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Kwanmuang, Paradee
Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Kasetsart University

Songsasen, Apisit
Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Kasetsart University

Sirisaksoontorn, Weekit
Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Kasetsart University

Wannalerse, Boontana
Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Kasetsart University

https://doi.org/10.15017/2552933

出版情報：Proceedings of International Exchange and Innovation Conference on Engineering & Sciences (IEICES). 5, pp.49-52, 2019-10-24. 九州大学大学院総合理工学府
バージョン：
権利関係：

Synthesis of a novel sensor based on orcinol-dansyl derivative for fluoride ion detection

Paradee Kwanmuang, Apisit Songsasen, Weekit Sirisaksoontorn and Boontana Wannalerse*
Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Kasetsart University, Chatuchak, Bangkok, 10900, Thailand
*e-mail: fscibnw@ku.ac.th

Abstract: *A novel chemosensor (PK1) has been designed and synthesized in three steps. The binding ability of sensor PK1 with different anions (F^-, Cl^-, Br^-, $C_6H_5COO^-$, CH_3COO^-, $H_2PO_4^-$) in DMSO was evaluated by using ^1H NMR, UV-vis and fluorescence spectroscopic techniques. Upon addition of fluoride ion, the NH proton of PK1 disappeared because of deprotonation process. The sensor PK1 exhibited the spectral changes of selectivity to fluoride anion (F^-) over other anions, and the new absorption was found at 308 nm due to the internal charge transfer. The fluorescence emission at 415, 438, and 560 nm was quenched due to the complexation of PK1-F^-. The stoichiometric complexation was studies by Job's method as a 1:1 ratio of PK1 with F^-. The association constant between PK1 and fluoride was 4.5×10^4 M^{-1} in the DMSO solution.*

Keywords: Chemosensor; Dansyl; Fluoride ion.

1. INTRODUCTION

The new chemosensors for anion detection have been extensively developed and gained much attention for several years [1,2]. Anions display in many important aspects such as biochemical, environmental and industrial systems including things in daily life. Fluoride ion (F^-) is mixed in the gradient of toothpaste for protecting caries in human teeth. However, the risk of fluoride ion depends on extreme concentration levels. The excess fluoride level can cause many problems in the human body such as, thyroid problem, bone disease and dental fluorosis [3-4]. According to United States environmental protection agency (USEPA) and world health organization (WHO), the limitation of fluoride in water is 1.5 mg/L (79 µM) [5]. Host-guest chemistry is a simple and fast method for anion detection. The design and synthesis of host molecules have greatly concentrated on the selectivity and sensitivity of binding sites for anion sensing. Generally, chemosensors can interact with anions via hydrogen bonding, electrostatic, or hydrophobic interactions [6]. The dansyl fluorophore is well known due to its high fluorescence quantum yield and tremendous sensitivity to response in its system. Furthermore, dansyl fluorophore is easy to modify the molecule under simple reactions [7]. In this research, we report the synthesized sensor PK1 which consists of the amide moiety as a binding unit and the dansyl group as a signaling unit for fluoride ion detection. The complexation between sensor PK1 and fluoride ion was investigated by ^1H-NMR, UV-visible and fluorescence techniques.

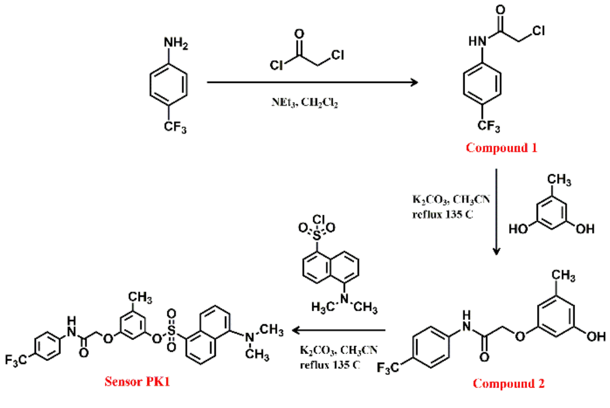
2. EXPERIMENT

2.1 Chemicals and instrumentation

All reagent and solvents were obtained commercially at analytical grade and used without further purification. All the tetrabutylammonium (TBA) salts of various anions (F^-, Cl^-, Br^-, CH_3COO^-, $C_6H_5COO^-$, $H_2PO_4^-$) were purchased from Merck KGaA. The ^1H and ^{13}C NMR spectra were recorded on a Bruker Advance 500 using $CDCl_3$ and $(CD_3)_2SO$ as solvents. FT-IR spectra were taken with Perkin Elmer 2000 using KBr pellet technique in the range of 4000-400 cm^{-1}. High resolution mass spectra (HRMS) were measured on a Bruker microtof-Q III. Elemental analysis of all compounds was examined by SCIENTIFIC AND TECHNOLOGICAL RESEARCH EQUIPMENT CENTER. UV-vis spectra were recorded on a UV-visible spectrophotometer (SHIMADZU UV-1800).

