New Fluoride-selective Red Fluorescent Chemosensors Based on Perylene Derivatives

Jun Ren, Qiaochun Wang, Dahui Qu, Xueli Zhao, and He Tian*
Lab for Advanced Materials and Institute of Fine Chemicals, East China University of Science and Technology,
Shanghai, 200237, P. R. China

(Received April 30, 2004; CL-040494)

Two chemosensors based on perylene derivatives linked by urea were synthesized, and they show red color fluorescence and response to fluoride anion selectively with fluorescence quenching. The binding constants of these sensory systems to fluoride anion were high up to $\approx 10^5\ M^{-1}$.

Anions play an important role in numerous kinds of chemical and biological processes, and considerate efforts have been devoted to design the receptors or sensors that have the ability to selectively bind and sense anions.[1] Recognition and detection of fluoride anion are of special importance for monitoring fluoride metabolism in nature, the analysis of drinking water, and the detection of chemical warfare agents.[2] Therefore, there is a need to develop new selective and sensitive methods for fluoride detection. Of all detected signals, fluorescence of the chemosensor is particularly attractive on account of its simplicity and high sensitivity. Swager and co-worker,[3a] for example, had utilized a new fluorescence polymer for the detection of fluoride anions. Gale et al.[3b] had shown that deprotonation of a functionalized pyrrole provides a selective colorimetric method of sensing fluoride in acetonitrile solution. More recently, Kubo et al. reported the red fluorescence sensor based on porphyrin to detect fluoride anions, since that the red emission could avoid the noise from biological background with blue fluorescence.[4]

In this paper, we synthesized new fluoride-selective fluorescent chemosensors **TM1** and **TM2** (Figure 1), and they show significant red fluorescence quenching in the presence of fluoride anions and result in the ability to visually detect fluoride anions (from bright red color to fuchsia). The urea moiety was chosen for binding site because it is powerful hydrogen bond donor[5] that can bind anions solely via hydrogen bonding. The highly fluorescent perylene-3,4:9,10-tetracarbonyl-diimide (PDI) chromophore is chosen as fluorescent-monitoring unit because of its outstanding chemical, thermal, and photochemical stability as well as their near-unit fluorescence quantum yield with red colorful emission.[6]

The synthesis routes of **TM1** and **TM2** were outlined in the Supplementary Information (SI) based on the literatures.[7] The effect of anions (as tetrabutylammonium salts) on the fluorescent spectra of **TM1** and **TM2** were investigated in THF, and the results show that the presence of F^- resulted in decreasing of the red fluorescence, while $H_2PO_4^-$, AcO^-, Cl^-, Br^-, and I^- almost have no influence on the fluorescence. The compounds in this study are selective to fluoride.

As shown in Figures 2 and 3, the presence of F^- did not change the absorption spectra of the sensory systems, but results in the fluorescence quenching of **TM1** and **TM2**, and the quenching efficiency increases along with the increase of concentration of F^-. In particular, upon addition of F^- to the solution of the sensors in 32-fold excess, the fluorescence of the perylene almost quenched completely. The fluorescence quenching might be ascribed to a new charge-transfer process between electron-rich, urea-bound fluoride, and the electron deficient perylene moiety and/or intramolecular energy transfer.[1,8,9] However, when Br^-, Cl^-, I^-, $H_2PO_4^-$, or AcO^- added in 32-fold excess, nearly no obvious fluorescent change was observed (shown in the SI).[10] The selectivity for F^- can be attributed to its high charge density and small size, which enables it to be a strong hydrogen bonding acceptor. F^- coordination to the binding site of the sensors results in a quenching of the perylene emission. The association constants[11] were calculated to be $1.03 \times 10^5\ M^{-1}$ for **TM1** and $1.017 \times 10^5\ M^{-1}$ for **TM2**. The fluorescence quenching efficiency achieved to about 35% when the concentration of F^- was one equiv. to **TM2** sensor. The different sensitivity between **TM1** and **TM2** might result from the steric repulsion between the methyl group and the carbonyl group in the diaryl urea "bridge" in **TM2**. When binding with F^-, the diaryl urea would make a cofacial configuration or a π-stacked configuration between two perylene units, which should quench obviously the fluorescence of the perylene.[5b–d]

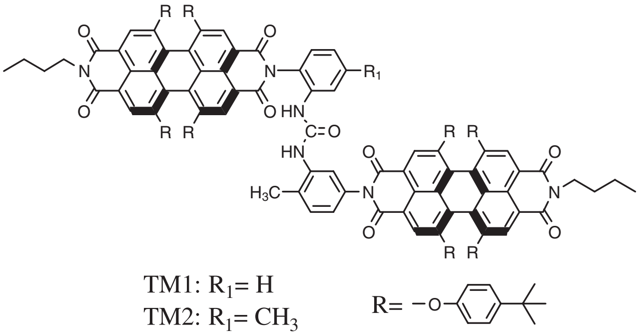

Figure 1. The molecular structures of the sensors.

