



Chemodosimeter approach: Selective detection of fluoride ion using a diketopyrrolopyrrole derivative



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ABSTRACT

A diketopyrrolopyrrole derivative was synthesized and designed with two trimethylsilyl groups to allow for sensitive, selective and fast recognition of fluoride ions by using a chemodosimeter approach. The probe exhibited a blue shift in the absorption and emission spectra in the presence of fluoride ions due to deprotection of the electron donating trimethylsilyl groups in the probe. UV–vis absorption, fluorescence, density functional theory and cyclic voltammetry studies indicated fluoride triggered cleavage of the Si–C bond resulting in the blue spectral shift.

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1. Introduction

Selective recognition of key anions that have biological importance has gained significant attention because of the vital roles they play in both biotic functions and industrial processes [1–4]. Among the various anions (i.e. fluoride, chloride, cyanide and phosphate), fluoride (F^-) ions are of great interest because of their well-known application in dental cavity prevention and osteoporosis treatment [5–11]. However, fluoride present in drinking water is highly toxic when its concentration exceeds the maximum permissible level, 1.0–4.0 mg L^{-1} [standard regulated by the United States Environmental Protection Agency (EPA)] [12,13] therefore, a precise determination of the F^- levels in drinking water is mandatory. Thus, the scientific community is interested in new fluorescent probes for F^- detection that are highly sensitive, differentiating, fast, and dynamic in either completely aqueous or partially.

Until now, a variety of fluorescent molecular probes for F^- detection have been designed and characterized. Most of them are based on either a hydrogen, Lewis acid coordination or a chemodosimeter approach [14–27]. The probes promote hydrolysis of silyl ethers, i.e., *tert*-butyldimethylsilyl (TBDMS) and *tert*-butyldiphenylsilyl (TBDPS) via cleavage of the Si–O bond. This occurs not only

because the probes are derivatives of pyrenes, boron-dipyrromethene (BODIPY), naphthalimides, resorufin, and coumarins, but also because of the chemical affinity of fluoride for silicon [28–33].

A class of brilliant red high performance pigments exist, for example, diketopyrrolopyrrole (DPP) [34–36], which exhibit exceptional light, weather, and heat stability, and gives yellow fluorescent solution. These pigments are widely used in electronic/optoelectronic materials like organic semiconductors, photovoltaics [37–40], and two photon absorption materials [41–45] while, their ability to recognize the biologically important species are less studied. Recently, many research groups reported progress in the development of DPP-containing fluorescent probes, and they investigated their applications in selective detection of thiols, Zn^{2+} and cyanide [46–49]. There are only a few reports in the literature on the F^- detection using DPP derivatives. The first reports by Tian et al. and Qu et al., described a DPP-based fluorescent chemosensor for fluoride. The detection mechanism was ascribed to an intermolecular proton transfer between the hydrogen atom at the *N*-position on the lactam ring in the DPP moiety and the fluoride ion [50,51]. Later, Wang et al. synthesized a DPP derivative bearing a boronate group for fluoride ion detection based on the unique fluoride boron interaction [52]. Yet another report by Lin et al. was based on a DPP-[2]rotaxane derivative for selective optical sensing of F^- [53]. From these reports, it was concluded that derivatization of the DPP unit may provide a suitable receptor that is capable of interacting with both anions and cations.

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Recently, we reported a DPP-alkyne conjugate that acted as an optical chemosensor and demonstrated colorimetric and selective signaling behavior toward Hg^{2+} and Cu^{2+} [54]. As a continuation of this research program, the present manuscript demonstrates the synthesis of a fluorescent chemodosimeter for the optical detection of F^- . It is well known that F^- displays high selectivity towards silicon and the Si–C bond in $-\text{C}\equiv\text{C}-\text{SiMe}_3$ is cleaved readily [55]. The cleavage of Si–C bond with F^- occurs much faster, typically within five minutes after adding F^- , compared to that of Si–O bond. Therefore, based on this idea a new chemodosimeter is reported in this paper, and the rationale for the design of probe **2** is depicted in Scheme 1. The presence of F^- induces a blue spectral shift in the fluorescence emission and absorption of probe **2**. When F^- removes the trimethylsilyl groups of the probe, the optical and fluorescent characteristics are significantly changed. UV–vis absorption and fluorescence spectroscopic experiments were carried out to understand the observed spectroscopic changes and the results were supported by the density functional theory (DFT) calculations.

