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Colorimetric and Fluorescent Determination of Fluoride using a Novel Naphthalene Diimide Boronic Acid Derivative

Luis Ernesto Solís-Delgado

Centro de Graduados e Investigación en Química del Instituto Tecnológico de Tijuana, Tijuana,
México

Adrián Ochoa-Terán

Centro de Graduados e Investigación en Química del Instituto Tecnológico de Tijuana, Tijuana,
México

Anatoly K. Yatsimirsky

Facultad de Química, Universidad Nacional Autónoma de México, México

Georgina Pina-Luis*

Centro de Graduados e Investigación en Química del Instituto Tecnológico de Tijuana, Tijuana,
México

*Address correspondence to Georgina Pina-Luis. Tel: +52 664 6233772. Fax: +52 664 6234042.

E-mail: gpinaluis@tectijuana.mx; gpinaluis@yahoo.com

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Abstract

A new 1, 4, 5, 8-naphthalene diimide functionalized with two 3-phenylboronic acid groups (1) was prepared and employed as a selective sensor for fluoride. The proposed sensor is based on anion- π interactions between fluoride and naphthalene diimide core and the cooperative effect of boronic acid groups acting as Lewis acid anion receptors. The results show that the naphthalene diimide and boronic acid fragments participate in fluoride recognition. This modification significantly and positively affected the analytical response of the receptor. Interactions of 1 with fluoride were characterized by ultraviolet-visible, fluorescence, and nuclear magnetic resonance (NMR) spectroscopy. The influence of the boronic groups on the colorimetric and fluorescent properties was established by comparison with a non-functionalized aniline derivative. The sensor showed high selectivity in the presence of other anions. Colorimetric sensor 1 operated from 3.3×10^{-4} to 1.5×10^{-3} M with a detection limit of 3.6×10^{-4} M. The fluorescent sensor operated from 0 to 4×10^{-4} M allowing the measurement of 1.7×10^{-5} M. The results open the possibility of design and development of a new class of naphthalene diimide receptors based on cooperative effects.

Keywords: boronic acid, colorimetry, fluorescence, fluoride, naphthalene diimide

INTRODUCTION

Anions play an important role in chemistry, biology, and biotechnology. Accordingly, the detection and quantification of anionic species is important in many fields including clinical analysis (Jiao et al. 2015), food manufacturing (Grice et al. 2007), and environmental science (Boukhris et al. 2015). Fluoride is of interest because of use for tooth decay prevention (Van der Kaaij et al. 2015), biological assay (Goswami et al. 2014), in electrical transformers, industrial applications, and the human diet (Galvis-Sánchez, Santos, and Rangel 2013). An excess intake of

fluoride may lead to human disease. There are numerous methods for the determination of fluoride summarized in several recent reviews, which reflect current interest in this area (Galbraith and James 2010; Wade et al. 2010; Guo, Shin, and Yoon 2012; Zhou, Zhang, and Yoon 2014). Recently, a new principle of fluoride detection was discovered, which is based on unexpectedly strong and selective anion- π and charge/electron transfer supramolecular interactions of fluoride ions with π -electron-deficient colorless 1, 4, 5, 8-naphthalene diimides (Guha and Saha 2010; Guha et al. 2011; Guha et al. 2012). General properties of naphthalene diimides are provided by Bhosale, Janiab, and Langford (2008).

Strong electronic interactions between lone-pair electrons of F^- and π^* orbitals of the naphthalene diimide unit lead to a $F^- \rightarrow$ Naphthalene diimide electron transfer that produces the intensively colored naphthalene diimide radical anion. At higher F^- concentrations (>5 equivalents), further fluoride-promoted reduction of naphthalene diimide radical anion takes place to produce eventually naphthalene diimide radical dianion. The process is unique for fluoride that allows selective detection of this anion. Several naphthalene diimides derivatives with R = substituted phenyl, alkyl, or 4-pyridyl (Guha and Saha 2010; Guha et al. 2012; Li et al. 2014), its Pd(II) coordination polymer (Guha et al. 2012), amino acids (Jana et al. 2013) were reported as optical fluoride sensors. In this paper, we propose a new design principle for naphthalene diimide - based fluoride receptors where R contains a Lewis acid group capable of anion complexation. The presence of these groups is expected to increase the overall affinity of the receptor to anion as well as provide the binding cooperativity (dos Santos et al. 2008), potentially improving the selectivity and/or sensitivity of determination.

