A highly selective fluorescent sensor for fluoride anion based on pyrazole derivative: Naked eye "no–yes" detection

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ARTICLE INFO

ABSTRACT

A new pyrazole-based fluorescent sensor, 5-amino-3-(5-phenyl-1H-pyrrol-2-yl)-1H-pyrazole-4-carboxamide (compound 1), was studied for fluoride anion (F^-) detection in organic or water-containing solution. This compound displayed both changes in UV–vis absorption and fluorescence emission spectra upon addition of F^-. With increasing of F^-, blue emission intensity increases drastically and reaches saturation with 607-fold enhancement at 424 nm. The results indicate that compound 1 has highly selectivity for fluoride detection over other anions, such as Cl^-, Br^-, I^-, HSO_4^-, $H_2PO_4^-$ and AcO^- in DMSO or aqueous DMSO solutions. ^1H NMR titration and other experiments confirm that the sensing process is mainly from the deprotonation of the pyrazole–NH in compound 1.

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1. Introduction

The development of sensor and receptor for biologically important anions has received considerable attention because of their important roles in chemical and biological processes [1–6]. Charge neutral receptors have been used for anion sensor and most of them contain pyrrole, amide, indolocarbazole, guanidium, imidazolium and/or urea/thiourea moieties, and the anion was recognized via H-bonding or deprotonation of protons on the receptor-NH in organic solvents [7–16]. The urea/thiourea-containing receptors are dominated for the past two decades, which can particularly establish H-bonding interaction with Y-shaped oxoanions and deprotonation with more basic anions such as fluoride. Among the anions, fluoride has received more attention for its activities in nature or in human beings [17–20]. On the other hand, there is highly advantageous to develop high-effective sensor that can selectively detect fluoride anion with naked eye "no–yes" response.

In consideration of a new sensor, it must contain receptive groups toward anions and has no urea/thiourea moieties in avoidance of multi-anion sensitiveness. In recent years, we synthesized a series of pyrrol–pyrazole derivatives [21–22], and considered that the new compound 1 (shown in Scheme 1), 3-amino-5-(5-phenyl-1H-pyrrol-2-yl)-1H-pyrazole-4-carboxamide, which contains several common anion recognition moieties, a pyrazole N–H, a pyrrole N–H and an amide group, would be used as a biresponsive fluorescent chemosensor. Research on the mechanism of recognition toward anions may help to understand the biological activities of pyrrole–pyrazole derivative as insecticide. We have investigated the interactions of anions with compound 1 in DMSO solution through spectroscopic and ^1H NMR titration experiment. All the results indicate that the compound 1 is a unique interaction mode for detection of fluoride anion (F^-) with high selectivity and sensitivity over other anions.

2. Experiments

2.1. Materials

All organic solvents were commercially available, dried and distilled by appropriate methods before use. A detailed description of the synthesis of compound 1 has been given in Ref. [22].
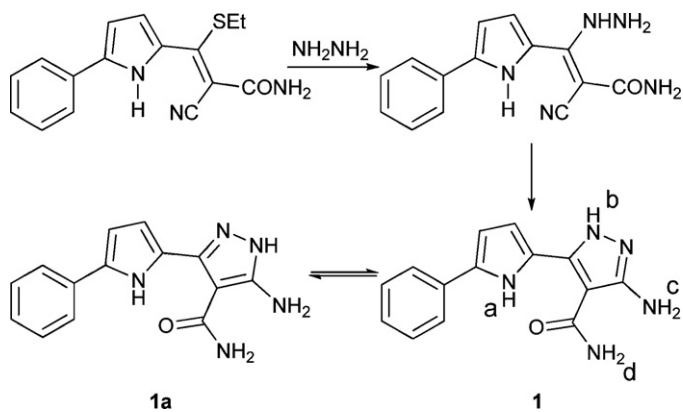
2.2. Methods

UV–Vis absorption spectra were recorded on a Hitachi U-3010 spectrophotometer. Fluorescence spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer. Fluorescence quantum yields (Φ_F) were determined by the comparative method using 1,4-di(5-phenyl-2-oxazolyl)benzene ($\Phi_F = 0.97$) as reference

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Scheme 1. Synthesis of compound 1.

