of the anisole unit. ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ (ppm) 1.28 (s, 24H), 3.64 (s, 3H), 3.67 (s, 3H), 3.70 (s, 3H), 3.70 (s, 3H), 7.02 (td, 1H, $J = 7.45$ and 0.77 Hz), 7.03 (td, 1H, $J = 7.43$ and 0.80 Hz), 7.06 (td, 1H, $J = 7.53$ and 0.70 Hz), 7.09 (td, 1H, $J = 7.45$ and 0.72 Hz), 7.18 (d, 1H, $J = 8.90$ Hz), 7.19 (d, 1H, $J = 8.05$ Hz), 7.20 (d, 1H, $J = 9.55$ Hz), 7.23 (d, 1H, $J = 8.30$ Hz), 7.26–7.32 (m, 4H), 7.35 (dt, 1H, $J = 7.50$ and 1.80 Hz), 7.37–7.41 (m, 2H), 7.44 (d, 1H, $J = 7.60$ Hz), 7.49 (td, 2H, $J = 7.93$ and 1.57 Hz), 7.51 (td, 2H, $J = 7.93$ and 1.55 Hz), 7.55–7.59 (m, 2H), 7.59 (d, 2H, $J = 0.70$ Hz), 7.74 (d, 2H, $J = 8.20$ Hz), 8.14 (d, 2H, $J = 8.20$ Hz), 8.16 (d, 2H, $J = 8.25$ Hz), 8.71 (s, 1H), 8.71 (s, 1H); ^{13}C NMR (125 MHz, $\text{DMSO}-d_6$) δ (ppm) 24.55, 55.43, 55.46, 55.50, 55.57, 83.69, 111.4, 111.5, 111.6, 117.3, 117.4, 118.9, 119.1, 119.1, 119.3, 119.5, 119.8, 119.9, 120.0, 123.2, 125.3, 126.2, 129.5, 129.5, 130.3, 130.3, 131.1, 131.2, 131.3, 133.4, 133.7, 157.3, 157.4, 157.5; FAB MS: m/z 630 $[\text{M}]^+$; elemental analysis: calcd for $\text{C}_{37}\text{H}_{34}\text{B}_2\text{F}_2\text{N}_2\text{O}_4$: C, 70.51; H, 5.44; N, 4.44, found: C, 70.28; H, 5.50; N, 4.44.

2.4 Determination of fluorescence quantum yield

The fluorescence quantum yield (ϕ_{exp}) of **1** was calculated from the equation below.²⁴

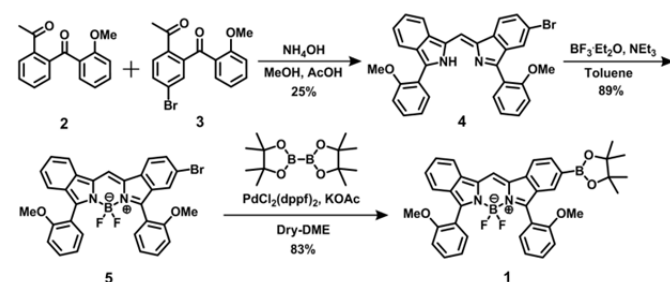
$$\phi_{\text{exp}} = \phi_r \times \frac{\int_0^\infty F(\lambda) d\lambda}{\int_0^\infty F_r(\lambda) d\lambda} \times \frac{A_r}{A} \times \frac{n^2}{n_r^2}$$

where $F(\lambda)$ and $F_r(\lambda)$ describe the measured fluorescence intensities of the dye and the reference, respectively, and A and A_r describe the corresponding absorbances at the excitation wavelength. Because Rhodamine B was used as the reference, the excitation wavelength was fixed at 535 nm. The refractive indexes are $n = 1.41$ for THF (solvent) and $n_r = 1.36$ for EtOH.