We selected the boronic acid group as the secondary binding site. Anion recognition by boronic acids and by other organoboron compounds occurs through donation of the anion

electron lone pair to the B(III) center, affording the respective tetrahedral adduct (Galbraith and James 2010; Wade et al. 2010; Guo, Shin, and Yoon 2012; Peters 2014). A number of anion receptors based on this interaction, typically selective for F^- , have been reported over the past decade (DiCesare and Lakowicz 2002; Koskela, Fyles, and James 2005; Kubo et al. 2005; Swamy et al. 2006; Thakur et al. 2012; Xue et al. 2012).

Previously water-soluble monoboronic acid functionalized N-phenyl-1, 8-naphthalene dicarboximides were reported as fluorescence sensors for saccharides (Cao, McGill, and Heagy 2004). In these as well as in other anion receptors (Gunnlaugsson et al. 2003; Gunnlaugsson et al. 2005; Ali, Kruger, and Gunnlaugsson 2008; Bhosale et al. 2009; Buckland, Bhosale, and Langford 2011; Lee et al. 2015), naphthalene diimides operate as a signaling moiety linked to the analyte recognition site through a suitable spacer. Here, we report a new naphthalene diimide, with two phenylboronic acid moieties capable of binding F^- through anion- π interactions between fluoride and the naphthalene diimide core and a Lewis acid-base interaction with the boronic acid groups as additional binding sites for the anions. The results show that naphthalene diimide and boronic acid fragments both participate in fluoride recognition. As far as we know, this type of receptor with two additional anion-binding boronic acid groups into the same naphthalene diimide has never been explored previously. We demonstrated that such modification significantly and positively affects the analytical response of the receptor. The sensor displays highly selectivity to fluoride in the presence of halides and other anions. The sensor operates in concentration ranges that depend on the detection method. The novelty is based on the operation of the naphthalene diimide as the signaling and a recognition site in cooperation with an additional for recognition.

MATERIALS AND METHODS

Reagents and Instrumentation

All reagents were purchased from Aldrich in the highest quality available and used without purification. All solvents were HPLC grade. Infrared spectra were obtained using a Perkin Elmer Fourier transform 1600 spectrophotometer. ^1H (at 200 MHz) and ^{13}C (at 50 MHz) nuclear magnetic resonance (NMR) spectra were recorded on a Varian Mercury 200 MHz spectrometer and on a Bruker Avance III HD 400 MHz in CDCl_3 and dimethyl sulfoxide- d_6 with tetramethylsilane as the internal standard. Fluorescence measurements were performed using a Horiba Jobin Yvon Model NanoLog Spectrofluorometer using a 10 mm quartz cell. Ultraviolet-visible absorptions measurements were performed using a Varian Cary 300 spectrophotometer utilizing a 10 mm quartz cell.

Synthesis of Receptor Compounds 1 and 2

The boronic acid receptor **1** was synthesized using 1, 4, 5, 8-naphthalenetetracarboxylic dianhydride and 3-aminophenylboronic acid. For comparison, a non-functionalized receptor **2** was prepared from aniline. **Figure 1** shows the synthetic route to obtain these receptors.

In a 100 mL round bottom flask, 2 mmol of 3-aminophenylboronic acid or aniline were added to 1 mmol of 1, 4, 5, 8-naphthalenetetracarboxylic dianhydride in dimethylformamide with constant stirring and refluxing for 3 h. Water was added to the hot solution to precipitate the product and the solution was stored at 4°C for 2 h. The precipitate was filtered and dried at room temperature.

