



A new fluoride ion colorimetric sensor based on dipyrrolemethanes

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ABSTRACT

Colorimetric fluoride ion sensors were developed using dipyrrolemethanes **1–4** synthesized from the reaction of aldehydes and pyrrole. The sensors showed a color change upon addition of fluoride ion with a substantial bathochromic shift. No significant color change was observed upon addition of any other anions. The significant changes of absorption bands and color show that chemosensor is selective toward fluoride ion over other anions such as Br^- , Cl^- , NO_3^- , HSO_4^- , SO_4^{2-} , AcO^- and H_2PO_4^- . The binding constants of sensors with fluoride ion were obtained in the order of $\sim 10^2$ which is enough to detect the fluoride ion.

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1. Introduction

Anion recognition is an area of growing interest in supramolecular chemistry due to its important role in a wide range of environmental, clinical, chemical and biological applications, and considerable attention has been focused on the design of host molecules that are able to selectively recognize and sense anion species [1–5]. Color changes, as signaling an event detected by the naked eye, are widely used owing to the low cost or lack of equipment required. Those chemosensors are constructed according to the receptor chromophore general binomial, which involves the binding of a specific anion substrate with receptor sites and a chromophore responsible for translating the receptor–anion association into an optical signal. This color variation can be related to either structural or conformational changes in the receptor structure when a complex is formed or to the formation of a charge-transfer complex [3,5,6]. Among the biologically important anions, fluoride is of particular interest due to its established role in dental care and osteoporosis [7]. The addition of fluoride in drinking water and toothpastes has become widespread due to the valuable effects of fluoride in human health. High doses of fluoride are hazardous and can lead to dental or skeletal fluorosis [8]. Therefore, noble methods for the detection of fluoride have become a hot topic. Even though some receptor compounds for fluoride ions have been reported [9–18], there is a paucity of reports on selective naked eye chemosensors for fluoride [19–23]. Nitrophenyl and nitronaphthalene urea, for the detection of fluoride have been reported as

colorimetric chemosensors [24,25], and also a naphthalene triphenylphosphonium ligand for fluoride ion has been reported [26]. So far these urea and phosphonium derivatives give excellent colorimetric property [23–26]. There is no report for the colorimetric sensor based on dipyrrolemethane derivatives, and this is new fluoride recognition by dipyrrolemethanes as a host. In pursuit of a selective fluoride ion chemosensor, dipyrrolemethane derivatives were synthesized, and their anion binding properties were investigated by ^1H NMR, UV–vis spectroscopy and color changes. To our knowledge, it is the first report of a colorimetric chemosensor based on dipyrrolemethane derivative. These results are comparable to those reported as the best colorimetric chemosensors [23–26].

2. Experimental

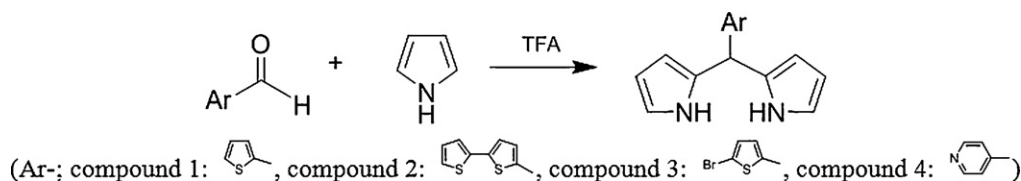
2.1. Chemicals and apparatus

All anions in the form of tetrabutylammonium salts were purchased from Fluka and used without further purification. All solvents used in the spectroscopic studies are spectroscopic grade. All other reagents used were of analytical grade. High purity argon was used for deaeration. All experiments were carried out at room temperature. All UV–vis spectroscopies were carried out in acetonitrile (MeCN) on a Scinco S-3100. All ^1H NMR were also determined in CDCl_3 on a Varian Unity Plus 300 (300 MHz).

2.2. Synthesis of dipyrrolemethane compounds

The synthetic procedure for dipyrrolemethane compounds **1–4** was adapted from the literature [27,28] (Scheme 1). Dipyrrolemethane compounds **1–4** were prepared using the

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Scheme 1. Preparation of dipyrrolemethane compounds 1–4.

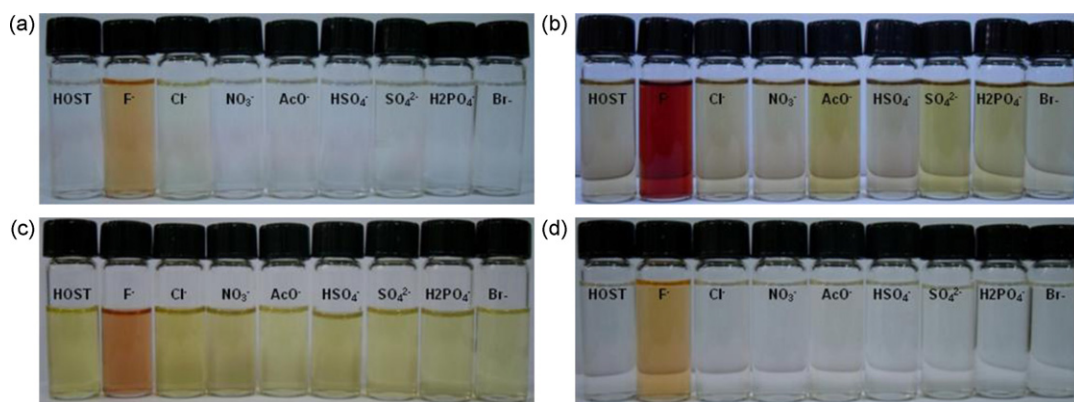


Fig. 1. Color changes upon addition of 10 equiv. of various anions in 0.1 mM MeCN solution of compounds 1(a)–4(d).

