



Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

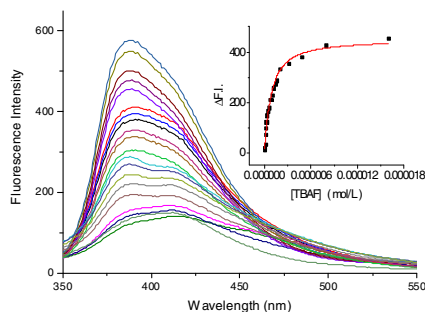
Investigation on the photophysical properties of ESPT inspired salicylaldehyde-based sensor for fluoride sensing

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HIGHLIGHTS

- A simple, highly selective and sensitive chemosensor **QP** has been developed.
- Sensor **QP** exhibited fluorescence enhancement for biologically important fluoride ion.
- ESPT resulted in the fluoride-triggered 'turn on' fluorescence.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 6 August 2014

Received in revised form 2 December 2014

Accepted 15 December 2014

Available online 3 January 2015

Keywords:

'Turn on' fluorescence

Anion recognition

ESPT

Deprotonation

ABSTRACT

A simple, highly selective and sensitive chemosensor (E)-2-((quinolin-8-ylimino) methyl) phenol (**QP**) has been developed for the fluoride, as demonstrated by the photophysical properties obtained by UV–vis and fluorescence methods. Excited-state inter/intramolecular proton transfer (ESPT) was suggested to be responsible for the fluoride-induced 'turn on' fluorescence and the blue shift of 25 nm in the emission spectrum.

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Introduction

The development of artificial neutral receptor for anions has attracted growing interest in recent years [1,2], due to the important role of anion in the biology, medicine and environment. Among these, hydrogen bond, especially the NH group [1–7], was usually used to design the anion receptor. However, OH subunit, being a well-known site to involve in natural anion binding and

transfer of proton, was paid less attention in the design of synthetic anion receptor [1,2,8,9].

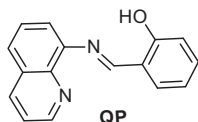
Many anion fluorescent sensors [1,2,10–12] have been developed due to their simplicity, high selectivity and impressive detectability. And numerous signal mechanisms [10], such as intramolecular charge transfer, photoinduced electron transfer, metal-to-ligand charge transfer and competitive binding, were used extensively to design the fluorescent anion sensors. Whereas excited-state intra/intermolecular proton transfer (ESPT), as a well-established signal mechanism [13–15], was poorly applied in anion recognition and sensing [8,11,16–20]. Generally, ESPT occurs in the excited state through five or six-member intramolec-

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ular hydrogen bonded ring [13–15,20], in which a proton is transferred to an electronegative atom. And the enhancement of the acidity of the hydrogen bond donor, e.g. OH group, was advantageous to ESPT upon excitation [16,17,20–22].

With the aforementioned considerations in mind, herein we reported the interaction and sensing properties of the (E)-2-((quinolin-8-ylimino) methyl) phenol (QP) for biologically important fluoride sensing. ESPT was responsible for the fluoride-triggered fluorescence enhancement.



Experimental

Tetrabutylammonium (TBA) salts of various anions were obtained from Sinopharm Chemical Reagent Co. Ltd., which were stored in desiccators under vacuum. Acetonitrile for spectroscopy was purchased from the J&K Scientific Ltd. Other chemicals were of analytical grade from commercial suppliers and were employed as received without further purification.

^1H NMR spectra were recorded on a Bruker 400 MHz spectrometer using TMS as an internal standard. Absorption spectra and fluorescence spectra were acquired on Shimadzu UV 2550 spectrophotometer and Shimadzu RF-5301PC spectrofluorometer, respectively.

QP was synthesized by condensation of 8-aminoquinoline and salicylaldehyde according to literature [23].

Results and discussion

UV–vis spectral studies of QP

Fig. 1 depicted the spectral changes of QP upon addition of 50 equiv. various anions. QP produces a maximum absorption at 338 nm, which was ascribed to the π – π^* transition [24] favored by intramolecular hydrogen bonding [8,25]. From the Fig. 1, it was seen that only F^- induced the obvious red shift of QP from 338 nm to 433 nm. Other anions (Cl^- , Br^- , I^- , H_2PO_4^- , NO_3^- and AcO^-) produced insignificant changes in absorption, even at higher concentration. This suggested the weak coordination interaction between these anions and QP.