Characterization of Compound 1: Gray solid, 0.040 g, 0.320 mmol, 32% yield. Infrared: 3625, 3463, 3200, 3068, 1706, 1653 cm^{-1} . ^1H NMR (dimethyl sulfoxide- d_6 , 200 MHz): 8.72 (s, 4H), 8.21 (s, 2H), 7.92 (d, $J= 5.8$ Hz, 2H), 7.79 (s, 2H), 7.52 (m, 6H). ^{13}C NMR

(dimethyl sulfoxide- d_6 , 50 MHz): 163.1, 134.9, 134.5, 134.2, 130.6, 130.5, 128.2, 127.0, 126.7.

ESI-MS: 507[M+H]⁺.

Characterization of Compound 2. Brown solid, 0.056 g, 0.450 mmol, 45% yield. Infrared: 3367, 3070, 1977, 1709, 1658 cm⁻¹. ¹H NMR (dimethyl sulfoxide- d_6 , 200 MHz): 8.73 (s, 4H), 7.52 (m, 10H). ¹³C NMR (dimethyl sulfoxide- d_6 , 50 MHz): 163.4, 136.1, 130.9, 129.5, 129.4, 128.9, 127.5. ESI-MS: 419 [M+H]⁺.

Detection Limit for Fluoride

Following IUPAC recommendations, the detection limit was obtained using the equation $3S_{bl}/m$, where S_{bl} is the standard deviation of the blank signal for ten measurements and m is the slope of the calibration curve.

Anion Titrations

Ultraviolet-visible and fluorescence titrations were performed by adding successive amounts of 2 microliters of the stock solution of anions to a known volume (typically 3 mL) of the ligand solution (5×10^{-5} M). The addition was limited to 0.06 mL, so that dilution remained insignificant.

¹⁹F NMR Titrations

¹⁹F NMR experiments were performed by adding successive amounts of 5 microliters of the stock solution of compound **1** to a known volume (500 microliters) of the tetrabutylammonium fluoride (5 mM). The addition was limited to 0.05 mL.

RESULTS AND DISCUSSION

Synthesis of Receptors

The receptors **1** and **2** were synthesized in 32% and 45% yields, respectively, under relatively mild conditions, by the methodology outline in Scheme 1. The synthetic route is a one-step reaction between two equivalents of the corresponding arylamine with one equivalent of the 1, 4, 5, 8-naphthalenetetracarboxylic anhydride in dimethylformamide. The compounds were precipitated adding water to the hot reaction, stored at 4°C, and filtered to give a gray and brown solid. The synthesized receptors were characterized by infrared spectroscopy, ¹H and ¹³C NMR, and mass spectrometry.

Optical Properties

The ultraviolet-visible and fluorescence spectra of **1** and **2** were nearly identical. The absorption spectra show sharp peaks in the near ultraviolet at 362 and 382 nm due to characteristic π - π^* transitions of naphthalene diimides core. The absorption spectrum of **1** is shown in **Figure 2** (black line). The emission spectra of **1** and **2** show two principal emission bands at 408 nm and 436 nm that correspond to the mirror image of the absorption and fluorescence spectra with a 25 nm Stokes shift. The fluorescence spectrum of **1** with excitation at 362 nm (red line in **Figure 2**) shows an additional emission band at 530 nm as a shoulder. Such additional red-shifted emission band was reported for several naphthalene diimide N-phenyl derivatives and was attributed to a twisted conformation of the molecule with N-phenyl groups coplanar with the naphthalene diimide core (Demeter et al. 1996; Cao, McGill, and Heagy 2004). The intensity of this band depends strongly on the substituents and solvent polarity. On the other hand, similar long wavelength emission was attributed to an excimer formation favored by low polar solvents (Andrich et al. 2004; Kumar and George 2011). An intense emission band at

550 nm was observed with excitation at 475 nm (blue line in **Figure 2**). Similar emission was observed for naphthalene diimide amino acid derivatives (Jana et al. 2013), although the nature of the respective electronic transition is not clear.

