Chromogenic and fluorescent chemodosimeter for fluoride ion based on novel anion-catalyzed intramolecular hydrogen transfer†‡

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We have developed a chromogenic and fluorescent chemodosimeter **3**, based on a novel anion-catalyzed intramolecular hydrogen transfer, which displayed drastic changes in UV-Vis absorption as well as fluorescence emission intensities showing selectively for F^- over other anions.

Introduction

The naked fluoride ion has potential as a very strong Lewis base for use in catalysis and is of significant interest in inorganic and organic synthesis.[1] Many intriguing patterns and applications of the fluoride ion in the synthesis of organic compounds,[2] materials,[3] and biological catalysis,[4] have been reported which clearly indicate its extraordinarily strong basicity and nucleophilicity. Therefore, conceptually, the finding of novel patterns to more broadly realize applications is still being intensively investigated.

The development of anion-sensing systems[5] has attracted much attention in recent years as the important role of anions in biological and chemical processes has become increasingly understood. Especially, the sensing of the fluoride ion has attracted growing attention because of the importance of this anion in dental caries and in the treatment of osteoporosis.[6]

Most of the receptors for the fluoride ion described so far[7] are mainly based on the approach of a binding site–signalling subunit. The binding site usually explores Lewis acids, triarylboranes, macrocycles, protonated polyammonium pyrroles, guanidiniums, metalloreceptors, amides, (thio)ureas, or designed hydrogen-bonding with the fluoride ion. The signalling subunit based on a chromogenic and/or fluorogenic response upon receptor–anion interaction appears particularly attractive.

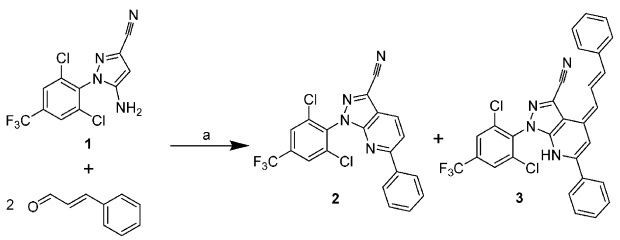
While considerable progress has been made in sensing of fluoride, the chemodosimeter approach,[8] which involves the use of specific chemical reactions induced by the presence of target anions, has received much less attention comparatively. This is an attractive approach which usually shows high selectivity, large spectroscopic shifts and different electronic properties. Martínez-Máñez *et al*. reported several chemodosimeters for fluoride detection based on the selective attack of hydrofluoric acid on a silica matrix grafted with a certain dye.[9] Kim and Swager reported a fluorescent self-amplifying wavelength-responsive sensory polymer for the fluoride ion based on fluoride induced Si–O bond cleavage.[10] Tamao *et al*. reported colorful fluoride detection based on the reaction between fluoride and the boron atom of the receptors that led to an interruption of the π-conjugation.[11] Besides, Lam *et al*. reported cyanide detection by chemodosimeters based on the coordination of cyanide to metal complexes.[12] Ahn *et al*. reported *N*-acyl triazenes as tunable and selective chemodosimeters for cyanide ion detection on the basis of a displacement reaction.[13] And also, several chemodosimeters for cation (Hg^{2+}, Cu^{2+}) detection based on a specific reaction was also reported.[14] An exciting approach involving a catalytic reaction reported earlier by Zhu and Anslyn,[15] is used for signal amplification. Therefore, it is possible to find an anion catalytic reaction for development of a more elegant chemodosimeter for a specific anion.

In our recent investigations to develop Fipronil[16] derivatives containing pyrazolopyridine (Scheme 1), the unexpected compound (*Z*)-1-(2,6-dichloro-4-(trifluoromethyl)phenyl)-6-phenyl-4-((*E*)-3-phenylallylidene)-4,7-dihydro-1*H*-pyrazolo[3,4-*b*]-pyridine-3-carbonitrile (**3**) was synthesized in moderate yield (Scheme 1), which can be further transformed to fluorophore **4** involving an intramolecular hydrogen transfer[17] in the presence of naked fluoride ion as catalyst. In this paper, we present a novel dosimeter **3**, which can be used as a fluorescent as well as chromogenic chemodosimeter for fluoride ion detection based on anion-catalyzed intramolecular[17] hydrogen transfer (Fig. 1).

Experimental section

General information

Melting points were taken on a micro melting point apparatus made in Beijing and were uncorrected. ^1H NMR (400 MHz)



Scheme 1 (a) Conc. HCl, acetonitrile, 50 °C.

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† The HTML version of this article has been enhanced with colour images.

