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COMMUNICATION

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

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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.

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

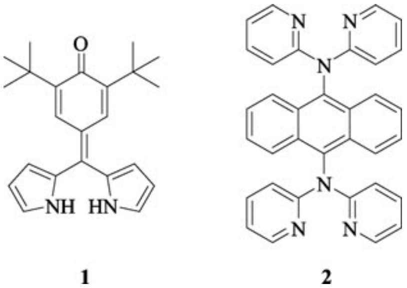

Figure 1 The chemical structures of sensor **1** and compound **2**.

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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).

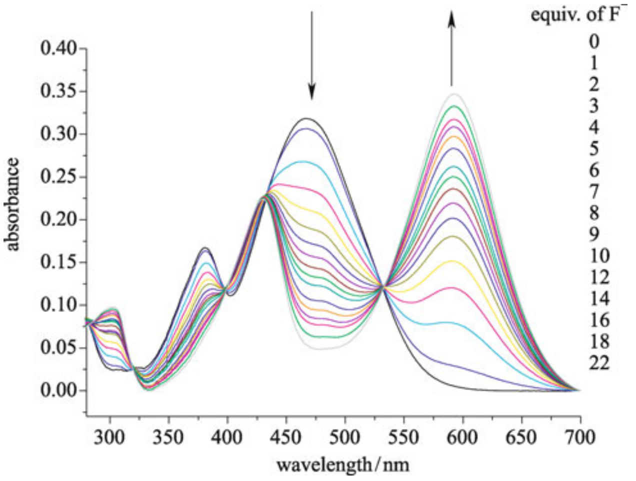

Figure 2 UV-Vis spectral changes of **1** (1.0×10^{-5} mol·L^{-1} in CH_2Cl_2) observed upon the addition of F^{-} (TBA salt) in CH_2Cl_2.

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

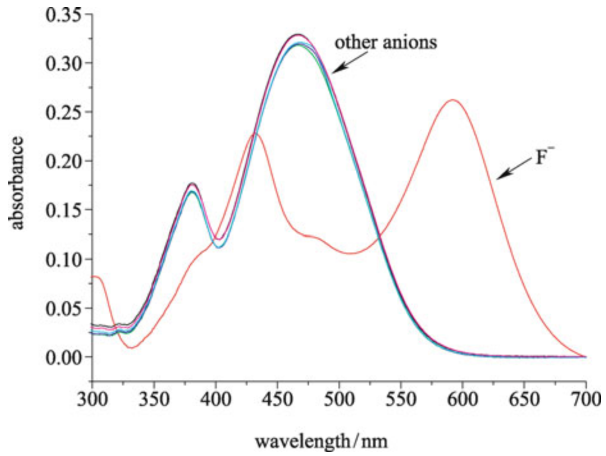

Figure 3 UV-Vis absorption change of **1** (1.0×10^{-5} mol·L^{-1} in CH_2Cl_2) upon addition of 10.0 equivalents of the anions (F^{-}, Cl^{-}, Br^{-}, or I^{-}).

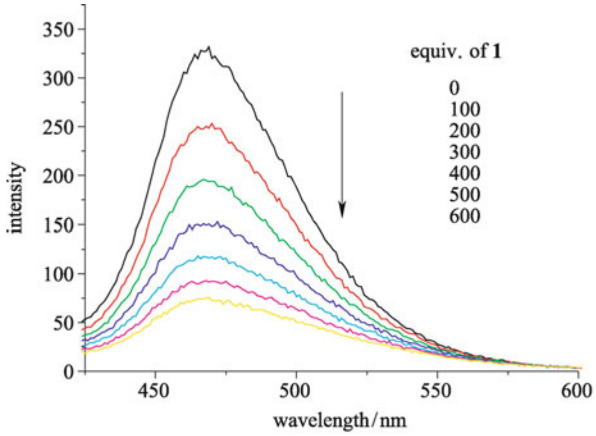

Figure 4 The fluorescence quenching of compound **2** (0.049 μmol·L^{-1} in CH_2Cl_2) upon the addition of **1**. Excitation wavelength was fixed at 397 nm (one of the isosbestic points).

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

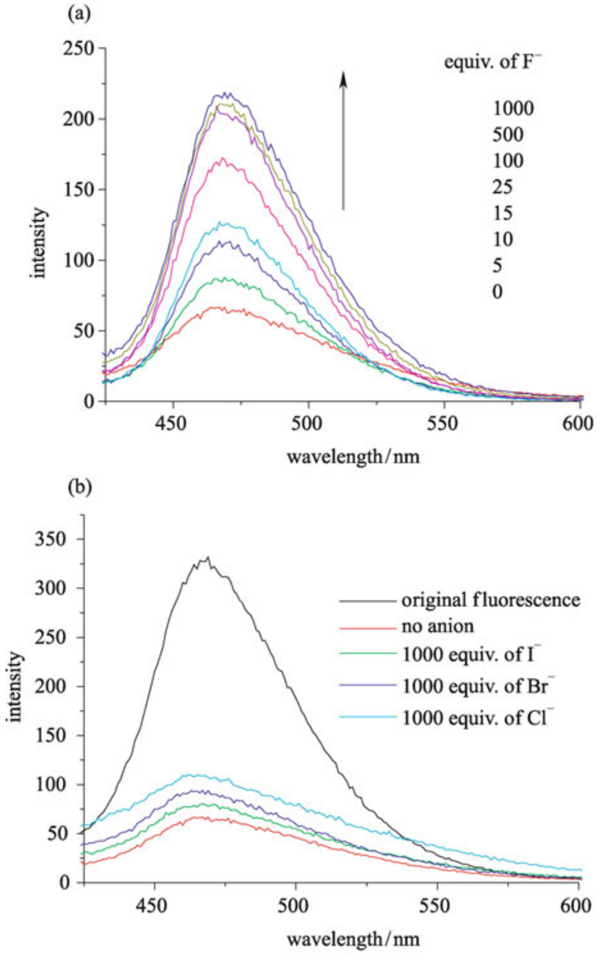

Figure 5 Fluorescence changes of the CH_2Cl_2 solution of compound **2** (0.049 μmol·L^{-1}) and sensor **1** (600 equivalents relative to **2**) upon the addition of (a) various equivalents of F^- (relative to **1**), and (b) Cl^-, Br^-, or I^- (1000 equiv. relative to **1**). Excitation wavelength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

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