

# Optical Fluoride Sensing with a Bay Region Functionalized Perylenediimide Dye

Funda YUKRUK<sup>1,2</sup>

<sup>1</sup>*Department of Chemistry, Middle East Technical University, 06531, Ankara-TURKEY*

<sup>2</sup>*Department of Chemistry, Balıkesir University, 10145, Balıkesir-TURKEY*

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A perylenediimide (PDI) derivative functionalized at the perylene core (bay region) to carry phenyl boronic acid groups was shown to interact with fluoride with changes in the emission and absorption spectrum. These changes are most likely due to fluoride-induced aggregation and/or quenching of the perylenediimide dye. The dye is also selective; among halide ions, fluoride anions generate a significant response. Thus, this class of PDI derivatives is likely to be useful in practical fluoride sensing.

**Key Words:** Chemosensor, fluorogenic sensors, chromogenic sensors, fluoride sensing, supramolecular chemistry.

## Introduction

The perylene-3,4:9,10-tetracarboxydiimide class of dyes are known to have remarkable properties like high photostability and high fluorescence quantum yield<sup>1</sup>, and as a result they have found many practical applications like as dichroic dyes, organic photoconductors and fluorescent collectors<sup>2–6</sup>. Their synthesis is straightforward: the reaction of tetracarboxylic acid anhydride with either aliphatic or aromatic primary amines yields corresponding diimide dyes in good yield. One disadvantage of these dyes is their low solubility and aggregation tendency in solutions. Various modifications of the parent structure yielded improved solubility characteristics<sup>7–9</sup>. Most important among these is the substitution at the bay region, positions 1, 6, 7 and 12 of the perylene core. Even then, fluorescence-sensing applications of this class of dyes are rare. In our laboratory, my collaborators' work is directed towards the development of novel chemosensors that operate at the long wavelength region of the visible spectrum<sup>10–15</sup>; they find these dyes to possess great potential in this regard as well.

Boronic acid derivatives, on the other hand, are known to interact with vicinal diols, and this was recognized by Czarnik<sup>16</sup> as a path for signaling opportunities in 1992. Later, a number of fluorescent chemosensors appeared based on this reversible esterification<sup>17–19</sup>. Recently, it was also shown that the boron center in boronic acids changes the hybridization state from  $sp^2$  to  $sp^3$  by the coordination of fluoride ions, and this change was exploited in the design of many fluorogenic or chromogenic sensors for fluoride<sup>20–22</sup>. In this study, I wanted to combine the advantages of perylenediimide dyes with the selective interaction of

boronic acids with fluoride in a perylenediimide-boronic acid derivative. Progress towards anion sensing in general was reviewed recently<sup>23</sup>.

## Experimental

### Materials and Methods

All chemicals and solvents were purchased from Aldrich and used without further purification. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded using a Bruker DPX-400 in CDCl<sub>3</sub> or DMSO-d<sub>6</sub> with TMS as internal standard. Absorption spectrometry was performed using a Shimadzu-1600PC spectrophotometer. The fluorescence spectra were recorded on a Perkin-Elmer 50B spectrofluorometer. Column chromatography of all products was performed using Merck Silica Gel 60 (particle size: 0.040-0.063 mm, 230-400 mesh ASTM) pretreated with eluant. Reactions were monitored by thin layer chromatography using fluorescent-coated aluminum sheets (20 x 20 cm). Elemental analyses and mass spectrometry were performed by the TÜBİTAK Elemental Analysis Laboratory, Ankara, Turkey.

