Front. Chem. China 2010, 5(2): 162–165
DOI 10.1007/s11458-010-0105-9

COMMUNICATION

A novel fluorescence enhancing F^- probe based on intermolecular energy transfer

Quanguo WANG, Yubin DING, Weihong ZHU and Yongshu XIE (✉)

A supramolecular fluorescent sensor of F^- based on intermolecular energy transfer is described. The maximum absorption wavelength of a pyrrolic compound 1 is 472 nm, which is coincident with the emission wavelength of a dipyridylamine-anthracene compound 2. In the CH_2Cl_2 solution of 1 and 2, the fluorescence of 2 was quenched because of the presence of intermolecular energy transfer from 2 to 1. When F^- was added to this solution, the absorption maximum wavelength of 1 shifted from 472 to 594 nm due to a deprotonation process. Simultaneously, the fluorescence of 2 was recovered because of the interruption of the intermolecular energy transfer. Based on these observations, the combination of 1 and 2 can be regarded as a novel supramolecular fluorescence enhancing F^- probe.

Keywords fluoride sensor, intermolecular energy transfer, fluorescence enhancement

1 Introduction

Over the past decade, great efforts have been devoted to fluoride sensing due to its importance in a wide range of chemical and biological processes [1–8]. Among the methodologies that have been reported, fluorimetric sensing plays critical roles in the recognition and sensing due to its simplicity and low detection limit [9–12]. As the most electronegative atom, F^- can form the strongest H-bond interaction with hydrogen-bond donors; such property has been adopted in F^- detection by neutral receptors [13–16]. Accordingly, the strategy for the design and construction of classical fluorescent fluoride sensors is to covalently link a fluorophore with a binding unit. When F^- interacts with the binding part to form H-bonding or to induce deprotonation, the fluorophore converts the changes into optical outputs, including the quenching or enhancing of the fluorescence [17–20]. Based on the intramolecular energy transfer, various fluorescent fluoride sensors have been synthesized. However, the linkage of the binding unit with a fluorophore through properly designed covalent bonds usually requires rather complicated multistep organic synthesis [21–24]. On the other hand, if a supramolecular sensor system is constructed through intermolecular energy transfer, the complicated organic synthesis could be avoided, and a wide range of well known fluorophores could be readily selected and utilized. Based on these considerations, we designed a novel and simple supramolecular fluorescence enhancing fluoride recognition system based on the intermolecular energy transfer mechanism, i.e., we selected a fluoride binding agent whose absorption maximum wavelength is coincident with that of the emission of a fluorescent compound. In the absence of F^-, the fluorescence was quenched by an intermolecular energy transfer process. The binding of F^- resulted in the shift of the absorption wavelength of the host molecule, and the intermolecular energy transfer was interrupted. Thus, the fluorescence was recovered.

Received January 13, 2010; accepted February 1, 2010
Key Laboratory for Advanced Materials and Institute of Fine Chemicals, East China University of Science and Technology, Shanghai 200237, China
E-mail: yshxie@ecust.edu.cn

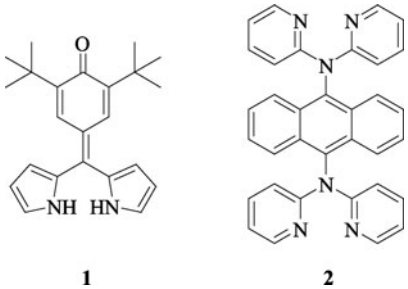
2 Experimental

2.1 Instruments and materials

Absorption spectra were measured on a Varian Cary 500 UV/Vis spectrophotometer (1 cm quartz cell was used). Fluorescence spectra were recorded on a Varian Cary Eclipse fluorescence spectrophotometer. All reagents used in this work were commercially available and used without further purification.

2.2 Preparation

The target sensor **1** (Figure 1) was synthesized in two steps with good yields. First, the condensation of 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde with pyrrole under acidic conditions



1 **2**

Figure 1 The chemical structures of sensor **1** and compound **2**.

afforded corresponding dipyrromethane, which was then oxidized with DDQ to afford **1** [25]. Compound **2** was synthesized according to a reported method [26].