2.5 Vapor detection

An EtOH solution (7 μL) containing **1** (25 μM) and TBAOH (250 μM) was spin-coated on a TLC plate (2 (length) $\times$ 1.5 (width) cm, RP-modified silica plate, Merck) at a rate of 1500 rpm for 20 s and dried for 5 min. Various concentrations of H_2O_2 were obtained by diluting the commercial 35 wt% H_2O_2 solution with pure water, and these were then put in a bottle containing the sensing plate and then sealed for 24 h to reach saturated vapor pressure. The vapor concentration was determined by using the following equation; $y_{\text{H}_2\text{O}_2} = (Y_{\text{H}_2\text{O}_2} \times X_{\text{H}_2\text{O}_2} \times P_{\text{H}_2\text{O}_2})/P$, where y , Y , X , P , and $P_{\text{H}_2\text{O}_2}$ are defined as the molar fraction in the vapor phase, the activity coefficient, the molar fraction in the liquid phase, the vapor pressure of H_2O_2 (1.801 mmHg), and atmospheric pressure (1 atm), respectively.²⁵ Because a binary system of $\text{H}_2\text{O}/\text{H}_2\text{O}_2$ was employed as the solution, the activity coefficient of H_2O_2 was calculated from Margules' equation; $Y_{\text{H}_2\text{O}_2} = \exp[-1.2661 + 0.2932 \times X_{\text{H}_2\text{O}}]$.²⁶ In this way, the vapor concentration of H_2O_2 could be evaluated. In addition, saturated vapor concentrations of the commonly used solvents were evaluated according to the literature.²⁷

3. Results and Discussion



Scheme 1 Synthesis of **1**.

The synthetic route to **1** is shown in Scheme 1. First, the condensation reaction of 1-(2-(2-methoxybenzoyl)-phenyl)ethanone (**2**) with its bromo-derivative (**3**) in the presence of NH_4OH gave the monobrominated and benzo-fused dipyrin (**4**) in 25% yield after purification by column chromatography. This was followed by BF_2 -chelation with **4** using $\text{BF}_3 \cdot \text{Et}_2\text{O}$ to give **5**. A subsequent $\text{PdCl}_2(\text{dppf})_2$ -catalyzed pinacolboronation afforded target **1** in reasonable yield. Structural assignments of these compounds were conducted

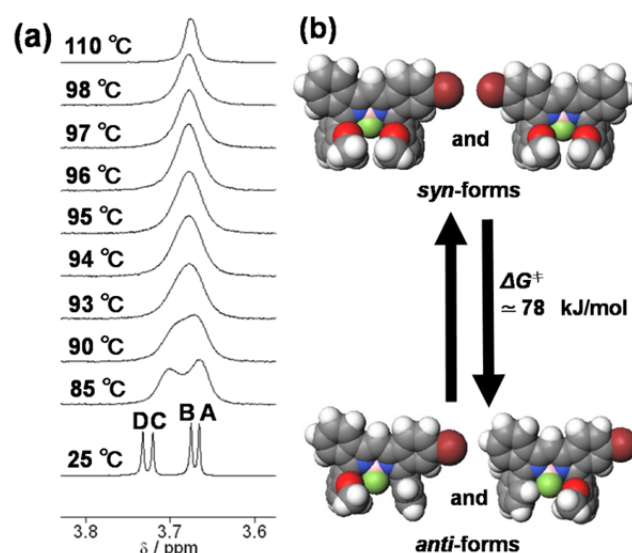


Fig. 1 (a) Variable temperature NMR of **5** in $\text{DMSO}-d_6$. (b) Proposed isomers of **5**.

using spectroscopic data, those ^1H NMR charts being shown in Figs. S1 – S4 in ESI†. In this context, the ^1H NMR spectra of **5** in $\text{DMSO}-d_6$ at room temperature are somewhat complicated (Fig. S2 in ESI†), containing four sets of signals assignable to the anisole segments; for instance, proton resonances arising from the methoxy groups were discretely observed as singlets at 3.665 (A), 3.675 (B), 3.720 (C), and 3.732 (D) ppm, respectively, (Fig. 1a). As inferred from our previous result,^{21c} one set of higher-field shifted signals (A, B) and another set of signals (C, D) would be assignable to either of the *anti*- and *syn*-forms of **5**, in which the anisole moieties are located on the opposite and same face of the dibenzopyrromethene core, respectively. Considering their unsymmetrical structures, each of *anti*- and *syn*-forms contains the corresponding unsymmetrical counterpart (Fig. 1b). To gain further insight into the structures, we recorded VT NMR spectra; with increases in the temperature of $\text{DMSO}-d_6$ solution of **5**, revealing a T_c value of 95 $^\circ\text{C}$ ($\Delta G^\ddagger = \text{ca. } 78 \text{ kJ mol}^{-1}$).²⁸ These results indicate that rotation about the two $\text{C}_{\text{anisole}}-\text{C}_{\text{isoindole}}$ bonds may be restricted by both the isoindole ring and BF_2 unit