2.2 Synthesis and structural characterization of PK1

The sensor PK1 was successfully prepared by the synthetic route as shown in scheme 1.



Scheme 1. The synthetic route of sensor PK1

2.2.1 Synthesis of 2-chloro-N-4-(trifluoromethyl)phenyl) acetamide (Compound 1)

4-(trifluoromethyl) aniline (2.5 g, 0.0155 mol) and triethylamine (3.25 mL) in dichloromethane (10 mL) were stirred under nitrogen atmosphere for an hour. The chloroacetyl chloride (4.95 mL) in dichloromethane (2 mL) was added dropwise in ice bath. The mixture was stirred for 24 h. The reaction mixture was poured into water and extracted (3x20 mL) with dichloromethane. The organic layer was dried with anhydrous Na_2SO_4. The CH_2Cl_2 solvent was evaporated by using rotary evaporator. The compound 1 was afforded as a brown solid in yield of 85.03% ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.41 (s, 1H), 7.72 (d, J = 8.6 Hz, 2H), 7.65 (d, J = 8.7 Hz, 2H), 4.25 (s, 2H)

2.2.2 Synthesis of 2-(3-hydroxy-5-methylphenoxy)-N-(4-(trifluoromethyl)phenyl)acetamide (Compound 2)

3,5-dihydroxytoluene (1.0448 g, 8.42 mmol) and K_2CO_3 (1.7450 g, 0.0126 mol) in acetonitrile (15 ml) were stirred and refluxed at 135°C under nitrogen atmosphere for an hour. Then, 2-chloro-N-(4-(trifluoromethyl) phenyl) acetamide (2 g, 8.42 mmol) in acetonitrile (15 ml) was added dropwise. The mixture was stirred for 13 h. The reaction mixture was poured into water and extracted with dichloromethane. The organic layer was dried with anhydrous Na_2SO_4. The product was purified by column chromatography using $EtOAc/CH_2Cl_2$ = 1:9 (v/v) as an eluent to get compound 2 as white solid (26.61%yield). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.39 (s, 1H), 7.75 (d, J = 8.6 Hz, 2H), 7.68 – 7.54 (m, 2H), 6.50 – 6.25 (m, 3H), 5.32 (s, 1H), 4.63 (d, J = 13.0 Hz, 2H), 2.32 (s, 3H).

2.2.3 Synthesis of 3-methyl-5-(2-oxo-2-((4-(trifluoromethyl) phenyl) amino) ethoxy) phenyl 5-(dimethylamino)naphthalene-1-sulfonate (Sensor PK1)

Compound 2 (0.7 g, 2.15 mmol) and K_2CO_3 (0.4461g, 3.23 mmol) in acetonitrile (15 mL) were stirred and refluxed at 135°C under nitrogen atmosphere for an hour. Then, dansyl chloride (0.5805g, 2.15 mmol) in acetonitrile (15 mL) was added dropwise. The mixture was stirred for 7 h. The reaction mixture was poured into water and extracted with dichloromethane. The organic layer was dried with anhydrous Na_2SO_4. The product was purified by column chromatography using CH_2Cl_2 as an eluent to afford sensor PK1 as a yellow solid (77.54%yield). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.66 (d, J = 8.3 Hz, 2H), 8.49 (d, J = 8.6 Hz, 2H), 8.27 (s, 2H), 8.15 (dd, J = 7.3, 1.2 Hz, 2H), 7.77 – 7.66 (m, 6H), 7.63 (d, J = 8.6 Hz, 4H), 7.49 (dd, J = 8.4, 7.5 Hz, 2H), 7.35 – 7.25 (m, 3H), 6.66 (s, 2H), 6.51 (s, 2H), 6.40 (t, J = 2.1 Hz, 2H), 4.37 (s, 4H), 2.96 (s, 12H), 2.23 (s, 6H). ^{13}C NMR (400 MHz, $CDCl_3$, ppm): δ = 165.8, 157.1, 150.3, 141.4, 139.7, 132.1, 131.2, 131.0, 130.1, 129.1, 126.4, 125.3, 123.1, 122.6, 119.4, 116.9, 115.8, 114.2, 106.3, 67.4, 53.4, 45.5, 42.8, 32.2, 29.7, 26.4, 23.4, 21.5. FT-IR (KBr, cm^{-1}): ν = 3369, 1701, 1599, 1533, 1460, 1293,1067; HRMS (ESI): m/z $[M+H]^+$ calc.: $C_{28}H_{25}F_3N_2O_5S$, 559.57, and found: 559. 1499; Elemental Analysis : calc. $C_{28}H_{25}F_3N_2O_5S$, %C = 60.21, %H = 4.51, %N = 5.02, and found: %C = 60.61, %H = 4.28, %N = 4.67.