3 Results and discussion

In our previous work [25], sensor **1** has been demonstrated to be an efficient colorimetric fluoride sensor as a result of a deprotonation process. From the UV-Vis titration of **1** with F^- (TBA salt) (Figure 2), we noticed that upon the addition of F^-, the intensity of the band at 472 nm decreased, and a new band at 594 nm developed, which can be ascribed to internal charge transfer (ICT). The addition of other anions, such as Cl^-, Br^-, and I^-, did not induce noticeable spectral responses (Figure 3).

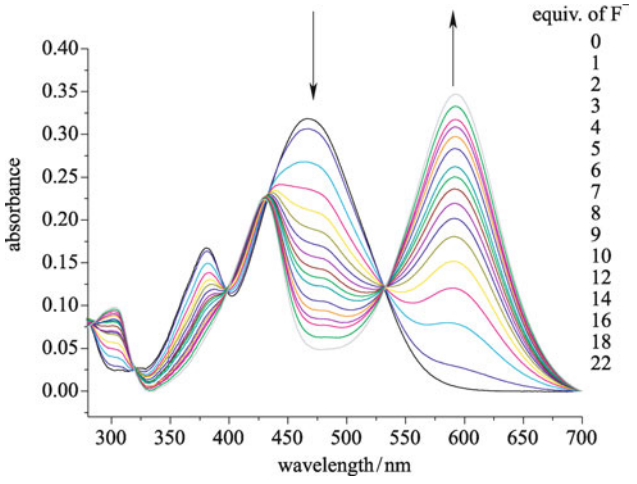


Figure 2 UV-Vis spectral changes of **1** (1.0×10^{-5} mol·L^{-1} in CH_2Cl_2) observed upon the addition of F^- (TBA salt) in CH_2Cl_2.

Based on the fact that the emission peak of **2** is 472 nm, which is almost equal to the λ_{max} at 472 nm for sensor **1**, we designed a novel supramolecular system for the fluorescent detection of F^- based on intermolecular energy transfer. When **1** was added to a CH_2Cl_2 solution of **2**, the energy of the excited state of **2** was transferred to **1**, and the fluorescence of **2** was quenched (Figure 4) due to the presence of the intermolecular energy transfer process. Thus, when 300 equivalents of **1** was added to the solution of compound **2,** the fluorescence of **2** was quenched by 48 percent (Figure 4), and 600 equivalents of **1** quenched the fluorescence by 71 percent.

When F^- was added to a mixture of compound **2** and 600 equivalents of **1**, a deprotonation process of **1** was caused by F^-, and the absorption maximum of **1** shifted from 472 to 594 nm, resulting in a cut-off of the intermolecular energy transfer accompanied with the recovering of the fluorescence of **2**. When 100 equivalents of F^- was added, the fluorescence

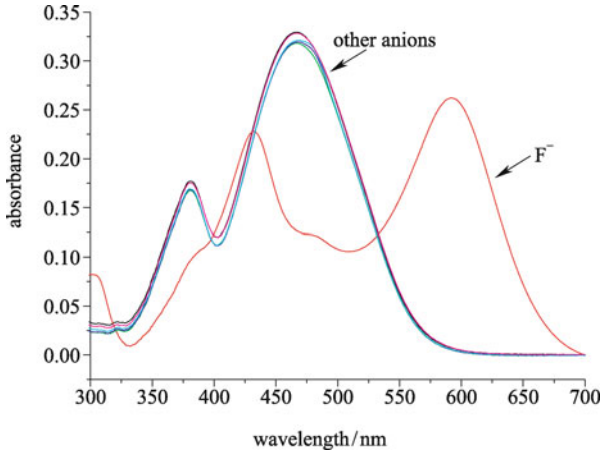


Figure 3 UV-Vis absorption change of **1** (1.0×10^{-5} mol·L^{-1} in CH_2Cl_2) upon addition of 10.0 equivalents of the anions (F^-, Cl^-, Br^-, or I^-).

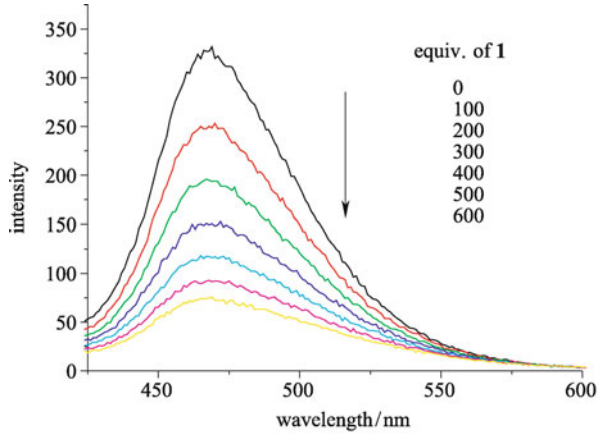


Figure 4 The fluorescence quenching of compound **2** (0.049 μmol·L^{-1} in CH_2Cl_2) upon the addition of **1**. Excitation wavelength was fixed at 397 nm (one of the isosbestic points).

increased by a factor of 2.2 (Figure 5(a)).

