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A tetra-sulfonamide derivative bearing two dansyl groups designed as a new fluoride selective fluorescent chemosensor

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Abstract—A new fluorescent chemosensor based on an acyclic tetra-sulfonamide derivative linked to two dansyl groups has been conveniently synthesized. Its high selective binding ability to fluoride ions over other halide ions was demonstrated by using fluorescence as well as ^{1}H NMR spectra.

The design of new receptors with electrochemical or optical properties for the selective detection of anions[1] has received considerable attention over the past several years, for anions not only are ubiquitous throughout biological systems but also play crucial roles in the areas of medicinal, catalysis, and environmental chemistry. Following a lot of successful examples of fluorescent chemosensors[2] for cations and neutral molecules, fluorescence is becoming of an important detection method for anions[3] as for its simplicity and high sensitivity. Generally, a typical fluorescent chemosensor is built by an appropriate ionophore for binding the substrate and a photoactive fluorophore attached for the signal detection.

The fluoride ion is one of the most important anions because of its biologically important role in dental care and clinical treatment for osteoporosis.[4] Thus some receptors, which can selectively bind and sense the fluoride ion through the naked eye,[5] electrochemical,[6] and NMR[7] procedures, have been designed. Recently, selective fluorescent chemosensor for the fluoride ion has received considerable attention.[8] In particular, Sessler and co-workers[8a,b] reported some fluorescent sensors for the fluoride ion based on calix[4]pyrrole as the anion recognition element, and more recently two fluoride selective fluorescent chemosensors based on bisphenylurea system were reported.[8d,e]

Compared with well-known types of hydrogen bonding for the anion with amides, pyrroles, and ureas, the sulfonamide-based receptors for anions are rare although they have strong binding ability with anions and are readily available.[1a,c] To the best of our knowledge, no fluoride selective chemosensors based on sulfonamide derivatives have been reported. In this paper, we present a new fluorescent chemosensor **1** based on four sulfonamide groups designed as the binding sites and two dansyl groups[9] linked as the fluorophore, which shows a high selective binding ability to the fluoride ion over other halide ions.

The synthesis of compound **1** was started from commercially available anthraquinone-1,8-disulfonic acid, disodium salt **2**, which was reduced by zinc in water and then treated with $SOCl_2$ to give 9,10-dihydroanthracene-1,8-disulfonyl chloride **3** in 83% yield for two steps. 9,10-Dihydroanthracene-1,8-disulfonamide **4** was obtained in 91% yield from the reaction of compound **3** with excess ethylenediamine. Treatment of compound **4** with dansyl chloride in the presence of triethylamine gave the target compound **1** in 50% yield (Scheme 1). The structures of **1** and **4** were identified by ^{1}H NMR, ^{13}C NMR, MALDI-TOF MS, and elementary analyses.[10]

All of the fluorescence experiments were carried out in acetonitrile, and the fluorescence spectrum of receptor **1** was characterized by the maximum emission wavelength at 518 nm along with 341 nm as excitation wavelength.

Keywords: Tetra-sulfonamide; Fluoride ions; Fluorescent spectra; Chemosensor.
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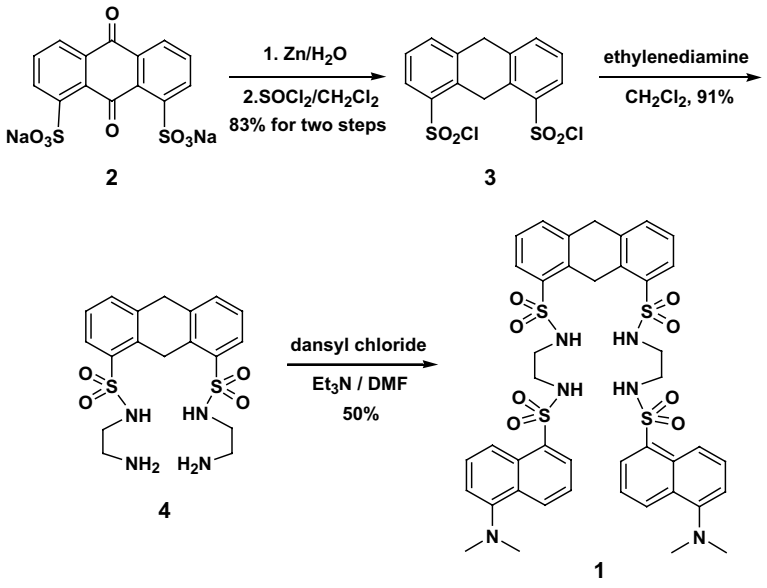


Scheme 1. Synthesis of tetra-sulfonamide compound **1**.