2.3 The preparation of stock solution for binding study between sensor PK1 and various anions

Stock solutions of analytes (F^-, Cl^-, Br^-, CH_3COO^-, $C_6H_5COO^-$, $H_2PO_4^-$ in the form tetrabutylammonium salts) with the concentration of $1x10^{-3}$ M were prepared in DMSO. Sensor PK1 was dissolved in DMSO to give the stock solution with the concentration of $5x10^{-4}$ M.

3. RESULTS AND DISCUSSION

3.1 The binding behavior between sensor PK1 and various anions

3.1.1 ^1H NMR study

To investigate the sensing mechanism of sensor PK1 towards various anions, adding 4 equiv anions to PK1 was studied in DMSO-d_6 as a solvent in Fig 1. When adding fluoride ion, the NH proton of sensor PK1 disappeared because of deprotonation process. And also, the deprotonation NH proton of PK1 gave the signal of H_2F^- at 16.07 ppm. [8] Moreover, the aromatic proton shifted to upfield, indicating the increase of electron density. For chloride, bromide, benzoate, acetate and phosphate, the NH signal of PK1 displayed to downfield shift under hydrogen bonding interaction. Meanwhile, thearomatic protons slightly shifted to upfield. These results indicated that the sensor PK1 has high selectivity to the fluoride ion.

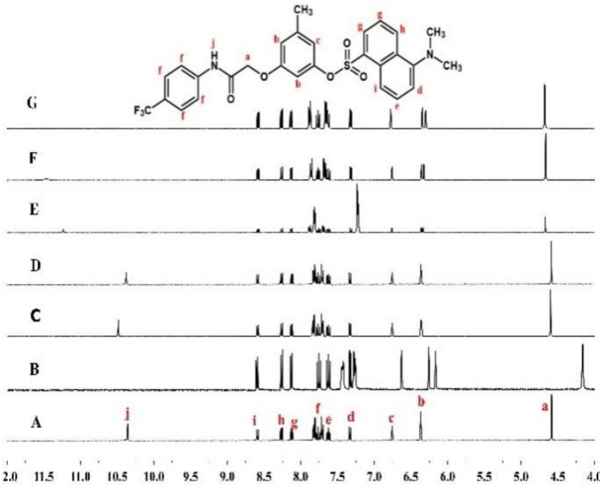


Figure 1. ^1H NMR spectra of (A) PK1 = $5x10^{-4}$ M. (B) PK1 + 4 equiv of F^- (C) PK1 + 4 equiv of Cl^- (D) PK1 + 4 equiv of Br^- (E) PK1 + 4 equiv of $C_6H_5COO^-$ (F) PK1 + 4 equiv of CH_3COO^- (G) PK1 + 4 equiv of $H_2PO_4^-$ in DMSO-d_6

3.1.2 UV-vis spectroscopic studies

The anion binding affinity of sensor PK1 with different anions (F^-, Cl^-, Br^-, $C_6H_5COO^-$, CH_3COO^-, $H_2PO_4^-$) was performed by UV-vis absorption spectroscopy. Upon addition of 20 equiv. F^- to PK1 solution, the absorption band at 358 nm was decreased and a new absorption band at 308 nm was found as shown in Fig.2A. The results occurred under internal charge transfer process [9-11]. Moreover, the graph bars exhibited that only F^- ion gave the new band at 308 nm in Fig 2B. Under the same condition, there was no the absorption band at 308 nm when adding other anions.