Fig. 1. ORTEP drawing of compound 1. Thermal ellipsoids are drawn at the 30% probability level.

standard [23]. ^{1}H NMR spectra were performed on a Bruker dmx 400 MHz NMR spectrometer at room temperature with DMSO-d_6 as solvent and tetramethylsilane (TMS) as internal standard.

2.3. X-ray crystallography

Accurate unitcell parameters were determined by a least-squares fit of 2θ values, measured for 200 strong reflections, and intensity data sets were measured on Rigaku Raxis Rapid IP diffractometer with Mo-Kα radiation ($\lambda = 0.71073$ Å) at room temperature. The intensities were corrected for Lorentz and polarization effects, but no corrections for extinction were made. All structures were solved by direct methods. The non-hydrogen atoms were located in successive difference Fourier synthesis. The final refinement was performed by full-matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F^2. The hydrogen atoms were added theoretically as riding on the concerned atoms. Crystallographic data for structure analyses are summarized in ESI Table S1, and selected bond lengths and angles data are listed in Table S2.

3. Results and discussion

3.1. Crystal structure of compound 1

Compound 1 as a precursor of purine analogs [21] was synthesized from 2-(1-ethylsulfanyl-2-carbamoyl-2-cyanoe-thenyl)-5-phenylpyrrole and hydrazine hydrate (Scheme 1) according to the literature procedure [22]. The expected structure of the target product should be compound 1a. We obtained the crystals of compound 1 suitable for analysis by single crystal X-ray diffraction through recrystallisation from CH$_3$CN. As a matter of fact, however, the X-ray analysis of the single crystal of compound 1 (Fig. 1) revealed that it exists, at least in the solid state, as 3-amino-tautomer instead of tautomer 1a, 5-amino-3-(5-phenylpyrrol-2-yl)-pyrazole-4-carboxamide, as-signed previously [22].

3.2. Colorimetric and fluorescence anion-sensing in DMSO solution

The changes of UV–vis absorption and fluorescence emission of compound 1 (5 μM in DMSO) upon addition of F$^-$, Cl$^-$, Br$^-$, I$^-$, HSO$_4^-$, H$_2$PO$_4^-$ and AcO$^-$ (70 equiv. as their tetrabutylammonium salts) are shown in Figs. 2 and 3, respectively. Free compound 1 displayed an absorption peak at 342 nm. Upon addition of F$^-$ it moved to 368 nm with a red shift of 26 nm. Addition of other anions did not affect the absorption of the free compound 1.
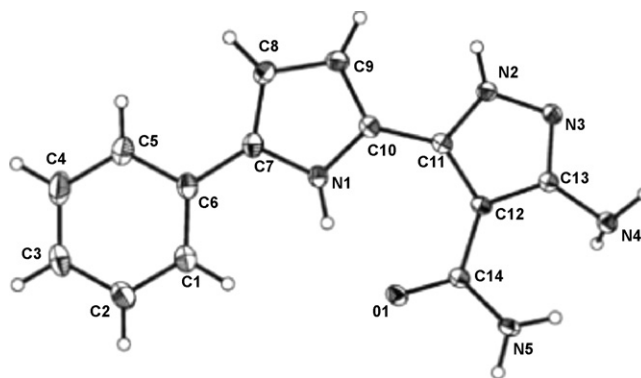

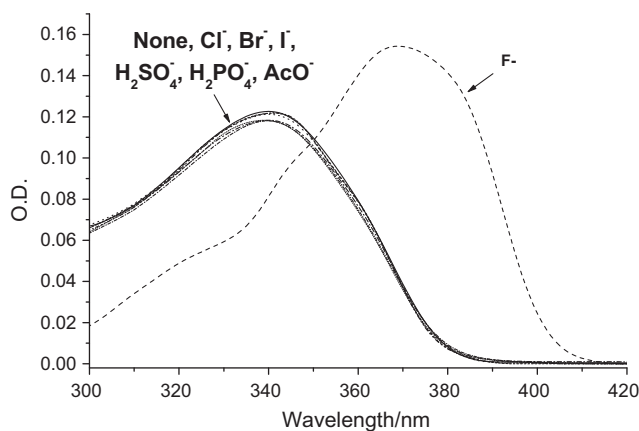Fig. 2. UV–vis absorption changes of compound 1 (5 μM) upon addition of tetrabutylammonium salts of F$^-$, Cl$^-$, Br$^-$, I$^-$, HSO$_4^-$, H$_2$PO$_4^-$ and AcO$^-$ (70 equiv.) in DMSO.