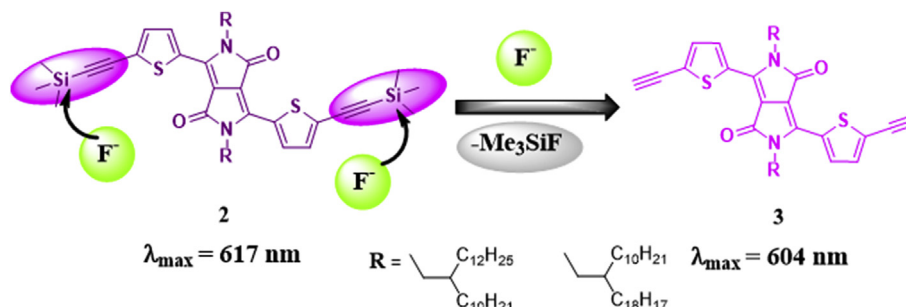
2. Experimental

2.1. Materials and instruments

All solvents used were of analytical grade. Solvents were dried according to standard procedures. All reactions were magnetically stirred and monitored by thin-layer chromatography (TLC) using Spectrochem GF254 silica gel-coated plates. Chromatography was performed using 100–200 mesh silica. ^1H and ^{13}C NMR spectra were recorded on Varian Mercury NMR spectrometer (300 MHz and 400 MHz) using deuterated chloroform purchased from Cambridge Isotope Laboratories; chemical shifts are represented in ppm with tetramethylsilane (TMS) as the internal reference. Coupling constants (J) are given in hertz (Hz). Signals are abbreviated as follows: singlet, s; doublet, d; double-doublet, dd; triplet, t; multiplet, m. Elemental analyses were performed using an EA1112 (Thermo Electron Corp.) elemental analyzer. Mass spectra were recorded on a Shimadzu LCMS-2020 (Liquid Chromatograph Mass Spectrometer). UV–vis absorption spectra of the solution and film state (chloroform, 1×10^{-6}) were obtained using a UV–vis spectrometer (HP 8453, photodiode array type) in the wavelength range of 190–1100 nm. Fluorescence spectra were recorded with a Hitachi F-7000 fluorescence spectrophotometer with a slit width of 2.5 nm used for excitation and emission. Density functional theory (DFT theoretical calculations) was studied using the Spartan program ('10') with B3LYP/6-31G* basis set.

2.2. Determination of binding constant and detection limit

The binding constants for the probe **2**-fluoride complex were calculated using the Benesi–Hildebrand equation [56].



Scheme 1. Design strategy, structure, and detection mechanism of probe **2a** and **2b** with fluoride ion.

$$1/(A_f - A_{obs}) = 1/(A_f - A_{fc}) + 1/K(A_f - A_{fc})[\text{Ligand}]$$

where A_f is absorbance of the free host, A_{obs} is the observed absorbance, A_{fc} is the absorbance at saturation, and K is the binding constant.

The detection limit (DL) was determined from the calibration curve of fluorescence intensity versus F^- ion concentration. Using this graph, the DL was determined by multiplying the concentration at which there was a sharp change in the fluorescence intensity by the concentration of probe **2a**.

Equation used for calculating detection limit (DL):

$$\text{DL} = \text{CL} \times \text{CT}$$

CL = Conc. of ligand; CT = Conc. of titrant at which the change was observed.

2.3. Preparation of stock solutions for UV–vis and fluorescence study

The stock solutions of probe **2** (10^{-4} M) and tetrabutylammonium salts (10^{-3} M) were prepared in a THF/HEPES buffer (8:2, v/v, pH 7.4). In titration experiments, a 3 mL (total volume) solution of probe **2** was placed in a quartz cuvette (path length = 1 cm). UV–vis absorption and fluorescence spectra were recorded after incubation of the probe with appropriate anions. For fluorescence measurements, excitation was provided at 530 nm, and emission was collected from 540 to 800 nm.

2.4. Synthesis

Synthetic procedures of probe **2a** (Scheme 2).

2.4.1. Synthesis of 2,5-bis(2-decyltetradecyl)-3,6-bis(5-((trimethylsilyl)ethynyl)thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (**2a**)

A mixture of compound **1a** [57] (0.5 g, 0.442 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (15.4 mg, 0.022 mmol), CuI (4.1 mg, 0.022 mmol), and PPh_3 (0.8 mg, 0.003 mmol) in THF (2 mL) and triethylamine (8 mL) was placed in a 100 mL round bottom flask (RBF). Nitrogen purged ethynyltrimethylsilane (96 mg/ μL , 0.977 mmol) was added to this solution. The solution was then heated at 50°C for 3 h, cooled to room temperature and the solvent was removed by evaporation. The residue was extracted with chloroform and water. The combined organic phases were dried over Na_2SO_4 and purified via column chromatography using ethyl acetate:hexane (1:10) as the eluent to afford 0.420 g (84%) as a deep purple solid. Mp: $>250^\circ\text{C}$. IR (KBr) ν_{\max} (cm^{-1}) = 2918–2849 (C–H stretch), 2143 ($-\text{C}\equiv\text{C}$ stretch), 1668 (C=O), 1555 (C=C aromatic stretch), 1399 (C–N stretch), 1322 (C–O stretch); ^1H NMR (300 MHz, CDCl_3), δ (ppm):

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