

2-(4-Formylphenyl)phenanthroimidazole as a Colorimetric and Fluorometric Probe for Selective Fluoride Ion Sensing

Fanpeng Kong · Qingjian Liu · Xue Wu · Zhen Wang ·
Qing Chen · Lusheng Chen

Received: 23 December 2010 / Accepted: 13 February 2011 / Published online: 24 February 2011
© Springer Science+Business Media, LLC 2011

Abstract An easy-to-prepare chemosensor, 2-(4-formylphenyl)phenanthroimidazole **1**, synthesized by facile one-step condensation under microwave irradiation, has been indicated to be a colorimetric and fluorometric probe for fluoride anion with good sensitivity and high selectivity. This probe shows obvious red shift and absorbance intensity changes in UV absorption and fluorescence spectra in the presence of fluoride anions. Such color and absorbance intensity changes are attributed to the deprotonation of N-H on the imidazole moiety with fluoride anion.

Keywords Phenanthroimidazole · Fluoride anion · Chemosensor · Colorimetric and fluorometric probe

Introduction

The development of chemosensors for selective anion recognition has received much attention, as anions play a

fundamental role in a wide range of chemical, biological, medical, and environmental processes [1–4]. Fluoride ion, the smallest anion, has unique chemical properties, and its recognition and detection are of growing interest because it is associated with dental care, the treatment of osteoporosis, nerve gases, the analysis of drinking water, and the refinement of uranium used in nuclear weapons manufacture. A number of synthetic colorimetric [5–9], fluorometric [10–15], as well as dual mode [16–25] probes have been designed and made for this important analyte. All of these probes require complicated synthesis. Easily and simply preparable fluoride ion probes are therefore necessary and useful for practical applications.

The plane-structured molecule **1**, 2-(4-formylphenyl)phenanthroimidazole, synthesized by facile one-step condensation, has unique thermal stability and optical properties, and has been used as probes for copper ion [26], cysteine and homocysteine [27]. Herein, we report the studies of this compound as a highly selective fluoride ion probe in both colorimetric and fluorometric analyses.

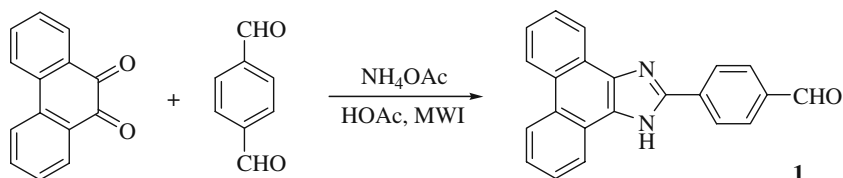
Experimental Section

Solvents and reagents were used as received. The NMR spectra were determined on a Bruker 300 MHz spectrometer using TMS as the internal standard in DMSO- d_6 ; UV–vis spectra were taken on a Pharmaspec TU-1901 spectrophotometer using quartz cells with path-length of 1 cm; Fluorescence spectra were recorded on a Varian Cray Eclipse fluorescence spectrophotometer with quartz cells of path-length 1 cm. All measurements were performed under ambient atmosphere at room temperature.

F. Kong
Department of Chemistry, College of Science, Tianjin University,
Tianjin 300072, People's Republic of China

Q. Liu (✉) · X. Wu · Z. Wang · Q. Chen · L. Chen
College of Chemistry, Chemical Engineering and Materials
Science, Key Laboratory of Molecular and Nano Probes,
Engineering Research Center of Pesticide and Medicine
Intermediate Clean Production, Ministry of Education, Shandong
Provincial Key Laboratory of Clean Production of Fine
Chemicals, Shandong Normal University,
Jinan 250014, People's Republic of China
e-mail: liujq@sdnu.edu.cn

Scheme 1 Synthesis of 2-(4-formylphenyl)phenanthroimidazole **1**



Synthesis of the Probe **1** (Scheme 1)

A mixture of phenanthraquinone 0.21 g (10 mmol), ammonium acetate 0.39 g (50 mmol), and terephthalaldehyde 0.40 g (30 mmol) in 20 mL acetic acid was irradiated in a microwave synthesizer for 10 min monitored with TLC [28]. The reaction mixture was neutralized with aqueous ammonia and the crude product was collected and recrystallized from nitrobenzene to afford the pure product, 71% yield, and mp 315–317°C. IR (KBr pellet): ν_{\max} 3442, 1678 cm^{-1} . ^1H NMR (300 MHz, DMSO-d_6): δ_{H} 13.77(s, 1 H), 8.82–9.10 (d, $J=8.2$ Hz, 2 H), 8.51–8.63 (m, 4 H), 8.41–8.61 (d, $J=8.2$ Hz, 2 H), 7.81 (s, 2 H), 6.80 (s, 2 H) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): 122.39, 122.66, 124.27, 124.63, 125.98, 126.30, 126.90, 127.28, 127.68, 127.79, 128.19, 128.52, 128.80, 130.67, 135.87, 136.51, 137.86, 148.15, 193.02 ppm.