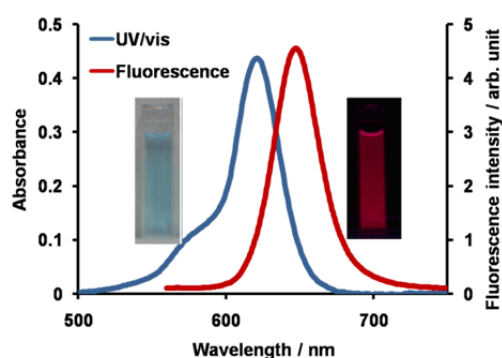


Fig. 2 Absorption and fluorescence spectra of **1** (5 μM) in THF at 25 $^\circ\text{C}$. The excitation wavelength was 550 nm.

in 5. A similar result was obtained for **1** (Figs. S3, S5, and S6 in ESI†). The absorption and fluorescence spectra were measured in a THF solution of **1** at 25 °C (Fig. 2), which showed an absorption with a λ_{max} value of 621 nm ($\epsilon = 8.74 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) and fluorescence bands ($\lambda_{\text{max}} = 643 \text{ nm}$, $\lambda_{\text{ex}} = 550 \text{ nm}$). In accordance with the optical properties, the solution is bluein color, although a red emission can also be detected. In addition, the quantum yield (Φ) of **1** was evaluated to be 0.21 against Rhodamine B ($\Phi_{\text{R}} = 0.97$)²⁹ when excited at 535 nm.³⁰

Encouraged by its optical properties, we investigated how **1** responds to the addition of H_2O_2 . First, the time-dependent responses of **1** toward H_2O_2 were examined by absorption and fluorescence spectrophotometries (Fig. 3). When adding H_2O_2 (500 μM) into an EtOH/ H_2O (1:1 v/v) solution of **1** (5 μM) at 25 °C, a slow kinetic change in the absorption spectra showed a bathochromic shift of 19 nm, with an isosbestic point at 635 nm. On the other hand, we observed a steep decrease in the fluorescent intensity at 643 nm, accompanied by a slight red shift in the band. The reaction product was successfully assigned as deboronated dye **6**³¹ through H_2O_2 -mediated oxidation (Scheme 2), with the ^1H NMR spectrum showing proton resonance arising from Ar-OH at 9.60 ppm (Fig. S8 in ESI†). A linear relationship was observed between the exponential decrease in the fluorescence spectra and the reaction time, giving a pseudo-first-order rate constant (k) of

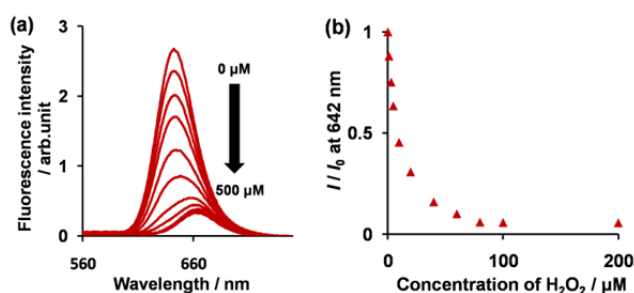


Fig. 4 (a) Change in the fluorescence of **1** (5 μM) upon adding incremental amounts of H_2O_2 in EtOH/ H_2O (1:1 v/v) in the presence of TBAOH (50 μM) at 25 °C. Each spectrum was acquired 2 min after the addition of H_2O_2 . (b) A plot of fluorescent intensity at 642 nm as a function of H_2O_2 concentration.