‡ Electronic supplementary information (ESI) available: UV-Vis and fluorescence emission titrations of **3**, and ^1H NMR and ^{13}C NMR spectra of compounds **2**, **3**, **4**. See DOI: 10.1039/b712554b

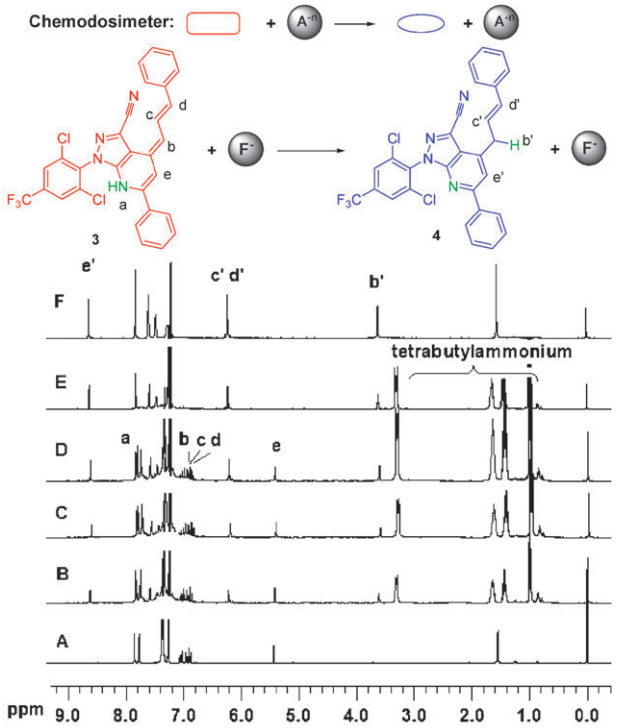

Fig. 1 ^{1}H NMR spectra ($CDCl_3$) of **3** (1.97×10^{-2} M) with different amounts of added F^- ions: (A) 0 equiv.; (B) 0.50 equiv.; (C) 0.65 equiv.; (D) 1.24 equiv.; (E) 1.24 equiv. (30 h); (F) **4** itself; NH and CH (except phenyl–H) shifts are shown.

and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker AVANCE 400 MHz spectrometer using $CDCl_3$ as solvent at 298 K and Me_4Si as an internal standard. IR spectra were recorded on a Nicolet Magna-IR 550 instrument using KBr pellets. High resolution mass spectra (HRMS) were obtained on a MicroMass GCT CA 055 spectrometer. Absorption spectra were determined on a TU-1901 UV-Vis spectrophotometer. Analytical thin-layer chromatography (TLC) was carried out on precoated plates (silica gel 60_{F254}), and spots were visualized with ultraviolet light. All chemicals or reagents were purchased from standard commercial suppliers. For ^{1}H NMR titrations a solution of receptor (1.97×10^{-2} mol L^{-1}) in $CDCl_3$ was prepared in an NMR tube. For UV-Vis and fluorometric titrations a solution of receptor (2×10^{-5} mol L^{-1}) in CH_2Cl_2 (or CH_3CN, CH_3CN–H_2O) was titrated with incremental amounts of appropriate anion (0.001–0.1 mol L^{-1}). A 10 mM aqueous HEPES buffer solution (pH 7.4) was used in a mixed solvent system. The anions (X) used in this study are all as $[Bu_4N]X$ salts.