Results and Discussion

The resonance signal at 13.77 ppm in the ^1H NMR spectrum of **1** was assigned to the hydrogen of N-H in the imidazole moiety of the molecule **1**. The probe **1** is composed of a phenanthroimidazole moiety and a formyl-

phenyl unit, the electron rich phenanthroimidazole ring acted as both a good fluorescent dye and a fairly strong electron donor [29].

Fluorescent anion titration studies as shown in Fig. 1, the probe exhibited greatly decrease of fluorescence intensity as well as a large emission peak red-shifted (80 nm) upon addition of fluoride anion, which is attributed to the deprotonation with fluoride anion of the phenanthroimidazole moiety of **1**, becoming a negatively charged core with stronger electron donation.

Changes in the fluorescence spectra of probe **1** caused by other halide anions were also investigated. With the addition of 10 equivalents of halide anions for 10 min, respectively, the fluorescence spectra of the solution **1** were measured and presented in Fig. 2. It can be observed that only fluoride ion give rise to dramatic changes in the fluorescence spectra, while the other anions did not cause obvious changes under the same conditions. Such result implies that the selectivity of **1** for fluoride ion over the other anions is remarkably high and efficient.

UV–Vis Anion Titration Studies

Titration of **1** as a function of fluoride ion (shown in Fig. 3) gave a decreasing intensity with the formation of red-shifted band at 440 nm. The fluoride ion induced colorimetric and

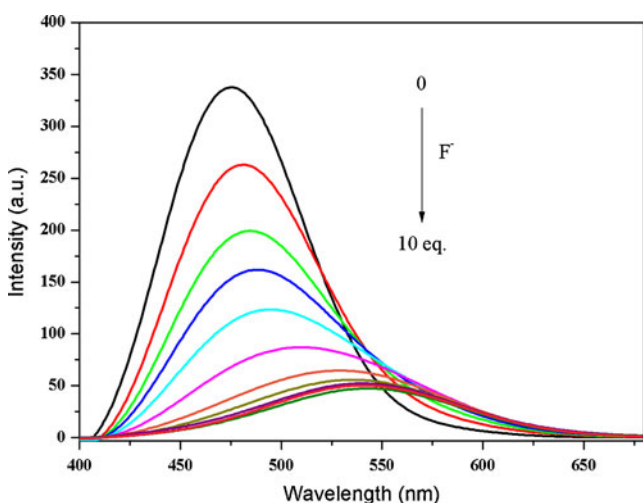


Fig. 1 Changes in emission spectra of **1** in Dichloromethane (DCM, 1.0×10^{-5} M) upon addition of F^- (1–10 equiv) in ($\lambda_{\text{ex}}=370$ nm)

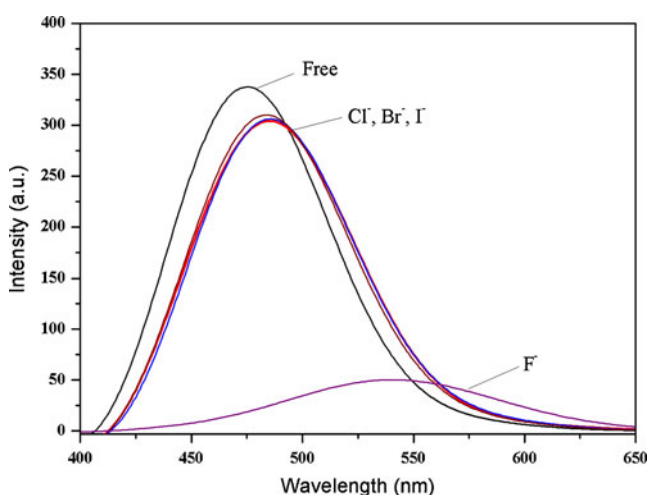


Fig. 2 Changes in absorption of **1** measured in DCM (1.0×10^{-5} M) upon addition of 10 equivalents of halide anions (as $n\text{-Bu}_4\text{N}^+$ salts)