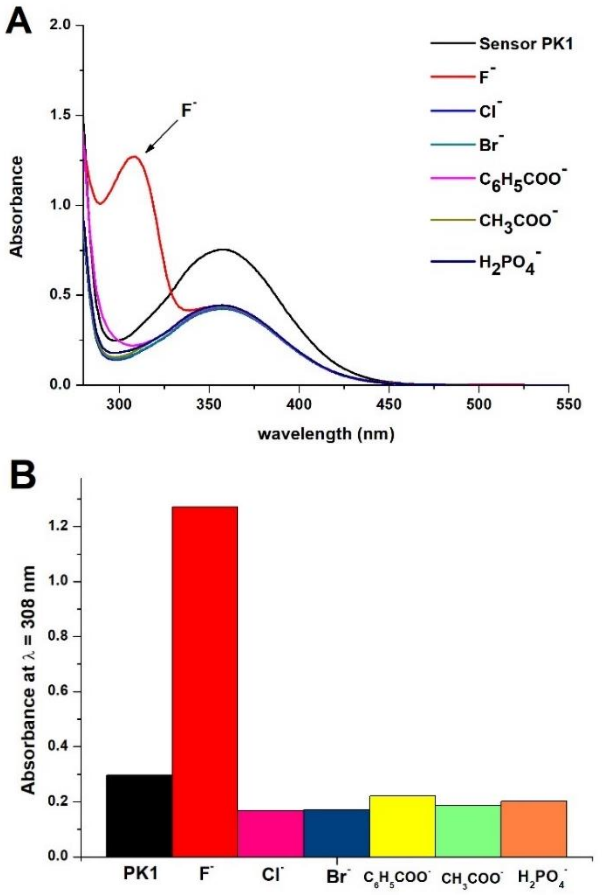


Figure 2. (A) UV-vis absorption spectra of PK1 (2x10^{-4} M) in DMSO/TBAPF$_6$ in the absence and presence of 20 equiv. of various anions: F$^-$, Cl$^-$, Br$^-$, CH$_3$COO$^-$, C$_6$H$_5$COO$^-$, H$_2$PO$_4^-$ (B) The graph bars at λ = 308 nm of PK1 and PK1 + various anions.

3.1.3 Fluorescence spectra

The fluorescent sensing properties of sensor PK1 to F$^-$ with different concentrations were performed by the titration experiment in Fig 3.

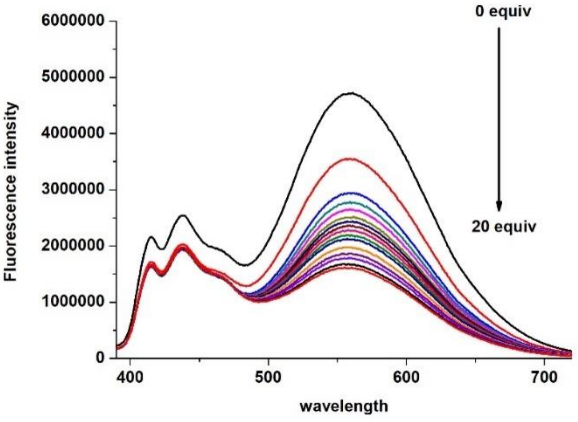


Figure 3. Fluorescence spectra of sensor PK1 (DMSO, 1x10^{-5} M.) upon the addition of F$^-$ ion (0-20 equiv.) λ_{ex} = 370 nm.

The fluorescence emission band at 415, 438, and 560 nm were quenched upon the addition of F$^-$ ion. This result indicates the complexation between PK1 and F$^-$ ion in the solution [12]. Moreover, the Job's plot of PK1 and F$^-$ ion suggests that the fluorescence intensity at 558 nm reached the maximum at 0.5 mole fraction (Fig. 4), which was identified as a 1:1 ratio complexation of PK1 and F$^-$.

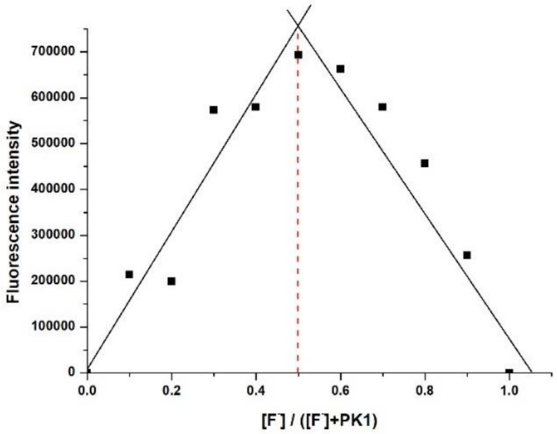


Figure 4. Job's plot of PK1 and fluoride ion in DMSO/TBAPF$_6$. The emission wavelength was 558 nm (λ_{ex} = 370 nm).

3.2 Calculation of the association constant

The association constant can be calculated by using the Benesi-Hildebrand equation [13]. From the relationship between 1/(F-F$_0$) and 1/[F$^-$], a linear plot was obtained with R^2 = 0.9923. The association constant between sensor PK1 and F$^-$ ion was equal to 4.5x10^4 M^{-1}.