The anion binding could be also investigated using ^{1}H NMR technique. The NMR spectral chemical shifts of **TM1** and **TM2** change dramatically in the presence of F^-, as shown in SI.[10] When 1 equiv. F^- was added into the $CDCl_3$ solution of the compound, the aromatic proton signals in benzene shift downfield or upfield. So the signals of the aromatic proton could be used as probes for stoichiometry complexion. In **TM1**, H_c, H_d, and H_g protons at the *ortho* position of urea group shown a moderate downfield shift ($\Delta\delta = 0.35$ ppm and 0.45 ppm, respectively).[10] On the other hand, slight upfield shifts are observed from H_a and H_f ($\Delta\delta = -0.11$ ppm).[10] Obviously, fluoride anions bind with urea N–H protons, which could cause H_c, H_d, and H_g protons to be downfield shifted by the hydrogen bond. An upfield shift of H_a and H_f could be the result of the enhanced resonance of phenyl electrons from the anionic character of urea nitrogen. To determine the stoichiometry of the anion complexation, the Job plots were constructed from ^{1}H NMR titration data, as

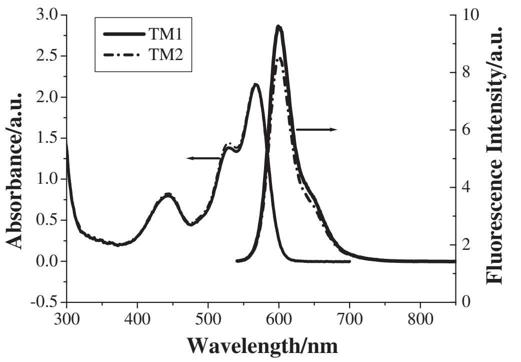

Figure 2. The absorption spectra and fluorescence spectra (excited at 450 nm) of **TM1** and **TM2** in THF.

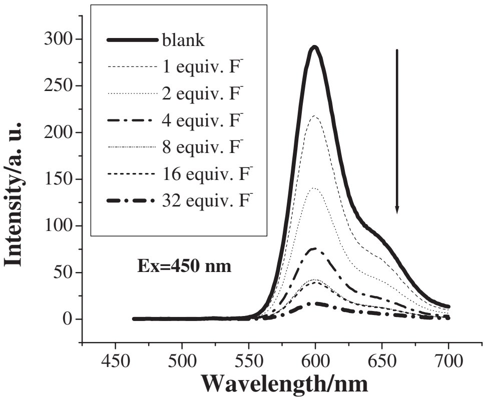

Figure 3. Fluorescence titration spectra of **TM2** (10^{-6} mol/L) with n-Bu$_4$N$^+$F$^-$ in THF at 25 °C (Ex = 450 nm).

shown in SI. The formation of the 1:1 complexes was clearly confirmed.[10]

In summary, new selective chemosensors with red fluorescent signal for fluoride anion had been constructed by binding the urea to a soluble perylene. In contrast to most anion sensors that rely on changes in color (absorption), this sensory system utilized more sensitively and red emission signal only probed fluoride anion. In spite of these successes, it is generally preferable for a fluorescence sensory signal to involve a new emission at a different wavelength rather than a modulation of an existing signal, because a new signal is inherently easier to be detected than intensity change.[1,3a] We intend to apply this approach to further analysis of interest.

Authors acknowledge the support from NSFC/China and Education Committee of Shanghai.

References and Notes

1 a) B. L. Feringa, in “Molecular Switches,” Wiley-VCH, Weinheim (2001). b) B. Valeur, “Molecular Fluorescence,” Wiley-VCH, Weinheim (2002). c) P. D. Beer and P. A. Gale, *Angew. Chem., Int. Ed.*, **40**, 486 (2001). d) P. A. Gale, *Coord. Chem., Rev.*, **199**, 181 (2000). e) M. Berger, *Chem. Rev.*, **97**, 1609 (1997). f) J. L. Sessler and J. M. Davis, *Acc. Chem. Res.*, **34**, 989 (2001). g) S. J. Coles, J. G. Frey, P. A. Gale, M. B. Hursthouse, M. E. Light, K. Navakhun, and G. L. Thomas, *Chem. Commun.*, **2003**, 568. h) L. Fabbrizzi, M. Licchelli, F. Mancin, M. Pizzeghello, G. Rabaioli, A. Taglietti, P. Tecilla, and U. Tonellato, *Chem.—Eur. J.*, **8**, 94 (2002).