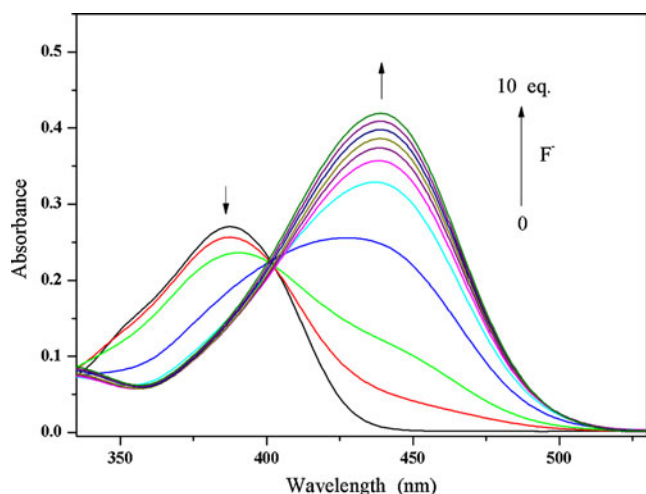


Fig. 3 Changes in absorption spectra of **1** in DCM (1.0×10^{-5} M) upon addition of tetrabutylammonium fluoride

fluorometric responses of **1** are simply driven by the intermolecular proton transfer between the imidazole ring and the fluoride anion. The spectral changes are due to the deprotonation [30–32] of the phenanthroimidazole moiety by fluoride ion. This would suggest that a negatively charged phenanthroimidazole has formed, which causes a significant increase in the charge density on the imidazole moiety associated with enhancement in the push-pull effect of the intermolecular charge transfer (ICT) transition [33]. As a result, when the imidazole moieties are deprotonated, charge redistribution takes place within the phenanthroimidazole molecules, the deprotonated push-pull chromospheres are responsible for the shift in both absorption (changes from colorless to yellow) and fluorescence (changes of fluorescence from cyan to yellow) (Fig. 4). The perceived color

Fig. 4 Color (left) and fluorescence (right, irradiation at 365 nm with UV lamp) changes of **1** in DCM (1.0×10^{-5} M) upon addition of 10 equivalents of tetrabutylammonium fluoride

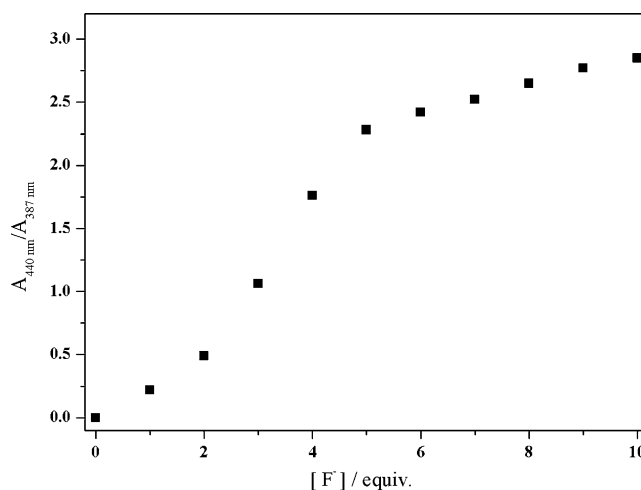
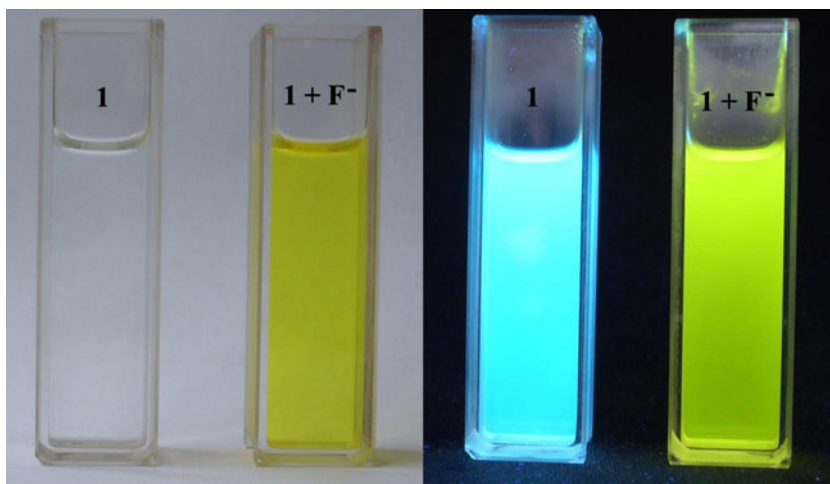


Fig. 5 Plot of the absorbance ratio of **1** in DCM (1.0×10^{-5} M) at 387 nm and 440 nm (A_{440}/A_{387}) vs. concentration of F^- in DCM

changes would be useful not only for the ratiometric detection but also for the rapid visual sensing.