The compound 1 revealed a peak at 407 nm in the fluorescence spectrum with a very low fluorescence quantum yield when it was excited at 365 nm ($\Phi_F \approx 0.008$). Upon addition of F$^-$, the fluorescence emission peak red shifted to 424 nm and the intensity increased drastically, while only slight changes occurred upon addition of other anions.

It is worth to point out that the absorption peak of compound 1 at 368 nm upon addition of F$^-$ is quite fit for the cheap UV lamp of 365 nm, while the fluorescence emission of 424 nm is in the range of blue luminescence. Hence, it can be foreseen that when excited
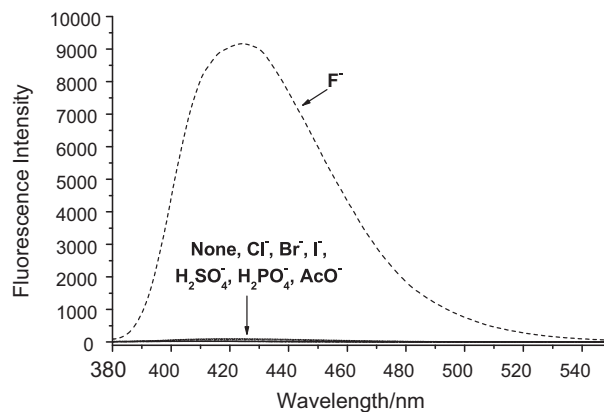

Fig. 3. Fluorescence emission changes of compound 1 (5 μM) upon addition of tetrabutylammonium salts of F$^-$, Cl$^-$, Br$^-$, I$^-$, HSO$_4^-$, H$_2$PO$_4^-$ and AcO$^-$ (70 equiv.) in DMSO (excited at 365 nm).
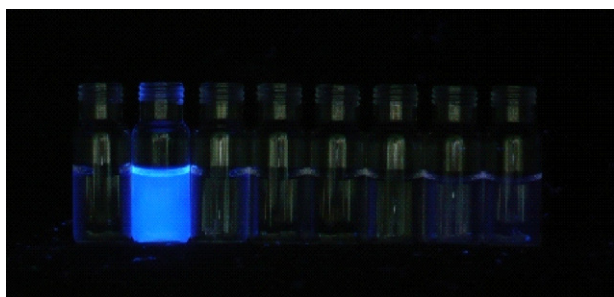
with a 365 nm UV lamp, a visible change of compound **1** in the emission from colorless to bluish color will be observed upon addition of F⁻ (as shown in Fig. 4).

The titrations were carried out using tetrabutylammonium salts for further investigation. Fig. 5 shows the UV–vis absorption spectra of compound **1** (5 μM) upon addition of different equiv of F⁻ in DMSO. The absorption at 342 nm decreased and a new peak appeared at 368 nm upon increasing the concentration of F⁻. The presence of a sharp isosbestic point at 350 nm indicated that only two species are present at equilibrium throughout the titration process [24]. The absorption peak at 368 nm in DMSO was partially returned to 342 nm when a protic solvent such as methanol or water was introduced, which leads to a suggestion that the interaction of compound **1** with F⁻ is hydrogen bonding [25–29] or deprotonation [30–33]. Considering the greater contribution of the electron density changing for the conjugated system in the deprotonated compound **1**, it could concluded that the interaction was deprotonation rather than the formation of hydrogen bonding because of the significant absoption shift. In the case of other anions, the UV–vis absorption were almost the same with that of free of anion during the titration experiments (see ESI, Figs. S1 and S2).