2 For recent fluoride chemosensors, see a) J. L. Sessler, H. Maeda, T. Mizuno, V. M. Lynch, and H. Furuta, *J. Am. Chem. Soc.*, **124**, 13474 (2002). b) S. Aldridge, C. Bresner, I. A. Fallis, S. J. Colesb, and M. B. Hursthouse, *Chem. Commun.*, **2002**, 740. c) T. Mizuno, W.-H. Wei, L. R. Eller, and J. L. Sessler, *J. Am. Chem. Soc.*, **124**, 1134 (2002). d) T. Gunnlaugsson, A. P. Davis, and M. Glynn, *Chem. Commun.*, **2001**, 2556. e) K. H. Lee, H.-Y. Lee, D. H. Lee, J.-I. Hong, *Tetrahedron Lett.*, **42**, 5447 (2001). f) H. Furuta, H. Maeda, and A. Osuka, *J. Am. Chem. Soc.*, **123**, 6435 (2001). g) M. Takeuchi, T. Shioya, and T. M. Swager, *Angew. Chem., Int. Ed.*, **40**, 3372 (2001).

3 a) T.-H. Kim and T. M. Swager, *Angew. Chem., Int. Ed.*, **42**, 4803 (2003). b) S. C. Philip, P. A. Gale, M. B. Hursthouse, and M. E. Light, *Org. Biomol. Chem.*, **1**, 741 (2003). c) X. Zhang, L. Guo, F. Y. Wu, and Y. B. Jiang, *Org. Lett.*, **5**, 2667 (2003).

4 Y. Kubo, M. Yamamoto, M. Ikeda, M. Takeuchi, S. Shinkai, S. Yamaguchi, and K. Tamao, *Angew. Chem., Int. Ed.*, **42**, 2036 (2003).

5 a) M. C. Etter and T. W. Panunto, *J. Am. Chem. Soc.*, **110**, 5896 (1988). b) S. Yagi, I. Yonekura, M. Awakura, M. Ezoe, and T. Takagishi, *Chem. Commun.*, **2001**, 557. c) S. Yagi, M. Ezoe, I. Yonekura, T. Takagishi, and H. Nakazumi, *J. Am. Chem. Soc.*, **125**, 4068 (2003). d) Q. C. Wang, J. Ren, D. H. Qu, X. L. Zhao, H. Tian, and P. Erk, *Dyes Pigm.*, **59**, 143 (2003).

6 a) J. Qu, C. Kohl, M. Pottek, and K. Müllen, *Angew. Chem., Int. Ed.*, **43**, 1528 (2004). b) H. Quante, P. Schlichting, U. Rohr, Y. Geerts, and K. Müllen, *Macromol. Chem. Phys.*, **197**, 4029 (1996). c) P. Tinnefeld, K. D. Weston, T. Vosch, M. Cotlet, T. Weil, J. Hofkens, K. Müllen, F. C. De Schryver, and M. Sauer, *J. Am. Chem. Soc.*, **124**, 14310 (2002). d) H. Langhals, J. Korolin, and L. B. A. Johansson, *J. Chem. Soc., Faraday Trans.*, **94**, 2919 (1998). e) H. Langhals and S. Saulich, *Chem.—Eur. J.*, **8**, 5630 (2002).

7 a) F. Würthner and A. Sautter, *Org. Biomol. Chem.*, **1**, 240 (2003). b) H. Tian, P. H. Liu, W. H. Zhu, E. Gao, S. M. Cai, and D. J. Wu, *J. Mater. Chem.*, **10**, 2708 (2000). c) H. Langhals, W. Jona, F. Einsiedl, and S. Wohnlich, *Adv. Mater.*, **10**, 1022 (1998).

8 H. Miyaji, W. Sato, and J. L. Sessler, *Angew. Chem., Int. Ed.*, **39**, 1777 (2000).

9 R. Martínez and F. Sancenón, *Chem. Rev.*, **103**, 4419 (2003).

10 The synthesis, NMR spectra, electrochemical data, fluorescent lifetimes and the fluorescent spectra sensing for other anions were described in the Supplementary Information in detail.

11 K. A. Conners, “Binding Constants,” John Wiley and Sons, New York (1987).

Published on the web (Advance View) July 5, 2004; DOI 10.1246/cl.2004.974