Tetrahedron Letters 59 (2018) 2473–2476

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

# Fluorescent sensor for fluoride anion based on a sulfonamido-chromone scaffold

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ARTICLE INFO

*Article history:*
Received 26 April 2018
Accepted 18 May 2018
Available online 19 May 2018

*Keywords:*
Fluorescent
Chromone
Fluoride sensor

ABSTRACT

New scaffolds of sulfonamido-chromone derivatives recently synthesized were found to be effective fluorescent sensors for fluoride anion. This new class of fluorophore showed a blue shift in the emission spectra upon addition of various equivalents of fluoride. These compounds also exhibit excellent selectivity for the fluoride anion via a deprotonation process. They were also shown to have a detection limit of $F^-$ down to 0.5 ppm.

Over the past several decades, the development of anion receptors has received significant attention.[1] In particular, the detection of fluoride anions is of continuing interest due to their presence in drinking water, nerve agents, and the refinement of uranium used in weapons manufacturing.[2] As a result, fluoride sensing technologies that provide information pertaining to fluoride contamination are in high demand. Fluorescent fluoride sensors can be divided into four main categories including hydrogen-bonding/deprotonation,[3] Lewis acid/Lewis base,[4] anion-pi interactions,[5] and fluoride anion mediated chemical reaction.[6] This report will focus on compounds that utilize the hydrogen bonding/deprotonation mechanism. These neutral anion receptors usually contain subunits such as pyrrole, urea/thiourea, amide, indole, imidazole, and sulfonamide groups that can act as H-bond donors.[7] Fluoride anion can also lead to deprotonation via a Bronsted-Lowry acid-base interaction. This has also shown to be a very effective method. These sensors typically contain an acidic N—H proton which undergoes rapid fluoride induced deprotonation.[8] Some sensors utilize a "turn-on" or "turn-off" fluorescence mechanism for detection.[9] Herein, we report a new class of chromone-based fluorescent fluoride sensors that result in a blue-shift in the emission spectrum via a deprotonation mechanism allowing for quantitative detection of sub-1 ppm fluoride concentrations.

Our group recently reported the synthesis of a new class of fluorescent chromones that used an inverse-demand hetero-Diels-Alder reaction between substituted chromones and silyl enol ethers.[10] These compounds exhibited large Stokes shifts (~5300–6600 $cm^{-1}$) and gave quantum yields up to 73% (Scheme 1). Due to their interesting spectroscopic properties, we were interested in exploring their capability as fluorescent fluoride anion sensors, particularly due to the presence of a key N—H-bond on the sulfonamide subunit found in their core structure.

The fluoride sensing study began by screening three different compounds from our small library of fluorescent chromone derivatives. Interestingly the sulfonamido-chromone **4** gave a significant decrease in fluorescent intensity (~2.7-fold) and the emission blue-shifted by approximately 33 nm (Fig. 1(a)) upon addition of fluoride as the tetrabutylammonium (TBA) salt. Chromone **6** (bearing two methoxy donating groups to the chromophore) gave a similar result (Fig. 1(c)); however, it was determined that compound **4** gave a greater fluorescence intensity change (via lowering) and wavelength shift. Surprisingly, we found that enol **5** resulted in almost no change in fluorescence upon addition of up to 20 equiv. of fluoride (Fig. 1(b)).

Using fluorophore **4** as the optimized fluoride sensor, we investigated different solvents. Fig. 2 depicts the fluorescent spectra of sulfonamido-chromone **4** with varying equivalents of fluoride (TBA salt) in three different solvents. Acetone (a) resulted in an intensity decrease of 23% with a negligible $\lambda_{em}$ change, and acetonitrile (b) gave a decrease in fluorescent intensity of 35% and blue-shifted the emission wavelength 25 nm ($\lambda_{em}$ = 484 nm with no fluoride and $\lambda_{em}$ = 453 nm with 20 equiv. of fluoride). Although there is an observed change in fluorescence in these two polar aprotic solvents, superior results were achieved in $CH_2Cl_2$ (c) (63% decrease in intensity and $\Delta\lambda_{em}$ = 33 nm, blue-shifted). It