### Synthesis of the phenoxy-derivative **3**

1,7-Dibromoperylene-tetracarboxylic acid dicyclohexylimide (**1**) was prepared according to the patent literature<sup>7</sup>. Fifty-five milligrams of **1** (0.077 mmol) was suspended in 8 mL of NMP. To this stirred suspension K<sub>2</sub>CO<sub>3</sub> (20 mg, 0.140 mmol) and phenol (24 mg, 0.253 mmol) were added, and this mixture was stirred for 48 h under argon atmosphere at 80 ° C. Then the mixture was cooled to room temperature and a 250 mL methanol-HCl mixture was added (100 mL 10% HCl and 150 mL methanol) and stirred for 2 h. The solution was filtered and dark purple precipitate washed with a methanol/water solution (60/40, v/v) and dried under vacuum at 100 ° C. The yield was 56 mg (96% ) in the form of a purple powder.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm), 1.05-1.50 (m, 6H), 1.69-1.75 (m, 6H), 1.82-1.91 (m, 4H), 2.44-2.52 (m, 4H), 4.93-4.98 (m, 2H), 7.08-7.41 (m, 10H), 8.21 (s, 2H), 8.49 (d,  $J=8.4$  Hz, 2H), 9.56 (d,  $J=8.4$  Hz, 2H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ (ppm) 24.8, 28.1, 31.0, 53.5, 112.9, 117.6, 121.9, 122.5, 123.1, 124.2, 126.8, 128.5, 130.5, 131.0, 131.2, 131.3, 150.1, 157.0, 159.2

### Synthesis of the boronic acid derivative **4**

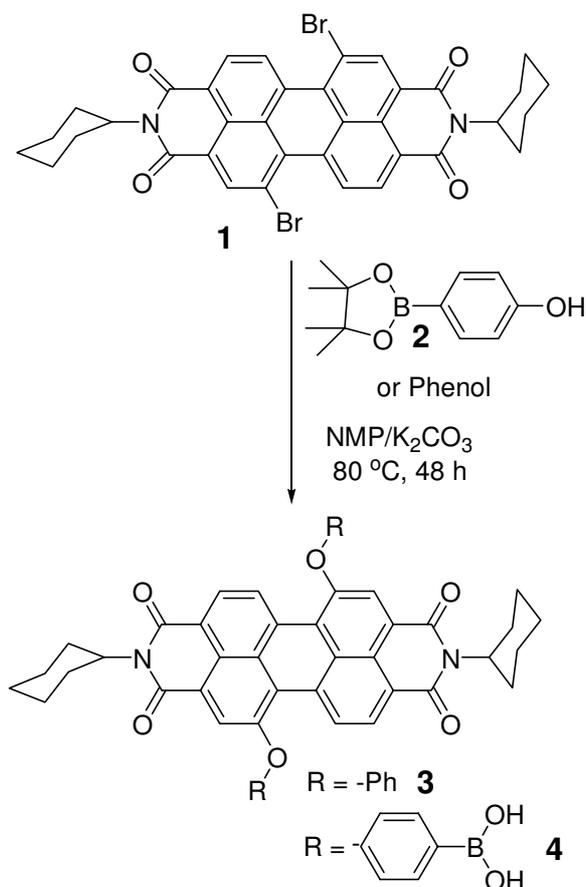
1,7-Dibromoperylene-tetracarboxylic acid dicyclohexylimide (**1**) (22.6 mg, 0.032 mmol) was suspended in 5 mL of NMP. To this stirred suspension K<sub>2</sub>CO<sub>3</sub> (7.33 mg, 0.053 mmol) and **2** (23.1 mg, 0.105 mmol) were added, and this mixture was stirred for 48 h under argon atmosphere at 80 ° C. Then the mixture was cooled to room temperature and a 250 mL methanol-HCl mixture was added (100 mL 10% HCl and 150 mL methanol) and stirred for 2 h. The solution was filtered and dark purple filtrate washed with a methanol/water solution (60/40, v/v) and dried under vacuum at 100 ° C. The yield was 25 mg (95% ) in the form of a purple powder.

<sup>1</sup>H NMR (400 MHz, CHCl<sub>3</sub>),  $\delta$  (ppm), 1.05-1.50 (m, 6H), 1.69-1.75 (m, 6H), 1.82-1.91 (m, 4H), 2.44-2.52 (m, 4H), 4.93-4.98 (m, 2H), 6.85 (d,  $J=8.7$  Hz, 4H), 6.97 (d,  $J=8.7$  Hz, 4H), 8.19 (s, 2H), 8.49 (d,  $J=8.4$  Hz, 2H), 9.56 (d,  $J=8.4$  Hz, 2H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm), 24.9, 28.0, 31.1, 53.6, 112.8, 117.5, 120.5, 122.5, 123.0, 124.2, 125.1, 126.7, 131.0, 133.6, 150.1, 152.1, 157.0. For  $\text{C}_{48}\text{H}_{40}\text{B}_2\text{N}_2\text{O}_{10}$ , calcd.: C 69.76, H 4.88, N 3.39%, found: C 69.94, H 4.82, N 3.47. EI-MS 826.3 ( $\text{M}^+$ ).