Fig. 6 shows the changes of fluorescence emission of **1** upon addition of F⁻ in DMSO, in which the emission maximum redshifted to 424 nm. With increase of F⁻ concentration, the emission intensity increased drastically and reached saturation with 607-fold enhancement at 424 nm when 50 equiv. of F⁻ was added. The quantum yield of fluoresceence is 0.74 in this case. The stoichiometry of the equilibrium was determined by fitting the experimental data to give a 1:2 ratio between compound **1** and F⁻. The stability
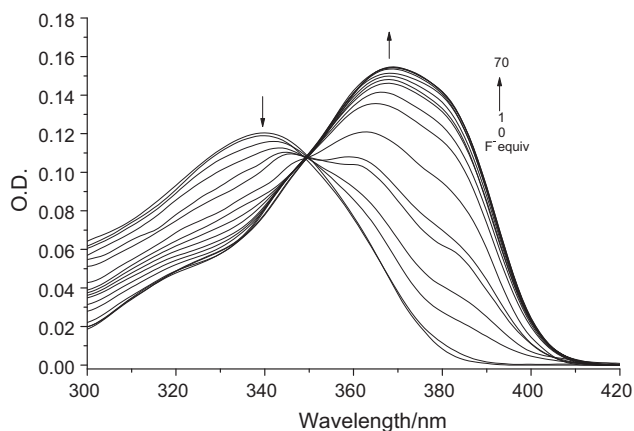
constant of the complex was also obtained to be $\log K_1 = 4.67 \pm 0.16$ and $\log K_2 = 4.68 \pm 0.05$ [34–35] (see Fig. 7).

Usually, presence of anions of $H_2PO_4^-$ and AcO^- interferes the detection of F⁻ in the solution [33,36–39]. Upon addition of $H_2PO_4^-$ and AcO^-, the emission maximum of compound **1** caused slight emission enhancement at 424 nm. Other anions such as Cl⁻, Br⁻, I⁻ and HSO_4^- did not affect both the emission maximum and the intensity during the titration. The results are shown in Fig. 8 and it indicates that the compound **1** is a very good sensor for recognizing F⁻ over other anions. The detection limit was determined as the threefold standard deviation of the fluorescence obtained from a blank sample, prepared as described above but without addition of compound **1**. The detection limit of the compound **1** for fluoride is measured to be less than 5 ppm. This result shows that the compound **1** has a high sensitivity in detecting fluoride in DMSO.

3.3. ¹H NMR titration

To confirm the assumption of deprotonation for the compound **1** with F⁻, ¹H NMR titration was carried out. A series of ¹H NMR spectra of compound **1** upon addition of TBAF in DMSO-d_6 are shown in Fig. 9. There are four kinds of NH proton signals for free compound **1**, which are designated as H_a, H_b, H_c, H_d, respectively (as shown in Scheme 1). The amide NH (H_d) proton signal (7.47 ppm) overlaps with the signal of the phenyl CH and displays as a shoul-
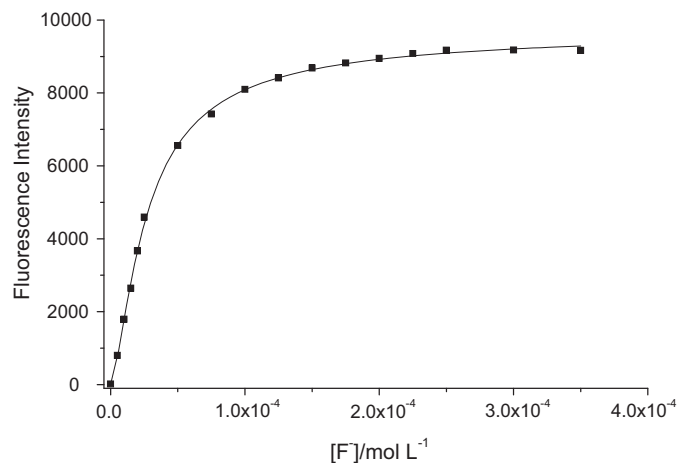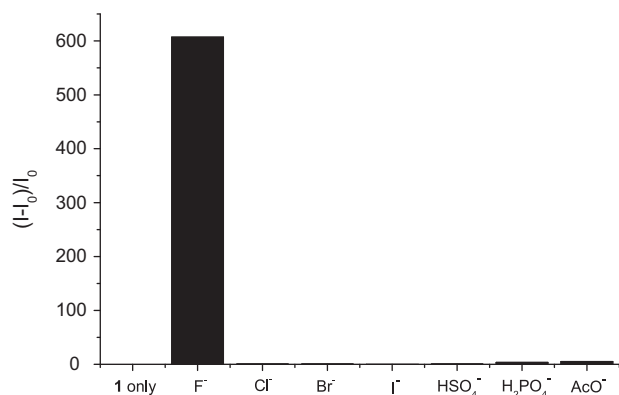
Fig. 8. Comparison of fluorescence emission of compound **1** (5 μM) in DMSO after the addition of 70 equiv. of different tetrabutylammonium salts.