As shown in Figure 1, when 2 equiv of tetrabutylammonium fluoride were added to the solution of **1** (2×10^{-5} M), a blue shift ($\sim$10 nm) with a concomitant increase of the fluorescence intensity was observed. This phenomenon, which is similar to that of a tripodal ligand containing the dansyl groups upon the addition of cations due to a deprotonation–complexation process,[9] indicated that a strong binding interaction took place between the fluoride ion and the fluoroionophore in **1**. Under the same conditions, however, there were no significant spectral changes upon the addition of tetrabutylammonium chloride, bromide, and iodide. Even in the presence of high concentration of halides, only the chloride displayed the similar behavior as the fluoride but smaller changes in the fluorescent spectrum of receptor **1**, while still no significant spectral changes occurred in the cases of bromide and iodide.[11] These results suggest that **1** has a high selectivity for the fluoride ion among the halides.

Figure 2 shows the dependence of fluorescence spectra of **1** upon the concentration of the fluoride ion. Because of the $\phi^{-}_{\mathbf{1}\text{-F}} \neq 0$, the Scatchart-type equation[12] was used to calculate the binding constant between **1** and the fluoride ion, which was about $2.44\times10^{4}\ M^{-1}$ (error $<10\%$) in acetonitrile. Similarly, the binding constant between **1** and the chloride ion was calculated to be $820\ M^{-1}$. The selectivity for fluoride ions over chloride ions is about 30-fold, which is comparable with that of the naphthalene urea system[8e] reported recently.

In order to look into the binding properties of receptor **1** with halides, NMR experiments were carried out. A partial ^{1}H NMR spectrum of **1** is shown in Figure 3, and each peak in **1** was assigned according to its ^{1}H–^{1}H COSY spectrum. When 1 equiv of fluoride was added to

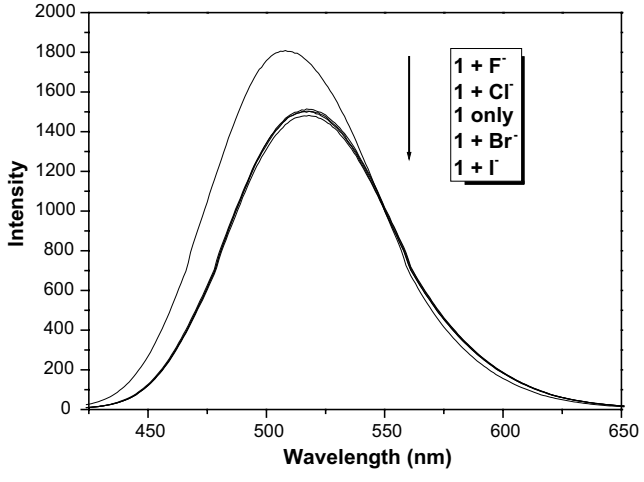


Figure 1. Fluorescent emission spectra of **1** (2×10^{-5} M) upon the addition of 2 equiv of tetrabutylammonium fluoride, chloride, bromide, and iodide in acetonitrile.

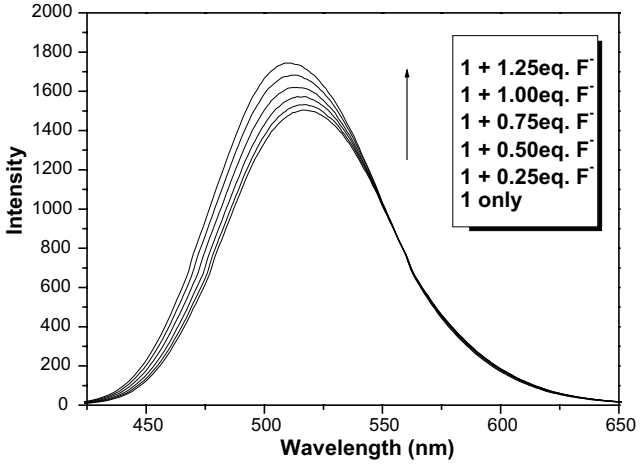


Figure 2. Fluorescent titrations of compound **1** (2×10^{-5} M) with tetrabutylammonium fluoride in acetonitrile. $\lambda_{ex} = 341$ nm.