^1H NMR and ^{19}F NMR Titrations

The interaction of **1** with F^- was studied by ^1H and ^{19}F NMR measurements in deuterated dimethyl sulfoxide. **Figure 3** shows the changes in the chemical shifts of **1** in the absence and in the presence of increased amounts of fluoride. The ^1H NMR spectrum of **1** reveals a singlet at 8.72 ppm corresponding to four identical naphthalene diimide core protons H_a , a peak at 8.13 ppm which belongs to $\text{B}(\text{OH})_2$ groups (H_f), and an aromatic region at 7.4 to 7.9 that correspond to the side chain phenyl protons. The charge transfer interaction generating naphthalene diimide radical leads to disappearance of core proton NMR signals (Guha and Saha 2010; Guha et al. 2012). A strong decrease in intensity of the H_a signal was observed. However, this signal does not disappear completely even in the presence of 2 equivalents of fluoride due to incomplete complexation of the receptor core. The signal of $\text{B}(\text{OH})_2$ groups initially exhibits a small downfield shift and then disappeared as observed in the titration of phenylboronic acid with tetrabutylammonium fluoride in dimethyl sulfoxide (Martínez-Aguirre and Yatsimirsky 2015). The aromatic signals of boronic acid fragment also showed a pattern similar to observed for phenylboronic acid (Martínez-Aguirre and Yatsimirsky 2015). The possibility of the formation of a covalent bond C-F was ruled out, since the H_a signal never split, which would have indicated a loss of symmetry. Thus, the NMR titration data reveal the simultaneous interactions of fluoride with both naphthalene diimide core and boronic acid fragments. The complex pattern of the signals of boronic acid protons indicates formation of an unsymmetrical anion-receptor complex with different degrees of complexation at the two boronate groups.

The ^{19}F NMR spectrum of tetrabutylammonium fluoride in deuterated dimethyl sulfoxide shows a singlet at -102 ppm corresponding to free fluoride. Addition of 1 equivalent of **1** caused the disappearance of this signal and the appearance of a new weak signal at -133.71 ppm which may be attributed to the formation of an $-\text{B}(\text{OH})_2\text{F}^-$ adduct (Martínez-Aguirre and Yatsimirsky 2015). This behavior is consistent with the high degree of formation of free radical F^\cdot lacking the NMR signal (Guha and Saha 2010; Guha et al. 2012) as a result of electron transfer from the electron-donating F^- ions to the naphthalene diimide core that generates naphthalene diimide boronic acid radical simultaneously with addition of a fraction of fluoride ion to boronic acid groups.

Determination of Fluoride by Ultraviolet-visible Titrations

Titrations of **1** and **2** with tetrabutylammonium fluoride were performed in dimethyl sulfoxide. The characteristics of both receptors toward fluoride were investigated by ultraviolet-visible spectroscopy. Upon the gradual addition of fluoride anion to the receptors, a new set of highly red shifted peaks at 475 and 605 nm appeared. **Figure 4** show the change in the absorption spectra of **1** following the addition of fluoride from 0 to 2.12 mM. Similar spectral changes were observed with **2**. Absorption titration profiles of **1** and **2** versus concentration of fluoride at 474 nm show a strong enhancement of the absorption signal for receptor **1** containing the boronic acid groups as compared to **2**, as shown in the inset in **Figure 4**. Considering that the bands of radical species increase after adding excess tetrabutylammonium fluoride to **1** more significantly than in **2**, it may be concluded that the anion- π interactions upon addition of fluoride ions are enhanced by a cooperative effect due to fluoride binding to the boronic groups.