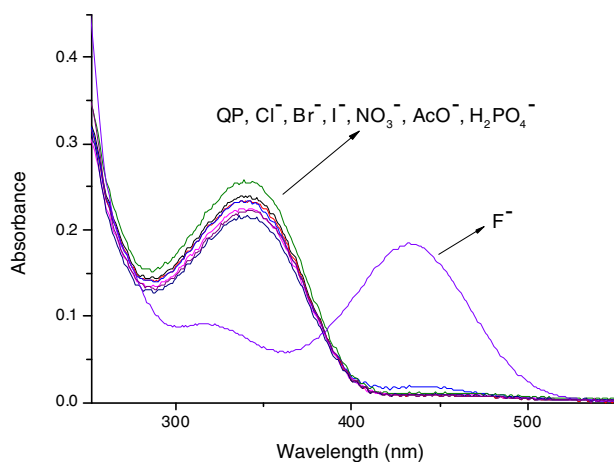


Fig. 1. UV–vis spectral changes of QP (2.0×10^{-5} M) in MeCN after the addition of 50.0 equiv. various anions.

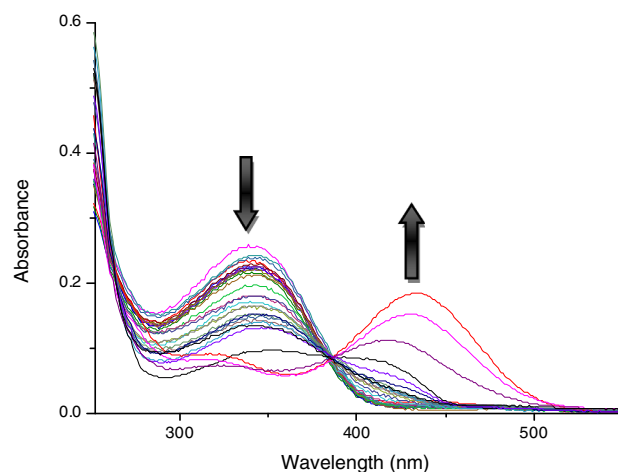


Fig. 2. UV–vis spectral changes of QP (2×10^{-5} M) in MeCN upon addition of 0–50.0 equiv. F^- .

Spectrophotometric titration was conducted by addition of TBAF to the CH_3CN of QP. As displayed in Fig. 2, with the gradual increase of F^- , the absorbance band at 338 nm of QP decreased and a new peak at 433 nm occurred and developed. These spectral changes were presumably attributed to the proton transfer from the phenolic OH group to F^- , and the formation of negative charged PhO^- enhanced the “push-pull” effect [8] of the intramolecular charge transfer in the ground state. Furthermore, the clear isosbestic point at 386 nm was observed. This indicated that the stoichiometry of F^- and QP was 1:1. Subsequently, TBAOH, which can remove the proton of OH binding site [2,8,10,18], was added to the QP solution. Similar spectral changes were observed for OH^- and F^- (Supporting Information, Fig. S1). This, therefore, confirmed our assumption. Furthermore, the binding strength between QP and fluoride were evaluated by non-linear least-square analysis of the titration curves according to the relation for 1:1 complexation. Satisfactory non-linear relationships ($R=0.982$) were observed for the spectrophotometer titration curve (Supporting Information, Fig. S2a). And the binding constant was calculated to be $2.85 \times 10^4 \text{ M}^{-1}$.

Fluorescence response of QP

To learn more sensing affinities of QP for various anions (F^- , Cl^- , Br^- , I^- , H_2PO_4^- , NO_3^- and AcO^-), fluorescence titration was carried out with excitation at 308 nm. Fig. 3 displayed the emission

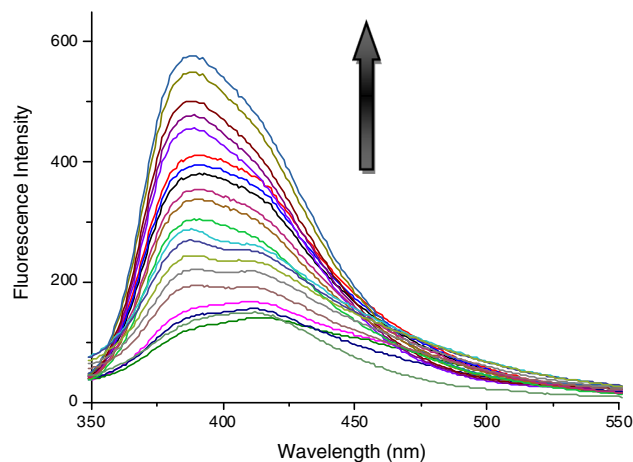


Fig. 3. Emission spectral changes of QP (2.0×10^{-5} M) in MeCN after addition of 0–40.0 equiv. F^- .

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