Figure 5 shows a correlation between intensity ratios of absorption at 440 nm and 387 nm (A_{440}/A_{387}) and concentration of fluoride ion in dichloromethane. This demonstrates the potential utility of probe **1** for calibrating and determining fluoride ion concentration in dichloromethane in the presence of other halide ions, which did not cause any changes of the absorption of **1**. Figure 6 reveals that the changes in spectral absorption of **1** measured in DCM upon addition 10 equivalents halide anions, respectively. Without fluoride anion, **1** exhibits a characteristic absorption band centered at 387 nm, but the addition of fluoride ion leads to a sharp decrease in this absorption and a development of red-shifted absorption centered at

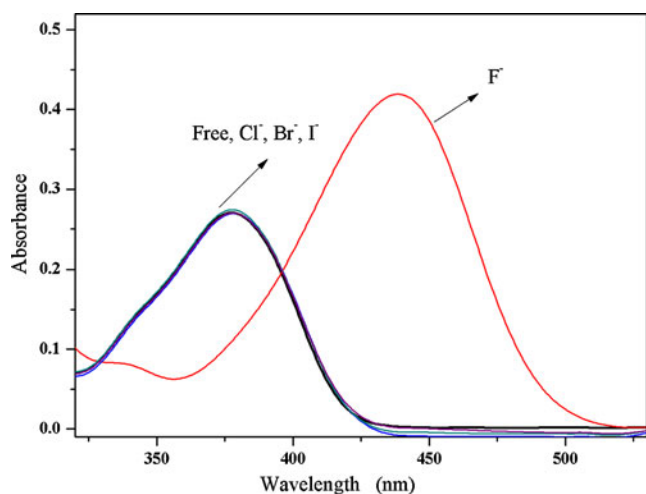


Fig. 6 Changes in absorption of 1DCM (1.0×10^{-5} M) measured in DCM upon addition of 10 equivalents of halide anions (as $n\text{-Bu}_4\text{N}^+$ salts)

440 nm. In contrast, the addition of other halide anions does not produce any spectral change.

^1H NMR Titrations

To further elucidate the nature of the intermolecular interactions between anions and probe **1**, we carried out the ^1H NMR analysis of the probe in the presence of TBAF in $\text{DMSO-}d_6$ (Fig. 7). Obviously, the resonance signal at 13.77 ppm, which was assigned to the hydrogen of N-H group on the imidazole moiety of the molecule **1**, can be observed in the absence of fluoride anion. The disappearance of the NH signal in the presence of TBAF confirms the deprotonation of N-H by F^- .

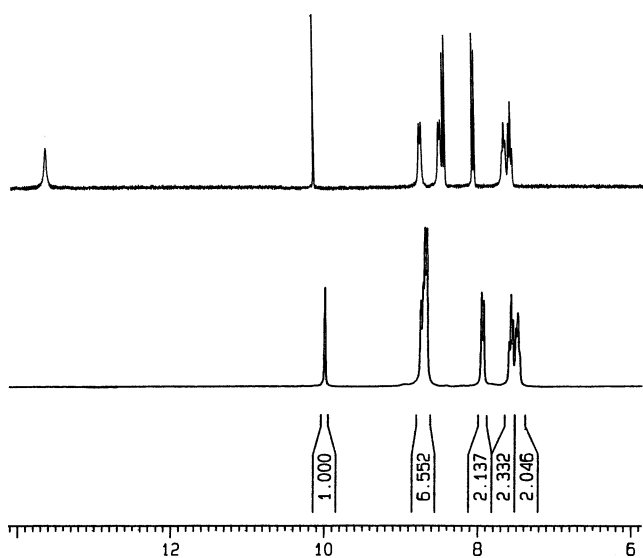


Fig. 7 ^1H NMR (300 MHz) of **1** (up) and **1** + TBAF (1:10) in $\text{DMSO-}d_6$

Analytical Applications

Experimental results given show the performance of probe **1** with high selectivity for F^- anion. Color changes were observed obviously, turning from cyan to yellow upon addition of F^- to the solution of **1** (1.0×10^{-5} M). However, no detectable color responses were observed while adding other halide anions such as Cl^- , Br^- and I^- ions.