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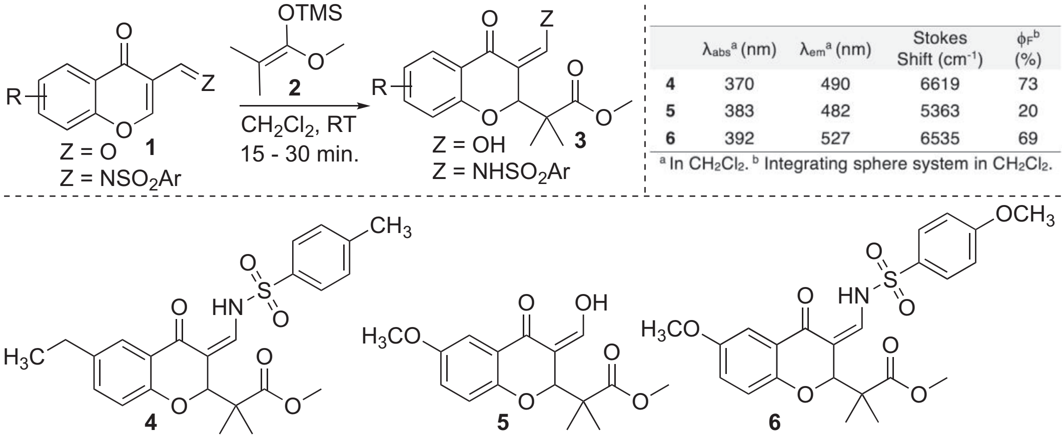
https://doi.org/10.1016/j.tetlet.2018.05.050



| | $\lambda_{abs}$[a] (nm) | $\lambda_{em}$[a] (nm) | Stokes Shift (cm$^{-1}$) | $\phi_F$[b] (%) |
|---|---|---|---|---|
| 4 | 370 | 490 | 6619 | 73 |
| 5 | 383 | 482 | 5363 | 20 |
| 6 | 392 | 527 | 6535 | 69 |

[a] In CH$_2$Cl$_2$. [b] Integrating sphere system in CH$_2$Cl$_2$.

**Scheme 1.** Synthesis of chromone fluorescent sensors.

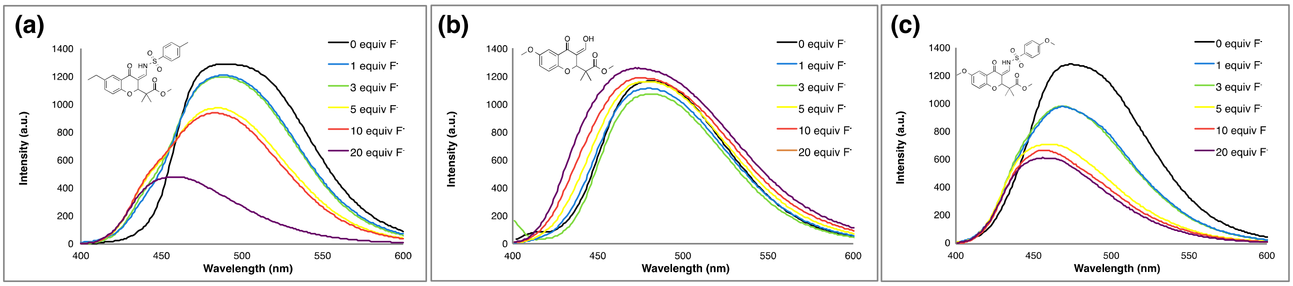


**Fig. 1.** (a) Fluorescent spectra of 1.0 µM **4** with fluoride equivalents in CH$_2$Cl$_2$ (b) fluorescent spectra of 1.0 µM **5** with fluoride equivalents in CH$_2$Cl$_2$ (c) fluorescent spectra of 1.0 µM **6** with fluoride equivalents in CH$_2$Cl$_2$.