$7.7 \times 10^{-2} \text{ min}^{-1}$. This means that its fluorescence was decreased by 80% within 22 min after adding H_2O_2 . However, setting up basic conditions by adding TBAOH led to an acceleration of the reaction. The k value was calculated to be 1.69 min^{-1} , being 21-fold larger than that under TBAOH-free conditions. As a result, it took only 2 min to attain 80% decrease in the fluorescence after adding H_2O_2 .³² With this in mind, fluorometric titrations of **1** were carried out by adding incremental amounts of H_2O_2 in the presence of TBAOH (50 μM) in EtOH/ H_2O (1:1 v/v) at 25 °C, the data being collected within 2 min. Fig. 4 shows that the fluorescence intensities gradually reduced as a function of H_2O_2 concentration. No further change was observed when 80 μM of H_2O_2 was added to the solution. Given the relation between the fluorescence intensities and concentrations of H_2O_2 (Fig. 4b), this allowed us to determine a detection limit of 0.127 μM . Such a H_2O_2 -induced change in the optical properties could be detected by the naked eye, which was followed by the trajectory of Commission Internationale de l'Éclairage (CIE) coordinates in the chromaticity diagram. When irradiated under UV (365 nm) under a natural white fluorescent lamp in a laboratory, a red emission with CIE coordinates $x = 0.54$ and $y = 0.29$ of the solution shifted to a blue emission with CIE coordinates $x = 0.25$ and $y = 0.13$ upon adding H_2O_2 under basic conditions (Fig. 5). The image data are also shown in Fig. S10 in ESI†.

Our motivation in studying the possibility of using **1** as a fluorescent probe for vapor detection led us to test how **1** coated on a TLC plate could respond to the presence of H_2O_2 vapor. An EtOH solution of **1** (25 μM) and TBAOH (250 μM) was spin-coated on a RP-modified silica plate to fabricate a sensing plate, a bright red dot could be observed under UV light irradiation at 365 nm. As expected, when the plate was exposed to the H_2O_2 vapor, the red emission was quenched under UV light irradiation. The images upon H_2O_2 exposure were converted into red values (ΔR) using an image-processing program³³ to evaluate the fluorescence response of **1** to various concentrations of H_2O_2 . As inferred from Fig. 6a, the sensing plate could monitor H_2O_2 vapor at a level lower than 1 ppm. As such, the H_2O_2 vapor detection limit for the plate was evaluated to be 8.43 ppb, *i.e.*, lower than the value of the permissible exposure limit (OSHA).³⁴ For comparison, the **1**-coated plate was tested against the saturated vapor of common solvents such

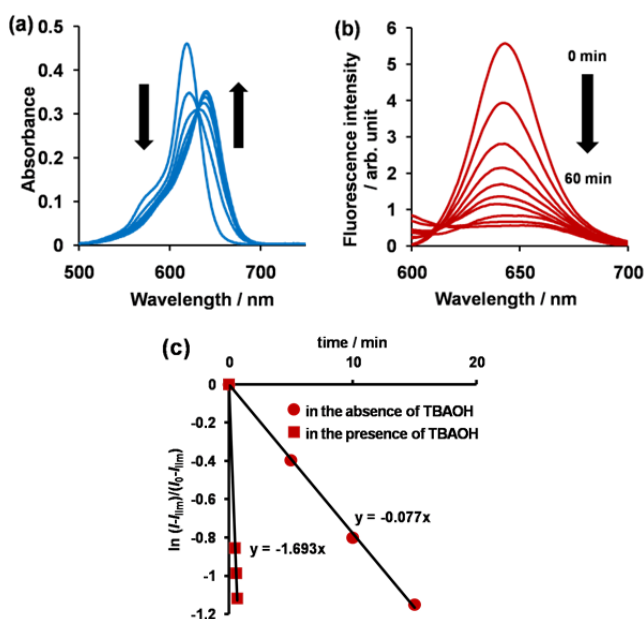
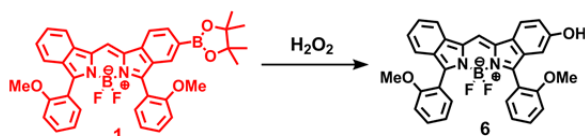


Fig. 3 Time course of absorption (a) and fluorescence (b) spectra of **1** (5 μM) in EtOH/ H_2O (1:1 v/v) at 25 °C, $\lambda_{\text{ex}} = 550 \text{ nm}$, and (c) a plot of $\ln[(I_0 - I_{\text{lim}})/(I - I_{\text{lim}})]$ at 642 nm as a function of time in the presence or absence of TBAOH (50 μM).