Fig. 10. Fluorescence emission changes of compound **1** (5 μM) upon addition of tetrabutylammonium salts of F^-, Cl^-, Br^-, I^-, HSO_4^-, $H_2PO_4^-$ and AcO^- (2000 equiv.) in DMSO/H_2O (95:5, v/v) (excited at 365 nm).

der. The pyrrole NH (H_a) and pyrazole NH (H_b) proton signals in the downfield gradually broaden, weaken and finally disappear or occur as new signals with increase of the F^- concentration. Meanwhile, the signal of amide NH (H_d) upfield shifts, broadens and also disappears upon addition of F^-. The disappearance of such signals indicates the formation of hydrogen bonded complex N–H⋯F^- or the deprotonation of N–H fragment to form N^-, but it is difficult to distinguish one from the other. However, the signal of amino NH (H_c) just undergoes a slight downfield-shift (0.44 ppm) with no broadening and weakening during the same process upon addition of F^-. This observation clearly supports that during the interaction of compound **1** and F^-, the pyrrole NH (H_a), pyrazole NH (H_b) and amide NH (H_d) moieties may play more important roles than amino function NH (H_c).

The most important result from the ^1H NMR titration is that a new signal appeared at 16.1 ppm ($J_{HF} = 119$ Hz) after 0.6 equiv. of F^- was added, which indicates the formation of a stable bifluoride

hydrogen-bonding self complex (HF_2^-) [30,40–45]. The occurrence of bifluoride points to the deprotonation of either the N–H group or of the solvent. The strong up-field shifts of all the CH proton signals, indicating an overall change of the electron distribution in the conjugated system, give evidence of the deprotonation of the N–H moiety [46]. Because of the high charge density and small size, fluoride as strong base can deprotonate the compound **1** to afford deeply the heterocyclic conjugated anion [9,12,47,48], which gives strong emission when excited at 365 nm. The deprotonation site could be fixed by the ^1H NMR titration spectra (Fig. 9) upon addition of enough amount of fluoride, which indicates clearly that the bifluoride signal comes from deprotonated pyrazole NH (H_b). Actually the acidity of pyrazole NH is much stronger than other NHs in compound **1** [49], leading to the formation of deprotonated pyrazole–N^- easily. All the CH protons of compound **1** and amino NH protons can be excluded as candidates for the interaction with F^-, since their signals are almost not changed after appearance of the bifluoride signal.

3.4. OH^- detection in DMSO

Another evidence for deprotonation of compound **1** is that the similar phenomenon could be observed upon addition of tetrabutylammonium hydroxide. Changes of fluorescence emission of **1** upon addition of tetrabutylammonium fluoride and hydroxide in DMSO are almost the same (see ESI, Figs. S3 and S4). The fluorescence emission intensity of compound **1** gave 393-fold enhancement at 424 nm when 5 equiv. of OH^- was added. It is slightly higher than that of addition of F^- (303-fold for 5 equiv. of F^-), which is caused by the stronger basicity of OH^- than F^- in leading to the deeper deprotonation [50].

3.5. Anion recognation in aqueous DMSO

As a potential candidate for fluoride prober, compound **1** can also be used in aqueous DMSO solution. In DMSO/H_2O (95:5, v/v) the fluorescence emission of compound **1** was increased about 400-fold upon addition of F^-. Other anions did not affect the absorption or fluorescence spectra of compound **1** in the aqueous DMSO solution (see Fig. 10 and ESI, Figs. S5–S7). Thus, the F^- in water can be detected with naked eye by dripping one drop of the real water sample containing F^- and other anions to the DMSO solution containing compound **1**. The "color" of DMSO solution will change from colorless to bluish when excited with a 365 nm UV lamp. Whereas, with increasing of water concentration in DMSO, the detection of F^- will become more and more difficult. For exam-
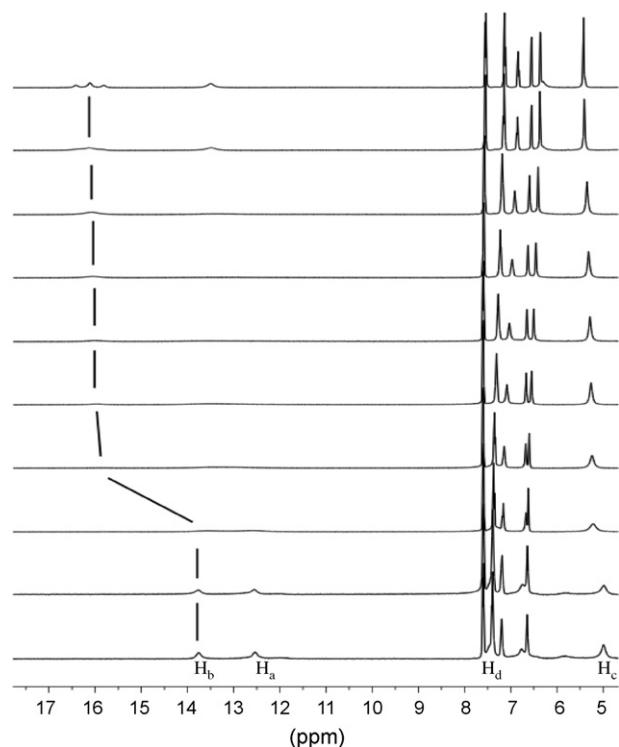