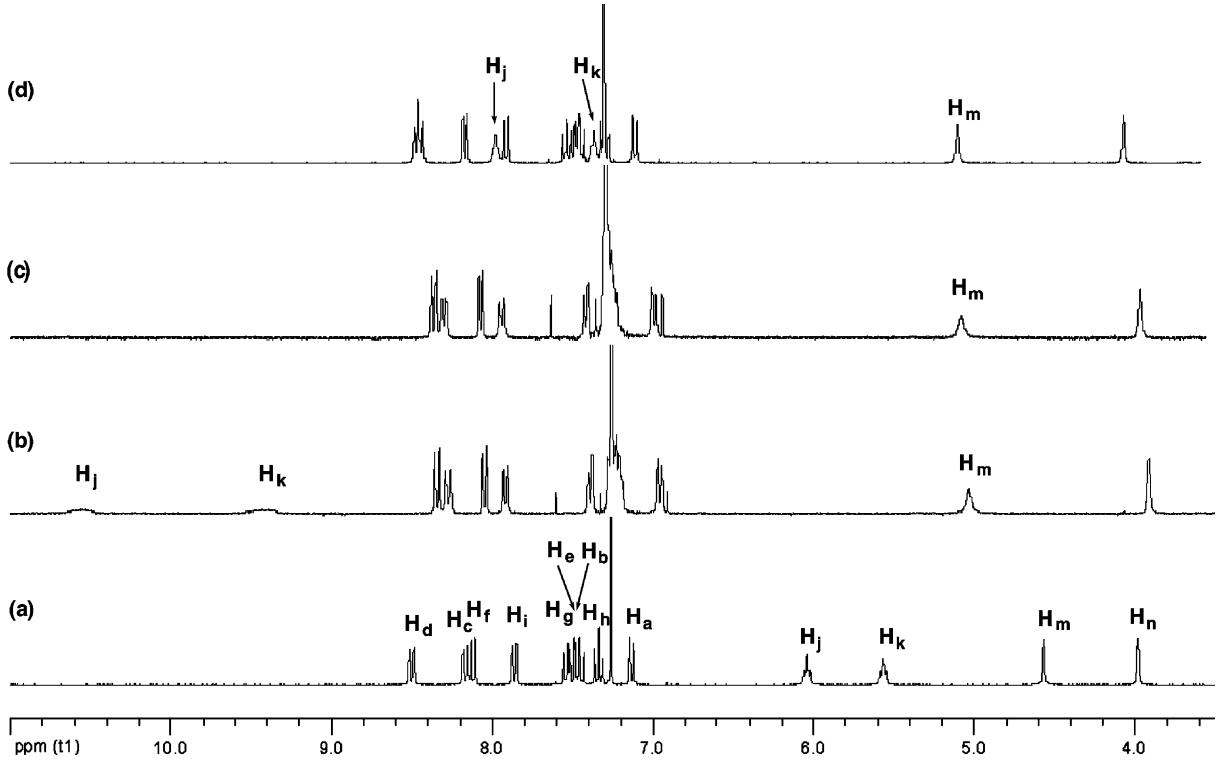
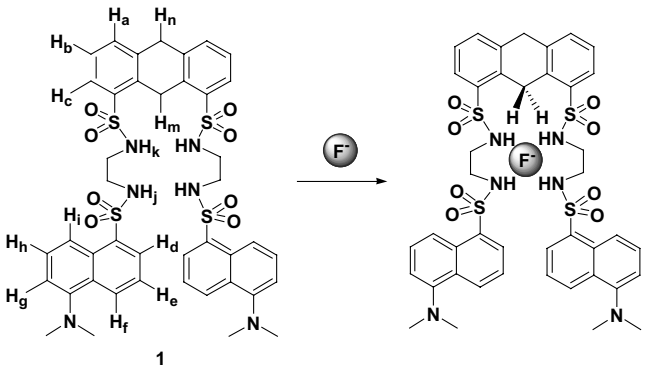