Scheme 2 H_2O_2 -mediated oxidation of **1** to give **6**.

as water (29000 ppm), toluene (34000 ppm), benzene (120000 ppm), hexane (180000 ppm), CHCl_3 (230000 ppm), and CH_2Cl_2 (440000 ppm). Contrary to the results obtained with H_2O_2 (300 ppm), a negligible response was obtained (Fig. 6b) with the other solvents. Taken together, we confirmed that the **1**-coated sensing plate exhibited a selective detection of H_2O_2 vapor over common solvents tested.³⁵

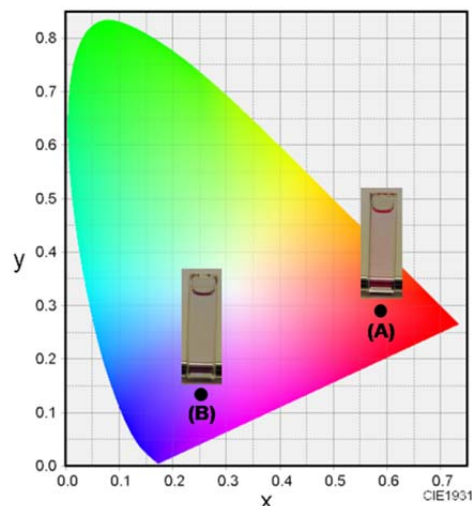


Fig. 5 The CIE coordinate diagram of the color of **1** (5 μM) (A) and **1** (5 μM) with H_2O_2 (80 μM) (B) in $\text{EtOH}/\text{H}_2\text{O}$ (1:1 v/v) in the presence of TBAOH (50 μM) at room temperature.

4. Conclusions

Our interest in exploring the functionality of a boron-dibenzopyrromethene dye led to the preparation of the corresponding pinacolboronyl derivative **1**. Taking advantage of the optical properties of **1**, we investigated its response to the presence of H_2O_2 , wherein the presence of H_2O_2 caused a significant decrease in the fluorescence of **1** due to the H_2O_2 -mediated oxidation of the pinacolboronyl unit. This change could also be detected visually. To the best of our knowledge, the **1**-coated TLC plate represents the first demonstrated example of BODIPY analogues being applied to the detection of H_2O_2 vapor.

5. Notes and references

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[†] Electronic Supplementary Information (ESI) available: Experimental data (Fig. S1 – S11). See DOI:10.1039/b000000x/

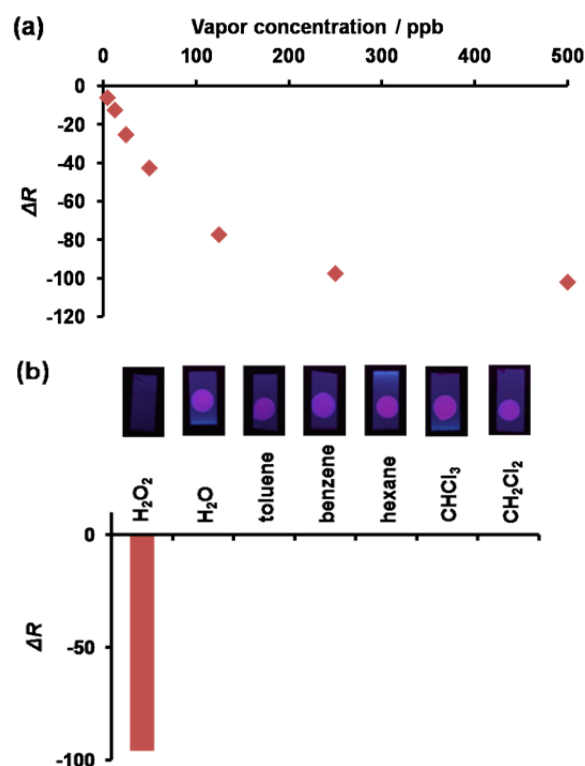


Fig. 6 (a) The emission response a **1**-coated TLC plate exposed to varying amounts of H_2O_2 vapor. (b) The emissive response of a **1**-coated TLC plate exposed to H_2O_2 and common solvents.

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32. As a control, time course of fluorescence spectra of **1** (5 μM) in the presence of TBAOH (50 μM) was measured in EtOH/H₂O (1:1 v/v) at 25 °C. Although, when excited at 550 nm, the fluorescent intensity at 642 nm was somewhat decreased within 30s, the intensity remained at 72% of the initial value (Fig. S9 in ESI†).
33. Image J was used as image-processing program.
34. Internet website of US-Occupational Safety & Health Administration (OSHA)
35. As a preliminary result, we found that saturated vapor of I₂ led to a decrease in fluorescence intensity of **1**, suggesting that **1** would be applicable to the detection of radioactive iodine-131.