This anion sensing system based on the fluorescence enhancement has good selectivity for F^- over other halides. As mentioned above, Cl^-, Br^-, and I^- could not induce obvious changes in the UV-Vis spectra of **1** (Figure 3). Thus, no obvious fluorescence change could be observed even when 1000 equivalents of Cl^-, Br^-, or I^- was added to the solution of compound **2** and sensor **1** (Figure 5(b)). Based on these results, the combination of **1** and **2** may be developed as a novel promising supramolecular system for the detection of F^-.

4 Conclusions

In summary, we have developed a novel supramolecular approach for detecting F^- via fluorescence enhancement based

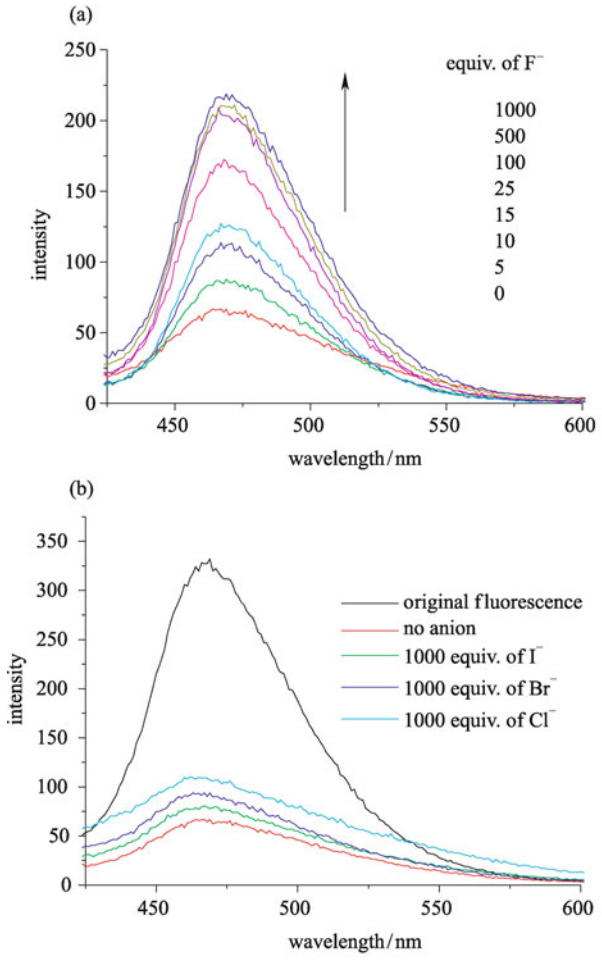


Figure 5 Fluorescence changes of the CH_2Cl_2 solution of compound **2** (0.049 μmol·L^{-1}) and sensor **1** (600 equivalents relative to **2**) upon the addition of (a) various equivalents of F^- (relative to **1**), and (b) Cl^-, Br^-, or I^- (1000 equiv. relative to **1**). Excitation wavelength was fixed at 397 nm (one of the isosbestic points).

on intermolecular energy transfer. The results indicate that the emission wavelength of the fluorescent compound **2** is coincident with the absorption maxima of a neutral receptor **1** containing NH fragments. In the absence of F^-, the fluorescence of **2** can be quenched by **1** due to an intermolecular energy transfer process. When F^- was added to this system, the shift of the absorption maxima of **1** results in the cut-off of the energy transfer process accompanied with fluorescence enhancement. This sensing behavior is highly selective for F^- over other halides based on the observation that Cl^-, Br^-, and I^- could not induce obvious changes in the absorption of **1** or the fluorescence of **2**.

Acknowledgements This work was financially supported by the Shanghai Pujiang Program (Grant No. 08PJ14037), the Program for New Century Excellent Talents in University (NCET), the National Natural Science Foundation of China, the Project Sponsored by the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry.