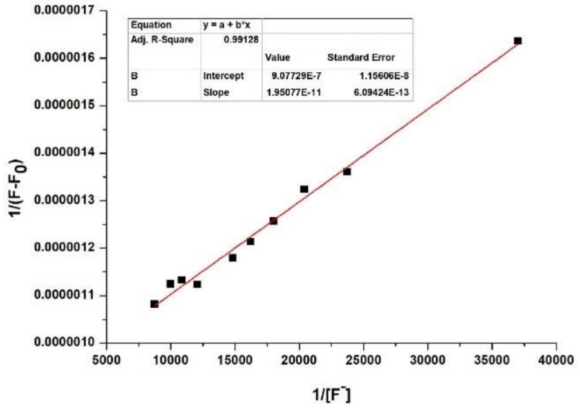


Figure 5. Benesi-Hildebrand plot (λ_{ex} = 370 nm) of 1/(F-F$_0$) vs 1/[F$^-$] based on a 1:1 complexation between PK1 and F$^-$.

4. CONCLUSION

In summary, we have successfully developed a new orcinol-dansyl derivative (sensor PK1). From ^{1}H NMR, UV-vis and fluorescence titration studies, the NH proton of PK1 can be deprotonated by F$^-$ ion. It was found that a new absorption band at 308 nm was ascribed to the internal charge transfer. Moreover, the fluorescence emission at 415, 438, and 560 nm was quenched due to complexation between PK1 and F$^-$.

5.ACKNOWLEGEMENTS

We would like to thank the Thailand Research Fund, Kasetsart University Research and Development Institute, the Department of Chemistry, Faculty of science, Kasetsart University and the Center of Excellent for Innovation in Chemistry (PERCH-CIC), the Ministry of Higher Education, Science, Research and Innovation for financial support.

6. REFERENCES

[1] Chen, C.-F. and Q.-Y. Chen, A tetra-sulfonamide derivative bearing two dansyl groups designed as a new fluoride selective fluorescent chemosensor, Tetrahedron Letters. 45(20)(2004) 3957-3960.

[2] Miao, R., et al, A C-linked peptidocalix[4]arene bearing four dansyl droups: a highly selective fluorescence chemosensor for fluoride ions, Tetrahedron Letter. 45(25)(2004) 4959-4962.

[3] Wu, Y.-C., et al, Design and application of tri-benzimidazolyl star-shape molecules as fluorescent chemosensors for the fast-response detection of fluoride ion, Sensors and Actuators B: Chemical. 237(2016) 865-875.

[4] Kaur, N. and G. Jindal, "Switch on" fluorescent sensor for the detection of fluoride ions in solution and commercial tooth paste, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. 223(2019) 117361

[5] Gowri, A., et al, A pyrene based colorimetric chemosensor for CO_2 gas detection triggered by fluoride ion, Chemical Physics Letters. 719(2019) 67-71.

[6] Kodlady, S. N., et al, Aromatic aldehyde based chemosensors for fluoride and cyanide detection in organic and aqueous media: Ascertained by characterization, spectroscopic and DFT studies, Inorganic Chimica Acta. 494(2019) 245-255.

[7] Ocak, Ü., et al, Calixarenes with dansyl groups as potential chemosensors, Inorganic Chimica Acta. 381(2012) 44-57.

[8] Liu, S. , et al, Distinctive fluoride fluorescent probes with ratiometric characteristics combinate desilylation, hydrogen bond and ESIPT process: Spectral and mechanistic studies, Sensor and Actuators B: Chemical. 255(2018) 401-407.

[9] Yao, K. , et al, A novel coumarin-based fluorescent sensor for Ca^{2+} and sequential detection of F^- and its live cell imaging, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. 216(2019) 385-394.

[10] Niu, Q., et al, A highly selective turn-on fluorescent and naked-eye colorimetric sensor for cyanide detection in food samples and its application in imaging of living cells, Sensors and Actuators B: Chemical. 276(2018) 13-22.

[11] Ashok Kumar, S. L., et al, Novel heterocyclic thiosemicarbazones derivatives as colorimetric and "turn-on" fluorescent sensors for fluoride anion sensing employing hydrogen bonding, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. 113(2013) 123-129.

[12] Liu, S.-y., et al, Fluorescent sensors for amino acid anions based on calix[4]arenes bearing two dansyl groups, Tetrahedron: Asymmetry. 16(8)(2005) 1527-1534.

[13] Zhou, T., et al, Synthesis and evaluation of a new furfuran-based rhodamine B fluorescent chemosensor for selective detection of $Fe3+$ and its application in living-cell imaging, Sensors and Actuators B: Chemical. 253(2017) 292-301.