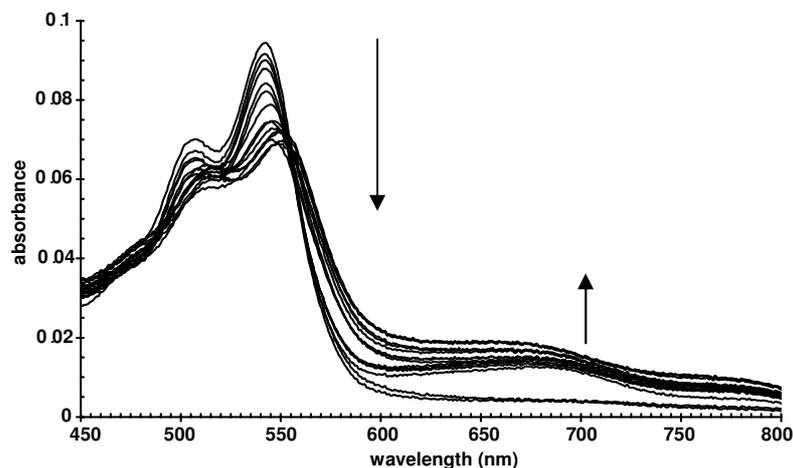
## Results and Discussion

The protected phenol-boronic acid was reacted with the dibromoperylene diimide (**1**) in NMP (Scheme). During the aqueous work-up steps, the protecting group was also removed. The product is soluble in a number of organic solvents, including THF. The anion binding studies were carried out in THF as it was a common solvent for both the tetrabutylammonium salts of the anions tested and the boronic acid derivative. The absorbance spectrum of the dye shows a typical PDI spectrum with 2 peaks (505 and 550 nm) and a shoulder (470 nm). The addition of fluoride ions results in a decrease in the absorption peak (mostly at 550 nm) and together with this decrease a broad peak (680 nm) and a shoulder (at 780 nm) appear (Figure 1). Similar changes were observed with acetate and to a much smaller extent with bromide and chloride (Figure 2). Iodide, not surprisingly, did not cause any changes at the concentration range studied (0-0.1 mM). The emission spectrum showed parallel changes: the addition of fluoride in the form of tetrabutylammonium salt resulted in a significant drop in the emission intensity. The change in the emission intensity at 540 nm demonstrates the highly selective nature of the interaction between fluoride anions and the boronic acid