Figure 3. Partial 300 MHz ^{1}H NMR spectra of compound **1** (4.8 mM) in $CDCl_3$ at room temperature: (a) **1** only; (b) **1** + 1 equiv of tetrabutylammonium fluoride; (c) **1** + 2 equiv of tetrabutylammonium fluoride; (d) **1** + 2 equiv of tetrabutylammonium chloride. The numbering of protons is given in Scheme 2.

the solution of **1** in $CDCl_3$, its ^{1}H NMR spectrum displayed dramatic changes. Two sulfonamide N–H signals shifted significantly downfield ($\Delta\delta = +3.86$ and $+4.51$, respectively), and at the same time the aromatic proton signals shifted slightly downfield or upfield. Interestingly, a considerable downfield shift ($\Delta\delta = +0.50$) for the signal of the methylene protons at the 9-position of 9,10-dihydroanthracene moiety in receptor **1** was observed. Furthermore, two sulfonamide N–H signals disappeared upon the addition of 2 equiv of fluoride. These results indicated that the fluoride ion has a strong hydrogen bonding interaction not only with the protons of sulfonamide, but also with the methylene protons (H_m) at the 9-position (Scheme 2). The interaction between H_m and fluoride ion may be an example of C–H hydrogen bonding. In the case of chloride, the spectral changes of **1** were similar to but smaller than those of fluoride, which is consistent with the results of the above fluorescent method.

In conclusion, we have presented a new fluorescent chemosensor based on an acyclic tetra-sulfonamide derivative linked to two dansyl groups, which displayed high selective fluorescent effects on the fluoride ion over other halides in acetonitrile. Studies on the ^{1}H NMR spectra of **1** show that the fluoride ion has a strong hydrogen binding interaction with the protons of sulfonamide and also with the methylene protons at the 9-position of 9,10-dihydroanthracene moiety.



1

Scheme 2. Proposed binding mode for **1** with fluoride ion.

Acknowledgements

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10. **4**. Yield: 91%; mp: 161–162 °C; ^{1}H NMR ($CDCl_3$): 2.74 (t, $J = 5.16$ Hz, 4H), 2.91 (t, $J = 5.16$ Hz, 4H), 3.00 (s, 4H), 3.99 (s, 2H), 4.62 (s, 2H), 5.31 (br s, 2H), 7.34 (dd, $J = 7.32$, 7.77 Hz, 2H), 7.52 (d, $J = 7.32$ Hz, 2H), 7.92 (d, $J = 7.77$ Hz, 2H); ^{13}C NMR (DMSO-d_6): 28.9, 36.0, 41.3, 46.1, 126.2, 126.4, 131.3, 134.2, 137.7, 139.8; MALDI-TOF MS (m/z): 425 (M^++1). Anal. Calcd for $C_{18}H_{24}N_4O_4S_2$: C, 50.93; H, 5.70; N, 13.20. Found: C, 50.75; H, 5.72; N, 12. 87. **1**. Yield: 50%; mp: 111–112 °C; ^{1}H NMR ($CDCl_3$): 2.86 (s, 12H), 2.93–3.02 (m, 8H), 3.98 (s, 2H), 4.57 (s, 2H), 5.57 (t, $J = 5.80$ Hz, 2H), 6.04 (t, $J = 5.76$ Hz, 2H), 7.13 (d, $J = 7.50$ Hz, 2H), 7.34 (t, $J = 7.73$ Hz, 2H), 7.45–7.51 (m, 4H), 7.54 (d, $J = 7.02$ Hz, 2H), 7.86 (dd, $J = 7.89$, 0.91 Hz, 2H), 8.11 (dd, $J = 7.30$, 1.14 Hz, 2H), 8.16 (d, $J = 8.63$ Hz, 2H), 8.50 (d, $J = 8.50$ Hz, 2H); ^{13}C NMR (DMSO-d_6): 28.6, 35.9, 41.9, 42.1, 45.0, 115.1, 118.8, 123.5, 126.1, 126.3, 127.9, 128.3, 128.8, 129.0, 129.5, 131.5, 134.0, 135.3, 137.1, 139.7, 151.3; MALDI-TOF MS (m/z): 891 (M^++1). Anal. Calcd for $C_{42}H_{46}N_6O_8S_4 \cdot H_2O$: C, 55.49; H, 5.32; N, 9.24. Found: C, 55.13; H, 5.08; N, 8.91.
11. In the case of I^-, a weak quenching of the fluorescent intensity of **1** was observed upon the addition of excess iodide because of heavy atom effect.[8f]
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