one-step reaction of pyrrole and appropriate aldehydes in a triethylamine solution in good yields as shown in Table 1. A typical synthetic procedure of dipyrrolemethane compound **3** is as follows: a 100 mL dry round flask was charged with pyrrole (1 mL, 8.6 mmol) and 5-bromo-2-thiophene (2.4 mL, 34.3 mmol). The mixture was degassed with N_2 for 5 min. A sample of TFA (83 μ L) was then added and the solution was stirred under N_2 gas at room temperature for 30 min, and quenching with triethylamine (1 mL). After cooling to room temperature, the precipitate was filtered off and the filtrate was purified by column chromatography on silica gel using hexane:ethylacetate (1:3) as the eluent to give compound **3** as a yellow–green solid (1.56 g, 56%). This compound was fully characterized by 1H NMR ($CDCl_3$, 300 MHz): δ (ppm) 5.65 (s, 1H), 6.04–6.07 (m, 2H), 6.15–6.18 (m, 2H), 6.63 (dd, $J=3.6$ and 1.2 Hz, 1H), 6.70–6.72 (m, 2H), 6.89 (d, $J=3.6$ Hz, 1H), 7.95 (br s, 2H), ^{13}C NMR ($CDCl_3$, 75 MHz): δ 39.41, 107.26, 108.60, 111.15, 117.68, 125.78, 129.44, 131.07, 147.38. M.P. 95–96 °C. HRMS calcd for $C_{13}H_{11}BrN_2S$ 306.9905, found 306.9999. Elemental Anal. calcd C, 50.83; H, 3.61; Br, 26.01; N, 9.12; S, 10.44; found C, 50.81; H, 3.78; N, 9.68.

3. Results and discussion

3.1. Visual sensing of fluoride anion

Optical inspection of solutions of compounds **1** and **4** (1.0×10^{-4} M) in MeCN before and after addition of 10 equiv. of tetrabutylammonium fluoride showed dramatic changes in color from colorless to yellow–red (Fig. 1a and d). The change could be detected by the naked eye. Meanwhile, visual examination of compounds **2** and **3** (1.0×10^{-4} M) in MeCN by the addition of 10 equiv.

of tetrabutylammonium fluoride showed dramatic changes in color from light yellow to deep red (Fig. 1b and c). The color intensity gradually increased corresponding to the increase of the anion concentration. It is noteworthy that there is no color change upon addition of protic solvents as water, methanol or ethanol. The addition of Br^- , Cl^- , NO_3^- , HSO_4^- , SO_4^{2-} , AcO^- and $H_2PO_4^-$ did not show any significant result of color changes.

3.2. UV–vis spectral responses of compounds 1–4

The interaction of compounds **1–4** with the anions was investigated through spectrophotometric titrations, by adding a standard solution of tetrabutylammonium salt in MeCN. Changes in UV–vis spectra of the free receptor and for the titration of compounds **1–4** with 10 equiv. tetrabutylammonium salt of the anion are shown in Fig. 2. The UV–vis experiments were carried out in MeCN solution. A receptor solution (5×10^{-4} M) was treated with the representative anions such as tetrabutylammonium fluoride (TBAF), chloride, bromide, dihydrogen phosphate, hydrogen sulfate, sulfate, nitrate and acetate. There is no absorption peak of compound **1** at used wavelength range, but a new peak appeared at 490 nm when compound **1** forms a complex with F^- . However, still there is no absorption peak when other anions were added to compound **1**. Fig. 2b shows the absorption spectra of compound **2** in the presence of several anions. The absorption peak at 330 nm was shifted to 510 nm when fluoride ion was added to compound **2** in the MeCN solution. On the other hand, the absorption peak at 413 nm of compound **3** was shifted to 501 nm. Meanwhile, no absorption peak of compound **4** in the absence of F^- was made a new peak at 487 nm when fluoride ion was added to compound **4** in the MeCN solution. UV–vis titration experiments were performed to understand the character of the receptor–anion interactions. Fig. 3 shows UV–vis titration results of dipyrrolemethanes with TBAF, and absorption peaks of dipyrrolemethane compounds **1–4** in the absence and in the presence of fluoride ion which were summarized in Table 2. All of the dipyrrolemethane compounds showed significant bathochromic shifts in the presence of fluoride, and also could be utilized as visible chemosensors owing to the noticeable color changes in the presence of fluoride ion.

Table 1
Synthesis of dipyrrolemethane compounds.

Compound	Temp (°C); time (h)	Yield (%)
1	25; 0.5	52
2	25; 0.5	48
3	25; 0.5	56
4	80; 12	54

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