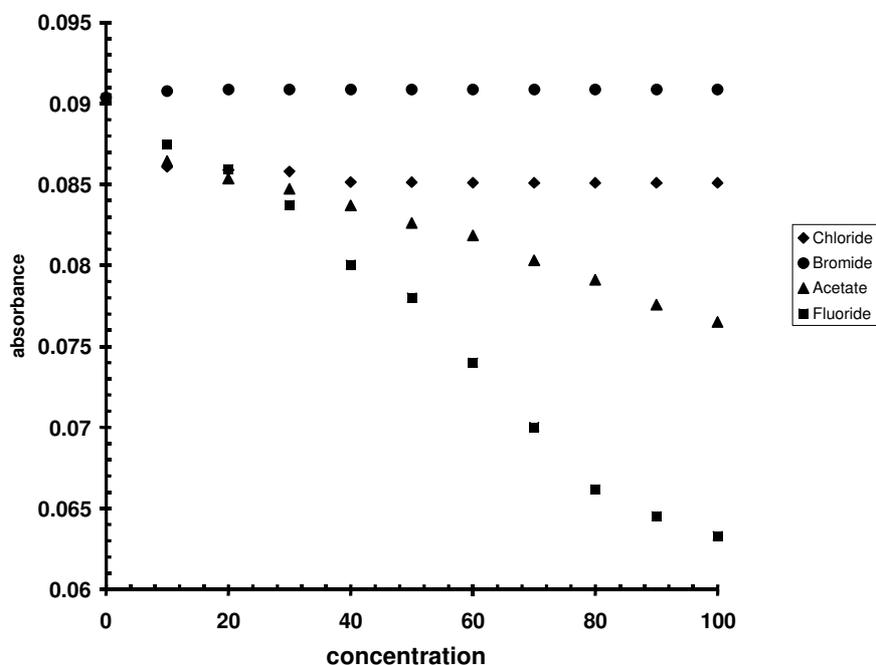


**Scheme.** Synthesis of the boronic acid derivatives used in this study.

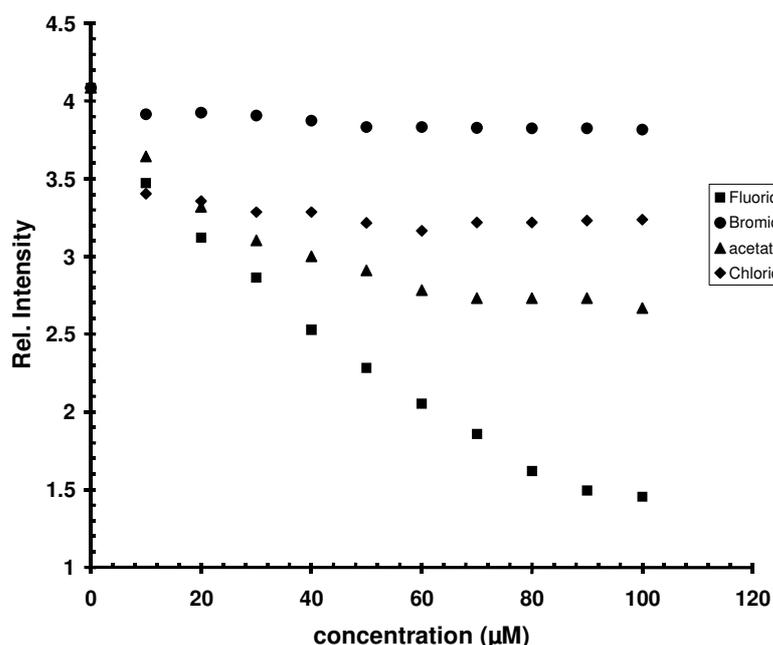
functionalities (Figure 3). In order to confirm the participation of boronic acid groups in the apparent fluoride signaling, diphenoxy derivative **3** was also synthesized. This compound lacks boronic acid moieties, and thus we did not expect significant changes in the absorption and emission spectra. Just as expected, tetrabutylammonium fluoride at a concentration of 100  $\mu\text{M}$  caused only minor changes in the spectra.



**Figure 1.** Absorption spectrum of compound **4** (1.4  $\mu\text{M}$ ) in THF on the addition of increasing amounts of tetrabutylammonium fluoride. The concentrations were varied as follows: 0, 10, 20, 30, 40, 50, 60, 80, 90, 100, 200, 300, 400, 500  $\mu\text{M}$ .



**Figure 2.** The change in the absorbance of **4** (1.4  $\mu\text{M}$ ) at 542 nm on the addition of indicated anions at increasing concentrations. The solvent is THF.



**Figure 3.** The change in emission intensity (at 560 nm) of 1.4  $\mu\text{M}$  **4** in THF, on the addition of various anions. Excitation wavelength was 490 nm.

## Conclusion

It was demonstrated that perylenediimide derived boronic acid **4** interacts with the strong Lewis base fluoride to cause changes in both the absorption spectrum and the emission spectrum. The changes appear to result from an alteration of the hybridization state and anion induced aggregation of the dye. I think, with further rational derivatization of the perylenediimide core, fluorogenic and chromogenic sensors of improved properties are likely to appear. My own work along these lines is in progress.

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