Fig. 9. Partial ^1H NMR (400 MHz) spectra of compound **1** in the presence of 0, 0.2, 0.4, 0.6, 0.8, 1.2, 1.6, 2.0, 2.4 and 2.8 equiv. of TBAF in DMSO-d_6.
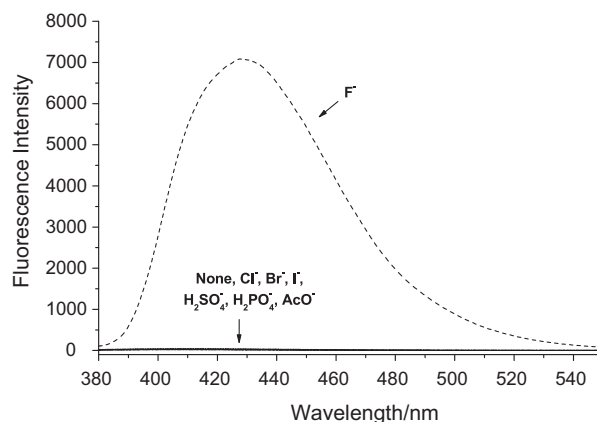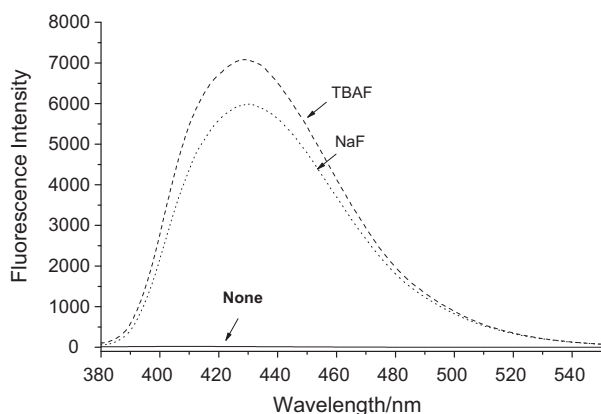
Fig. 11. Fluorescence emission changes of compound **1** (5 μM) upon addition of TBAF and NaF (2000 equiv.) in DMSO/H$_2$O (95:5, v/v) (excited at 365 nm).

ple, it needs 50 equiv. of F$^-$ to reach saturation in pure DMSO but about 1500 equiv. in DMSO/H$_2$O (95:5, v/v) when the concentration of **1** is 5 μM. Therefore, it is better to use pure DMSO as solvent when detecting F$^-$.

Another advantage of this prober is of possible in detection of the NaF, which is rarely reported in literatures. The fluorescence emission of compound **1** was increased about 337-fold upon addition of 2000 equiv. of NaF in DMSO/H$_2$O (95:5, v/v), only a little lower compare to addition of same equiv of TBAF (see Fig. 11).

4. Conclusions

We report a new pyrazole-based fluorescent compound suitable for floride sensing over other anions in DMSO. It is a very good naked eye "*no–yes*" detection sensor for the fluoride anion. Studies with spectroscopic techniques indicate that the mechanism of the anion recognition is the deprotonation of the pyrazole–NH. Compound **1** is also a good sensor in DMSO aqueous solution for the detectin of floride anion (TBA$^+$ and Na$^+$ salts).

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2010.09.012.

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