Synthesis

1-(2,6-Dichloro-4-(trifluoromethyl)phenyl)-6-phenyl-1*H*-pyrazolo[3,4-*b*]pyridine-3-carbonitrile (2) and (*Z*)-1-(2,6-dichloro-4-(trifluoromethyl)phenyl)-6-phenyl-4-((*E*)-3-phenylallylidene)-4,7-dihydro-1*H*-pyrazolo[3,4-*b*]pyridine-3-carbonitrile (3). 5-Amino-1-(2,6-dichloro-4-(trifluoromethyl)phenyl)-1*H*-pyrazole-3-carbonitrile[18] **1** (0.64 g, 2.0 mmol) and cinnamaldehyde (0.53 g, 4.0 mmol) were dissolved in 10 mL of CH_3CN. HCl (3 drops) was added to the stirred solution and the reaction mixture was heated at 50 °C for 6 h. The CH_3CN was removed in a vacuum and the residue purified by column chromatography on silica gel to give the pure products **2** (yield 35%) and **3** (yield 15%). Spectral data for **2**: mp 172.3–173.5 °C. IR (KBr, ν/cm^{-1}): 3071, 2918, 2239, 1597, 1319, 1128, 830. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45–7.50 (m, 3H), 7.85 (s, 2H), 7.93 (d, J = 8.5 Hz, 1H), 8.01 (m, 2H), 8.35 (d, J = 8.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.9, 151.1, 137.7, 136.4, 136.0, 134.3, 133.9, 130.5, 129.7, 129.0, 127.8, 126.1, 126.0, 121.0, 118.2, 115.2, 112.2. MS: m/z (relative intensity): 432 $[M]^+$ (18.32), 397 (100.00), 344 (9.58), 310 (10.77), 213 (3.65), 178 (4.34), 166 (2.41), 143 (3.91),140 (12.60), 115 (13.98), 77 (5.65), 64 (4.09), 51 (4.02). HRMS calcd for $([M])^+$, 432.0156; found: 432.0156. For **3**: mp 225.0–225.3 °C. IR (KBr, ν/cm^{-1}): 3071, 2225, 1590, 1550, 1320, 1128, 830. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.44 (s, 1H), 6.87–6.90 (d, J = 15.2 Hz, 1H), 6.93–6.96 (d, J = 2.4 Hz, 1H), 7.02–7.07 (m, 1H), 7.28–7.40 (m, 10H), 7.77 (s, 2H), 7.85 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.2, 146.0, 143.8, 143.5, 136.1, 135.7, 132.5, 130.0, 129.4, 129.0, 127.9, 127.8, 127.6, 127.3, 125.9, 125.0, 113.0, 113.0, 112.5. MS: m/z (relative intensity): 548 $[M]^+$, 457 (35.80), 421 (8.98), 409 (6.80), 92 (100), 77 (6.19). HRMS calcd for $([M])^+$, 548.0782; found: 548.0828.

4-Cinnamyl-1-(2,6-dichloro-4-(trifluoromethyl)phenyl)-6-phenyl-1*H*-pyrazolo[3,4-*b*]pyridine-3-carbonitrile (4). **3** (0.55 g, 1 mmol) and tetrabutylammonium fluoride, TBAF, (0.40 g, 1.5 mmol) were dissolved in 10 mL of CH_2Cl_2. The mixture was stirred at room temperature for 24 h. The CH_2Cl_2 was removed in a vacuum and the residue purified by column chromatography on silica gel to yield 85% of the pure product: mp 170.0–170.5 °C. IR (KBr, ν/cm^{-1}): 3071, 2918, 2229, 1569, 1310, 1132, 830. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.64 (d, J = 5.2 Hz, 2H), 6.25 (m, 2H), 7.20–7.62 (m, 10H), 7.85 (s, 2H), 8.66 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.9, 149.8, 143.7, 136.8, 136.5, 135.9, 134.5, 134.2, 132.9, 132.2, 130.2, 129.7, 129.0, 128.7, 128.6, 127.6, 126.1, 123.5, 120.9, 116.1, 111.7, 33.4. MS: m/z (relative intensity): 548 $[M]^+$ (18.35), 513 (5.25), 457 (100), 421 (20.24), 409 (15.13), 92 (7.51). HRMS calcd for $([M])^+$, 548.0782; found, 548.0772.

Results and discussion

Mechanism analysis from NMR study

The ^{1}H NMR spectra in $CDCl_3$ show dramatic changes for receptor **3** upon addition of increasing amounts of fluoride ions. A new set of peaks immediately appeared along with decreasing peak intensity from **3**, the internal –NH signal (s, 1H, δ = 7.85 ppm in the free receptor, Fig. 1A) disappears slowly and the double bond H_{b-d} signals also reduce gradually, which clearly indicate that the π systems are becoming reorganized involving a change in the proton above. Meantime, a new set of peaks ($H_{b'-e'}$) appears with a finer proportional relationship ($H_{b'} = 2H_{c'} = 2H_{e'}$), which could be assigned to a new compound obtained in this fluoride–receptor interaction system (Fig. 1B, 1C and 1D). On extending the reaction time, legible signals are shown in Fig. 1E, which intensively indicate that receptor **3** completely disappeared and only the new set of peaks was observed. Further, the new set of peaks was

coincident with that of compound **4** (Fig. 1F). The comparison of ^{1}H-NMR spectra in detail, is shown in Fig. 1. Thus, the fluoride-catalyzed intramolecular hydrogen transfer was confirmed.