Determination of Fluoride by Fluorescence Titrations

The determination of fluoride by **1** and **2** were also characterized by fluorescence titrations, which demonstrated stronger effects of the boronic acid group. The effect of fluoride on the fluorescence of receptor **1** shows significant fluorescence enhancement of emission at 430 nm with excitation at 362 nm (**Figure 5**) and a significant quenching of emission at 550 nm with excitation at 475 nm (**Figure 6**). In contrast, fluoride caused a small quenching on the fluorescence of aniline derivative **2** (not shown).

Since the effect was stronger for the emission at 550 nm, we believe that the role of boronate group is a conformational effect induced by the binding of fluoride to this group. The B(OH)₂ group as a substituent possesses weak electron-acceptor properties (Hansch, Leo, and Taft 1991). However, binding of fluoride causes conversion into an anionic B(OH)₂F⁻ group with strong electron-donor properties (Berionni et al. 2013). Apparently this donor effect increases the conjugation of the phenylboronic group with strongly electron accepting naphthalene diimide core which stabilizes the coplanar conformer emitting at 550 nm.

Table 1 summarizes the analytical characteristics of **1** as ultraviolet-visible and fluorescence sensors for the determination of fluoride. The fluorescent sensor provides better sensitivity than colorimetric sensor.

Interferences

The selectivity of probe **1** towards fluoride ions was investigated by observing the changes in the absorbance at 475 nm by the addition of 0 to 50 equivalents of Cl⁻, Br⁻, I⁻, NO₃⁻, acetate, benzoate, and H₂PO₄⁻. Only changes were observed in the absorption signal in the presence of fluoride ions. Amongst all the analytes tested, probe **1** was found to be highly selective for fluoride ions.

CONCLUSIONS

A new naphthalene diimide derivative with two boronic acid groups was synthesized and successfully used as a selective sensor for fluoride. The colorimetric signal involves anion- π formation between fluoride and the naphthalene diimide core with two boronic groups acting as cooperative binding sites for the analyte. The fluorescence process involves the stabilization of a planar conformer by complexation of fluoride to boronic acid groups. The results open the possibility to develop a new class of sensors based on these cooperative effects.

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Table 1. Detection limit, linear range, regression equation, correlation coefficient of the sensor 1 for absorption and fluorescence

Detection method	Detection Limit (μM)	Correlation Coefficient	Linear Dynamic Range (μM)	Calibration relationship
Fluorescence with excitation at 475 nm and emission at 545 nm	17	0.996	0–400	$Y = (2.98 \pm 0.02) \times 10^6 - (3.54 \pm 0.06) \times 10^3 [\text{F}^-]$
Fluorescence with excitation at 362 nm and emission at 530 nm	18	0.994	0–230	$Y = (2.77 \pm 0.06) \times 10^5 + (1.01 \pm 0.05) \times 10^3 [\text{F}^-]$
Absorption at 475 nm	360	0.997	330–1500	$Y = -0.023 \pm 0.003 + (1.13 \pm 0.03) \times 10^{-4} [\text{F}^-]$

Figure 1. Synthesis of naphthalene diimides.

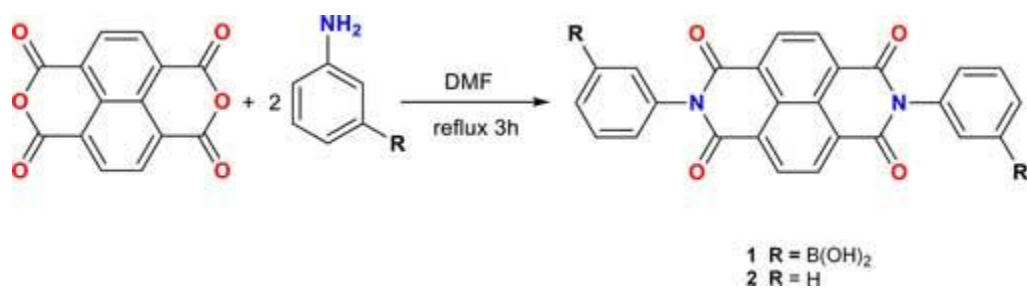


Figure 2. Absorption and emission spectra of 1 in dimethyl sulfoxide. The concentration ratio was 1:50 μM for absorption (black line) and for fluorescence with excitation at 475 nm (blue line); 10 mM for fluorescence with excitation at 362 nm (red line).