Conclusion

In summary, we have presented a chemosensor for fluoride anion, 2-(4-formylphenyl)phenanthroimidazole **1**, synthesized by facile one-step condensation under microwave irradiation, behaving as a highly sensitive fluoride anion probe in both colorimetric and fluorometric analyses. The sharp changes in UV absorption and fluorescence spectra are simply driven by the interaction between the imidazole N-H proton and fluoride ion. The remarkable photophysical properties of the probe would help to extend the design and development of colorimetric and ratiometric fluorescent chemosensors for fluoride anion.

Acknowledgments Tianjin University and College of Chemistry, Chemical Engineering and Materials Science, Key Laboratory of Molecular and Nano Probes, Engineering Research Center of Pesticide and Medicine Intermediate Clean Production, Ministry of Education, Shandong Provincial Key Laboratory of Clean Production of Fine Chemicals, Shandong Normal University are acknowledged.

References

- Martínez-Manêz R, Sancenón F (2006) *Coord Chem Rev* 250:3081
- Martínez-Manêz R, Sancenón F (2005) *J Fluoresc* 15:267
- Suksai C, Tuntulani T (2003) *Chem Soc Rev* 32:192
- Beer PD, Gale PA (2001) *Angew Chem Int Ed* 40:486
- He X, Hu S, Liu K, Guo Y, Xu J, Shao S (2006) *Org Lett* 8:333
- Cho EJ, Ryu BJ, Lee YJ, Nam KC (2005) *Org Lett* 7:2607
- Esteban-Gómez D, Fabbrizzi L, Licchelli M (2005) *J Org Chem* 70:5717
- Vázquez M, Fabbrizzi L, Taglietti A, Pedrido RM, González-Noya AM, Bermejo MR (2004) *Angew Chem Int Ed* 43:1962
- Jose DA, Kumar DK, Ganguly BD (2004) *Org Lett* 6:3445
- Swamy KMK, Lee YJ, Lee HN, Chun J, Kim Y, Kimand SJ, Yoon J (2006) *J Org Chem* 71:8626
- Liu XY, Bai DR, Wang S (2006) *Angew Chem Int Ed* 45:5475
- Wu JS, Zhou JH, Wang PF, Zhang XH, Wu SK (2005) *Org Lett* 7:2133
- Xu G, Tarr MA (2004) *Chem Commun* 1050
- Cho EJ, Moon JW, Ko SW, Lee JY, Kim SK, Yoon J, Nam KC (2003) *J Am Chem Soc* 125:12376
- Jiang X, Vieweger MC, Bollinger JC, Dragnea B, Lee D (2007) *Org Lett* 9:3579
- Batista RMF, Oliveira E, Costa SPG, Loderio C, Raposo MM (2007) *Org Lett* 9:3201

17. Lin CI, Selvi S, Fang JM, Chou PT, Lai CH, Cheng YM (2007) *J Org Chem* 72:3537
18. Luxami V, Kumar S (2007) *Tetrahedron Lett* 48:3083
19. Lin Z, Ou S, Duan C, Zhang B, Bai Z (2006) *Chem. Commun* 624
20. Kim SK, Bok JH, Bartsch RA, Lee JY, Kim JS (2005) *Org Lett* 7:4839
21. Liu ZQ, Shi M, Li FY, Fang Q, Chen ZH, Yi T, Huang CH (2005) *Org Lett* 7:5481
22. Kubo Y, Yamamoto M, Ikeda M, Takeuchi M, Shinkai S, Yamaguchi S, Tamao K (2003) *Angew Chem Int Ed* 42:2036
23. Hudnall TW, Gabbai FP (2007) *J Am Chem Soc* 129:11978
24. Lee MH, Agou T, Kobayashi J, Kawashima T, Gabbai F P (2007) *Chem Commun* 1133
25. Kim TH, Choi MS, Sohn BH, Park SY, Lyoo WS, Lee TS (2008) *Chem Commun* 2364
26. Lin W, Yuan L, Tan W, Feng J, Long L (2009) *Chem Eur J* 15:1030
27. Lin W, Long L, Yuan L, Cao Z, Chen B, Tan W (2008) *Org Lett* 10:5577
28. Day AR, Steck EA (1943) *J Am Chem Soc* 65:452
29. Tsai MS, Hsu YC, Lin JT, Chen HC, Hsu CP (2007) *J Phys Chem C* 111:18785
30. Qu Y, Hua J, Tian H (2010) *Org Lett* 12:3220
31. Zhang M, Li M, Li F, Cheng Y, Zhang J, Tao Y, Huang C (2008) *Dyes Pigm* 77:408
32. Lee SH, Kim HJ, Lee YO, Vicens J, Kima JS (2006) *Tetrahedron Lett* 47:4373
33. Liu B, Tian H (2005) *J Mater Chem* 15:2681