Anion-recognition studies

The changes observed in the absorption spectrum of receptor **3** in CH_2Cl_2 upon the addition of different anions are shown in Fig. 2. The spectrum of receptor **3** with tetrabutylammonium fluoride (TBAF) is observed with two new peaks at λ = 256 and 310 nm. Compared to **3** itself (λ = 386 nm), the larger blue-shift of **3** binding with TBAF, might be ascribed to the presence of a reduced π-conjugation network involving the phenylallylidene moiety and the 1*H*-pyrazolo[3,4-*b*]pyridine. A complete color change from yellow to colorless, was observed after the addition of ten equivalents of fluoride ions. The addition of acetate ions induced a less dramatic color change. Greater amounts of acetate ions were required to effect a commensurate change. On the other hand, exposure to Cl^-, Br^-, I^-, NO_3^- and HSO_4^- (as their tetrabutylammonium salts), did not lead to any obvious change in color. This indicates that the sensor shows a very typical response based on anion basicity.[19] Fluoride gives the biggest response mainly because it is more basic[20] than acetate. This dramatic chromogenic response or nonresponse for a specific anion can make receptor **3** a potential anion sensor. The changes observed when receptor **3** was treated with increasing quantities of TBAF in CH_2Cl_2 were also recorded (Fig. 3). The intensity of the peak at 386 nm reduced and that of two new peaks at λ = 256 and 310 nm increased upon addition of TBAF with a clear isosbestic point at 324 nm, and the absorbance intensity of dosimeter **3** was saturated with 40 equiv. of F^-. Meanwhile, a color change of dosimeter **3** was observed from yellow to colorless.

Fluorescence, on account of its simplicity and high sensitivity, is becoming of increasing importance for chemical trace detection. Therefore, fluorescent titrations of receptor **3** with TBAF were also recorded to evaluate it as a selective fluorescent receptor for the fluoride ion. In CH_2Cl_2 solvent, receptor **3** shows very weak fluorescence. Though it was donor–acceptor system, the hydrogen atom might be flexible

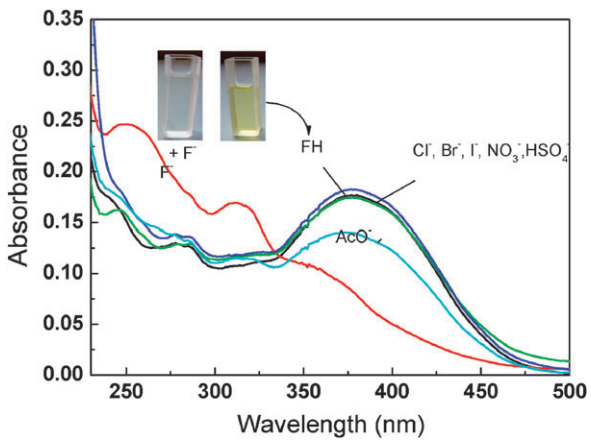

Fig. 2 UV-Vis spectra of **3** (10 μM in CH_2Cl_2) with different anions (*ca.* 10 equiv.). The inset shows color changes from yellow to colorless.

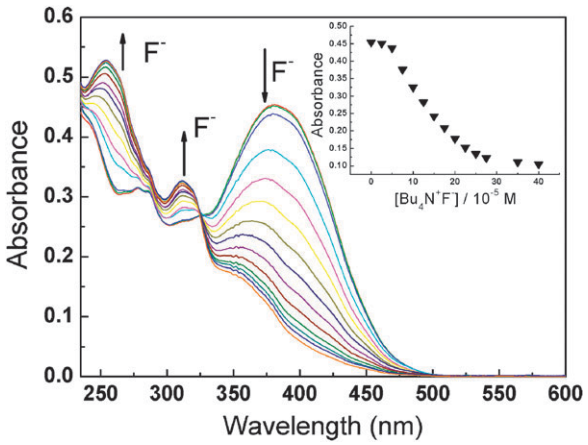

Fig. 3 UV-Vis titration of **3** (20 μM) with $Bu_4N^+F^-$ in CH_2Cl_2. Arrows show changes due to increasing concentration of F^-. The inset shows the absorbance at 386 nm as a function of [F^-].

enough to lose the excited energy easily through vibration or migration. However, upon the addition of fluoride ions, the emission spectrum displays an increasing strong band (λ_{max} = 400 nm, Fig. 4). This may be ascribed to the rigid pyrazolopyridine fluorophore[21] coming into being. Therefore, this process clearly demonstrates that receptor **3** can selectively detect fluoride ion by a fluorogenic "off–on" response.