Yongshu XIE received his Ph.D. degree in 1998 from Zhejiang University. He worked as a postdoctoral fellow and an associate professor in University of Science and Technology of China (1998–2006). He also worked as a visiting researcher in Prof. Shieming Peng's group at National Taiwan University (2003), in Prof. Hiroyuki Furuta's group at Kyushu University (2004–2006) and in Dr. Katsuhiko Ariga's group at National Institute for Materials Science, Japan (2006–2007). In 2007, he joined East China University of Science and Technology as a professor. He currently works on the synthesis of novel porphyrinoids and metal-organic compounds for supramolecular assemblies, optoelectronic and magnetic materials.

References

1. Gale, P. A.; García-Garrido, S. E.; Garric, J., *Chem. Soc. Rev.* **2008**, *37*, 151–190
2. Amendola, V.; Fabbrizzi, L., *Chem. Commun*. **2009**, *5*, 513–531
3. Kubik, S., *Chem. Soc. Rev*. **2009**, *38*, 585–605
4. Steed, J. W., *Chem. Soc. Rev*. **2009**, *38*, 506–519
5. Caltagirone, C.; Gale, P. A., *Chem. Soc. Rev*. **2009**, *38*, 520–563
6. Cametti, M.; Rissanen, K., *Chem. Commun*. **2009**, *20*, 2809–2829
7. Kirk, K. L., *Biochemistry of the Halogens and Inorganic Halides*, Plenum Press: New York, **1991**; p 58
8. Kleerekoper, M., *Endocrinol. Metab. Clin. North Am*. **1998**, *27*, 441–452
9. Li, Y.; Cao, L.; Tian, H., *J. Org. Chem*. **2006**, *71*, 8279–8282
10. Swamy, K. M. K.; Lee, Y. J. H.; Lee, N.; Chun, J.; Kim, Y.; Kim, S. J.; Yoon, J., *J. Org. Chem*. **2006**, *71*, 8626–8628
11. Liu, X. Y.; Bai, D. R.; Wang, S., *Angew. Chem. Int. Ed*. **2006**, *45*, 5475–5478
12. Jiang, X.; Vieweger, M. C.; Bollinger, J. C.; Dragnea, B.; Lee, D., *Org. Lett*. **2007**, *9*, 3579–3582
13. Liu, B.; Tian, H., *J. Mater. Chem*. **2005**, 2681–2686
14. Peng, X.; Wu, Y.; Fan, J.; Tian, M.; Han, K., *J. Org. Chem*. **2005**, *70*, 10524–10531
15. Gómez, D. E.; Fabbrizzi, L.; Licchelli, M., *J. Org. Chem*. **2005**, *70*, 5717–5720
16. Gale, P. A., *Acc. Chem. Res*. **2006**, *39*, 465–475
17. Jun, E. J.; K. Swamy, M. K.; Bang, H.; Kim, S. J.; Yoon, J., *Tetrahedron Lett*. **2006**, *47*, 3103–3106
18. Yamaguchi, S.; Akiyama, S.; Tamao, K., *J. Am. Chem. Soc*. **2000**, *122*, 6793–6794
19. Miyaji, H.; Sessler, J. L., *Angew. Chem. Int. Ed*. **2001**, *40*, 154–157

20. Choi, K.; Hamilton, A. D., *Angew. Chem. Int. Ed*. **2001**, *40*, 3912–3915
21. Shionoya, M.; Furuta, H.; Lynch, V.; Harriman, A.; Sessler, J. L., *J. Am. Chem. Soc*. **1992**, *114*, 5714–5722
22. Xu, G. X.; Tarr, M. A., *Chem. Commun*. **2004**, *9*, 1050–1051
23. Kubo, Y.; Kobayashi, A.; Ishida, T.; Misawa, Y.; James, T. D., *Chem. Commun*. **2005**, *22*, 2846–2848
24. Chung, Y. M.; Raman, B.; Kim, D. S.; Ahn, K. H., *Chem. Commun*. **2006**, *2*, 186–188
25. Wang, Q.; Xie, Y.; Ding, Y.; Li, X.; Zhu, W., submitted
26. Seo, J. D.; Kim, H. J.; Lee, K. H.; Oh, H. Y.; Kim, M. S.; Park, C. G., PCT Int. Appl. 2004, p 35