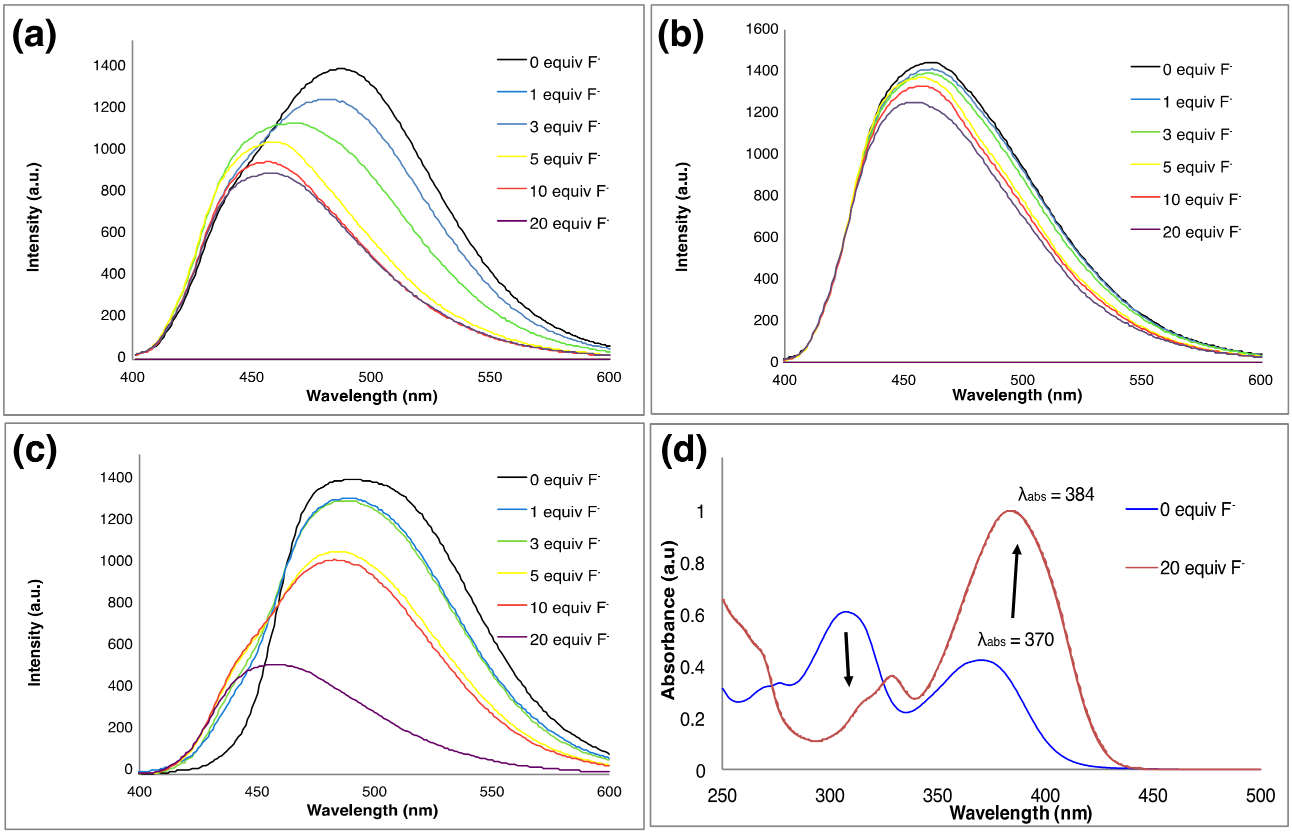


**Fig. 2.** Fluorescent emission spectra of 1.0 µM **4** with F$^-$ in (a) CH$_3$CN, (b) acetone, (c) CH$_2$Cl$_2$, and (d) absorbance spectra of **4** with and without F$^-$.