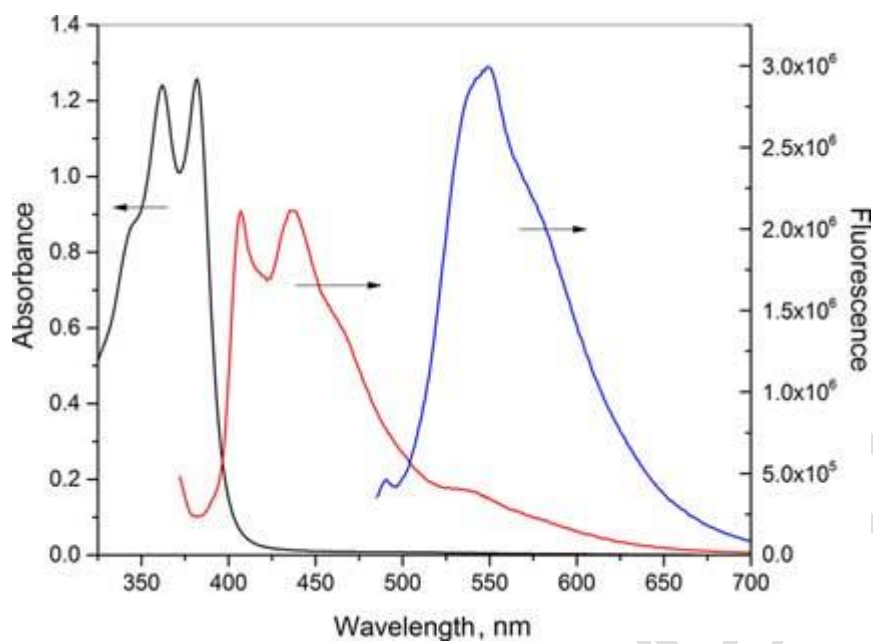


Figure 3. ^1H NMR spectra of 5 mM of **1** in deuterated dimethyl sulfoxide at 303 K (bottom spectrum) in the presence of increased fluoride as the tetrabutylammonium salt.