In view of the fact that the detection method described above is dependent on the fluoride-catalyzed reaction relating to intramolecular hydrogen transfer, its operation in a mixed solvent system, MeCN–water (19 : 1), was also carried out in similar titrations as above. In this medium, dosimeter **3** exhibited a similar color change in UV-Vis absorption (Fig. 5) and fluorescence enhancement (Fig. 6). But it required greater amounts of fluoride ions (20 000 equiv.) to effect a complete color change; this indicates that the fluoride ions show extraordinarily strong basicity in media of low polarity[22] (the titrations in CH_3CN solvent are shown in ESI‡). It should be noted that this is a novel approach to selectively recognize

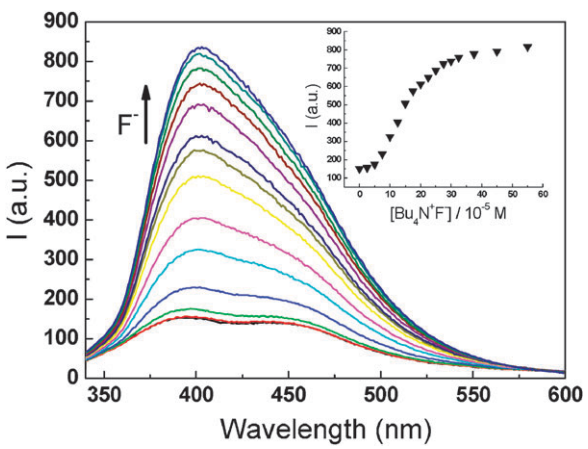

Fig. 4 Increase in fluorescence emission intensity (λ_{ex} = 324 nm) when sensor **3** (20 μM in CH_2Cl_2) is titrated with increasing concentration of F^-. Arrows show changes due to the increasing concentration of F^-. The inset shows the emission intensity at 400 nm as a function of [F^-].

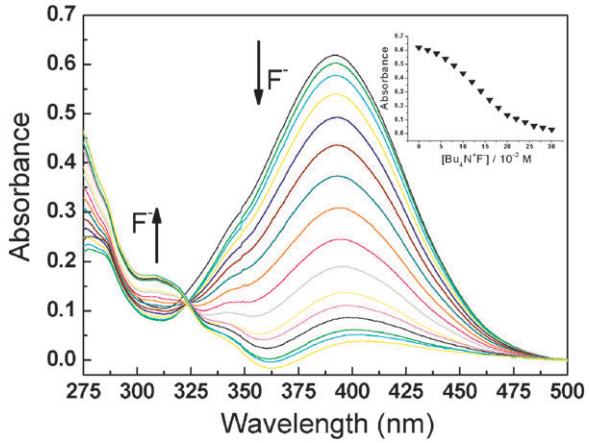

Fig. 5 UV-Vis titration of **3** (20 μM) with $Bu_4N^+F^-$ in MeCN–H_2O (19 : 1, v/v). Arrows show changes due to the increasing concentration of F^-. The inset shows the absorbance at 391 nm as a function of [F^-].

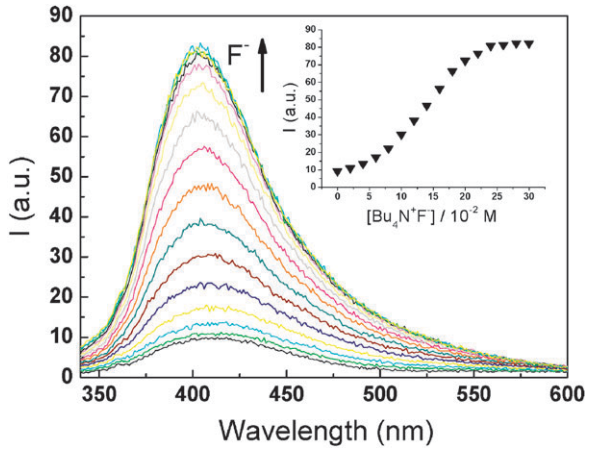

Fig. 6 Increase in fluorescence emission intensity (λ_{ex} = 324 nm) when sensor **3** (20 μM) in MeCN–H_2O (19 : 1, v/v) is titrated with an increasing concentration of F^-. The inset shows the emission intensity at 402 nm as a function of [F^-].

fluoride ions and acetate ions with drastic dual changes in UV-Vis absorption and fluorescence emission intensities.

Conclusions

In summary, we have demonstrated above (1) a previously undescribed organic reaction resulting in dosimetric fluoride ion determination; (2) obvious features such as high selectivity for F^- over other anions, fluorescence enhancement as well as dramatic color changes. A further study on the development of chemosensors/chemodosimeters based on analyte-specific reactions is in progress in our laboratory.

Acknowledgements

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20 In the case of the hydroxide, the titrations in CH_3CN solvent are shown in the ESI,‡ which further confirms that the sensing mechanism is mainly based on the basicity of anion.

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