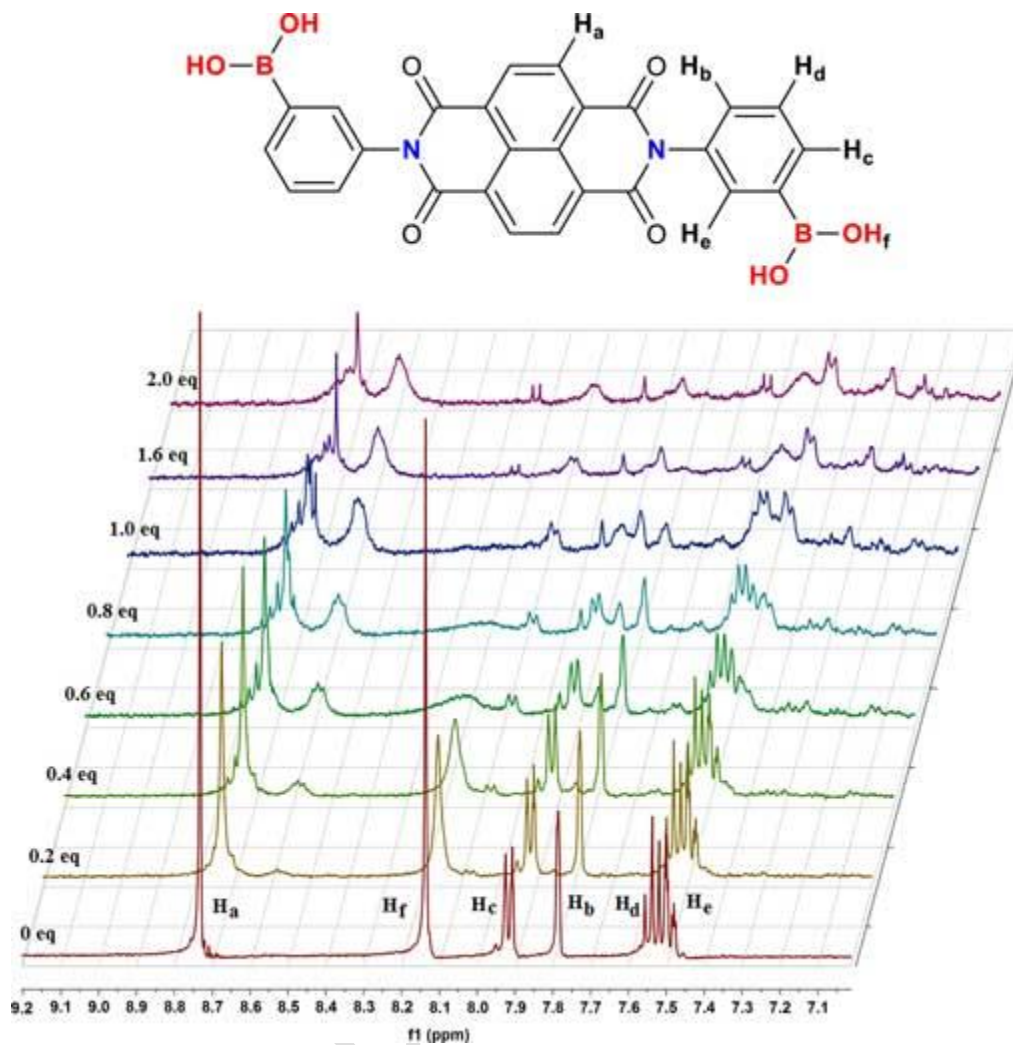


Figure 4. Absorption titration spectra of **1** (50 μM) following the addition of fluoride as the tetrabutylammonium salt in dimethyl sulfoxide. Inset: absorption titration profiles of **1** and **2** as a function of the concentration of fluoride at 474 nm.

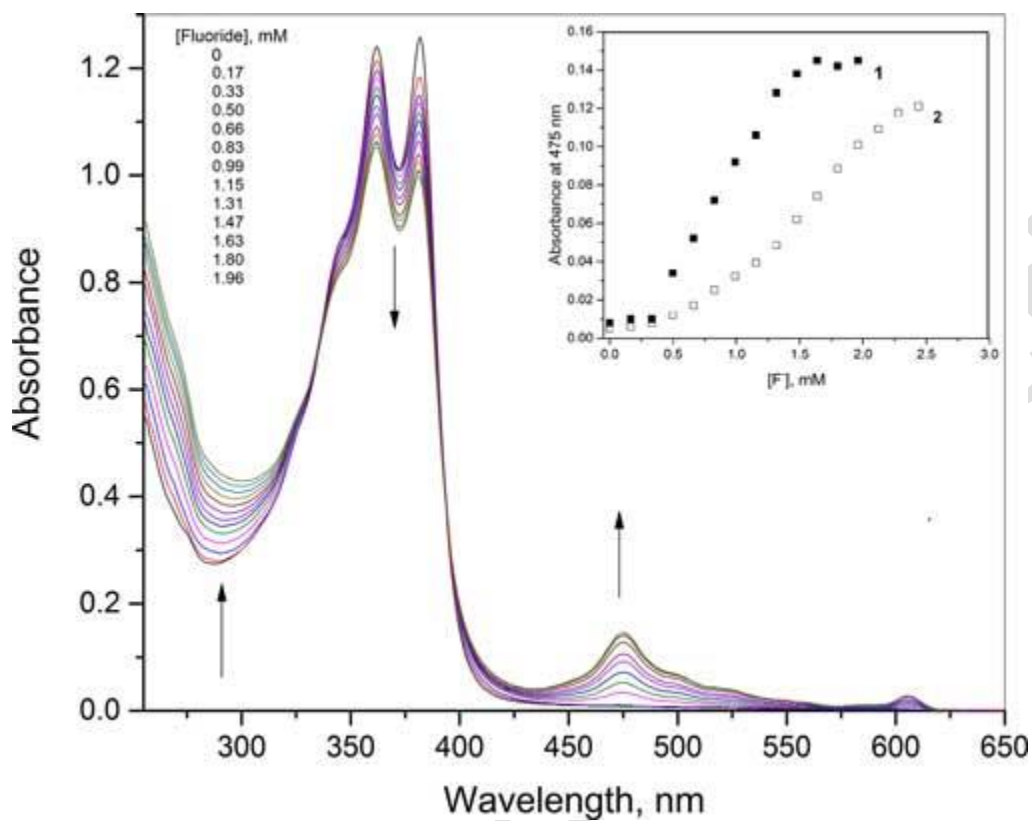


Figure 5. Fluorescence spectra of 1 (50 μM) in dimethyl sulfoxide with excitation at 362 nm following the addition of fluoride as the tetrabutylammonium salt. The arrow indicates the direction of spectral changes.

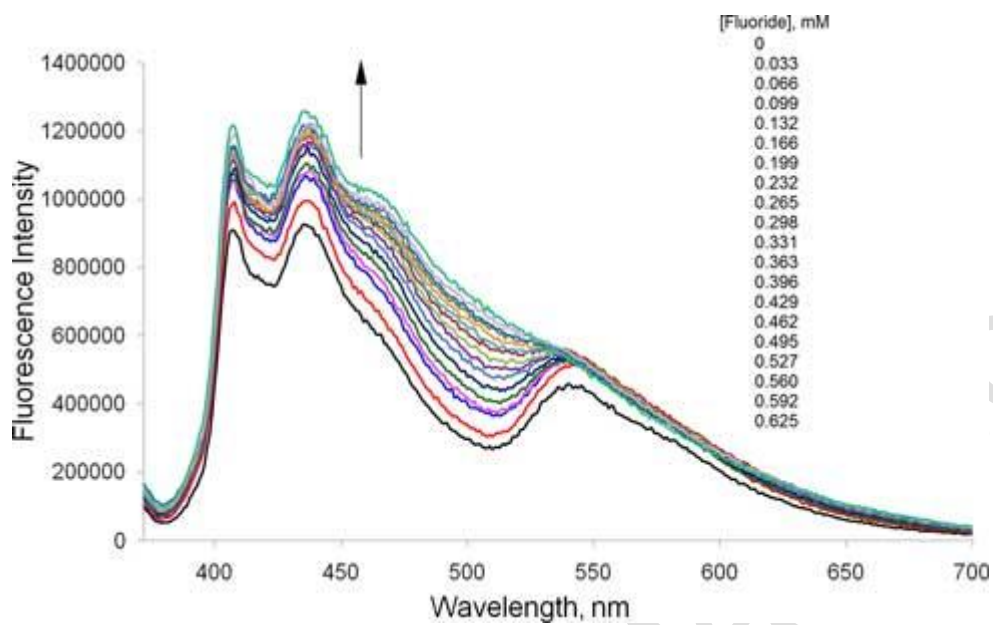


Figure 6. Fluorescence spectra of 1 (50 μM) in dimethyl sulfoxide with excitation at 475 nm following the addition of fluoride the tetrabutylammonium salt. The arrow indicates the direction of spectral changes.

