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ORIGINAL PAPER

A Colorimetric and Ratiometric Fluorescent Chemosensor for Fluoride Based on Proton Transfer

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Abstract N-Phenyl-N'-(3-quinolinyl)urea (**1**) has been developed as a highly selective colorimetric and ratiometric fluorescent chemosensor for fluoride ion based on a proton transfer mechanism. Evidences for the mechanism were provided by UV-vis and fluorescence titration and especially ^{1}H and ^{19}F NMR experiments. The sensor gave the largest ratiometric fluorescent response reported so far (R_{max}/R_{min}=2620) to fluoride. Taking H^{+} as the "recovering reagent", the sensor can be reversibly "used" and "recovered" for several cycles with only a slight decay of the response ability.

Keywords Fluoride · Chemosensor · Deprotonation · Reversible · Ratiometric fluorescence

Introduction

The design of chemosensors for fluoride ion is of continuous interest due to the importance of fluoride in dental care, treatment of osteoporosis and its possible toxicity when administered in high doses [1, 2]. Various kinds of fluoride sensors have been developed using urea or thiourea [3–12], amide- [13–21], phenol- [22–24], and cationic borane [25–27] receptors. Most of these sensors are based on colorimetric changes or fluorescence quenching, while only few of them experience fluorescence enhancement [12, 15, 16, 24]. However, in most practical applications, changes in fluorescence intensity are typically unreliable and require frequent calibration because of a variety of chemical, optical, or other instrument-related factors [17]. In view of such problems, the use of ratiometric fluorescent sensors [28, 29] may be an attractive choice which measure the ratio of the fluorescent intensities at two wavelengths and thus allow the estimation of the analyte independent of these influencing factors. Up to now, however, the reported ratiometric fluorescent sensors are mainly for cations, and only a paucity of reports are for fluoride ion [16, 17, 19, 29]. Hence, realization of ratiometric measurement for fluoride ion is still a challenge.

As an extension of our work in anion recognition [30, 31], we have developed a new urea-based chemosensor **1** [32] (Scheme 1) which showed dual emission channels in the presence of fluoride, thus allowing ratiometric fluorescence sensing of fluoride. The striking color and emission color changes of the sensor enable colorimetric naked-eye detection of fluoride as well.

Experimental

General

The tetra-*n*-butylammonium (Bu_4N^{+}) salts of different anions were purchased from Alfa Aesar. DMSO was used without further purification. ^{1}H NMR and ^{19}F NMR spectra were recorded on a Mercury plus-400 spectrometer at 400 MHz and 376.5 MHz, respectively, using TMS as an

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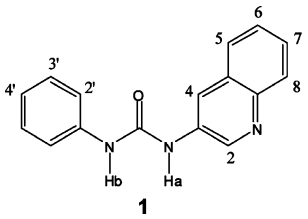

Scheme 1 The structure of compound 1

internal standard for ^{1}H and aqueous NaF (−122.4 ppm) as an external standard for ^{19}F NMR. IR spectra were measured with an HP5890II GC/NEXUS870. ESI-MS measurements were performed with a Waters ZQ4000 mass spectrometer. UV-vis spectra were performed on an HP8453 spectrophotometer (1-cm quartz cell) at room temperature. Fluorescence spectra were recorded on a Hitachi F4500 fluorescence spectrophotometer (1-cm quartz cell) at room temperature with slit width of 2.5 nm. Fluorescence lifetimes were measured using a time-correlated single photon counting FLS920 Spectrometer (1-cm quartz cell), and decays were monitored at the corresponding emission maxima of the samples. Fluorescence lifetimes were obtained through the fitting of the decay spectra (χ^2=1–1.2) by the in-built software.

Synthesis of N-phenyl-N'-(3-quinolinyl)urea (**1**)

Receptor **1** was synthesized using a method according to literature reports [30]. 3-Aminoquinoline (2.16 g, 15 mmol) was reacted with *in situ* prepared phenylisocyanate (15 mmol) in toluene. The precipitate was filtered off and recrystallized from ethanol to give the product as a white solid (3.16 g, 80%). IR (KBr, ν/cm^{-1}): 3379, 3055, 3020, 2970, 1716, 1619, 1597, 1532, 1492, 1441, 1292, 1229, 900, 740. ^{1}H NMR (DMSO-d_6, 400 MHz, 5 mM): 9.14 (s, 1H, NHa), 8.91 (s, 1H, NHb), 8.87 (s, 1H, H2), 8.53 (s, 1H, H4), 7.93 (t, J=8.0, 1H, H8), 7.90 (d, J=7.2 Hz, 1H, H5), 7.60 (t, 1H, J=8.2 Hz, H7), 7.55 (t, 1H, J=8.0 Hz, H6), 7.50 (d, 2H, J=8.0 Hz, H2'), 7.10 (t, 2H, J=8.0 Hz, H3'), 7.10 (t, 1H, J=8.0 Hz, H4'). ESI-MS: 264.4 ([M +H]$^{+}$, calcd. 264.1).

Results and discussion

UV-vis anion titration studies

The anion binding and sensing properties of receptor **1** were studied firstly by UV-vis spectroscopic techniques in DMSO (5×10^{-5} M, Fig. 1a). On addition of 20 equiv. of F^-, the ICT (intramolecular charge transfer) band of **1** at λ_{max} 331 nm was enhanced significantly, while the π–π* transition band displayed a bathochromic shift from 343 to 393 nm. On the other hand, AcO^- and $H_2PO_4^-$ only caused a slight enhancement and bathochromic shift (~5 nm) of the spectra which may be induced by hydrogen bonding of the anions with the urea subunit [3]. No obvious changes were observed upon addition of other anions, suggesting that **1** has an excellent colorimetric selectivity for F^- over other anions in DMSO, especially AcO^- and $H_2PO_4^-$ which have similar basicity and surface charge density with F^- [3, 4, 7, 11].

The interaction of receptor **1** with F^- ion was investigated in detail through UV-vis titration (Fig. 1b). On addition of 0–5 equiv. of F^-, only slight enhancement of the band at 331 nm (ε from 6016 to 6340 M^{-1} cm^{-1}) was observed due to the hydrogen bonding between this anion and the urea group [7]. With further addition of F^-, the absorption at 331 nm and a new band appeared at λ_{max} 393 nm began to increase significantly and reached the limit value after 20 equiv. of F^- were added (393 nm, ε= 6356 M^{-1} cm^{-1}; 331 nm, ε=27190 M^{-1} cm^{-1}), indicating that a fluoride-induced deprotonation of urea NH may have occurred [6, 16]. This was confirmed by adding OH^- (as Bu_4NOH) to the solution of **1**, which gave similar UV-vis spectral changes (Fig. S2) to those observed with F^- ion.

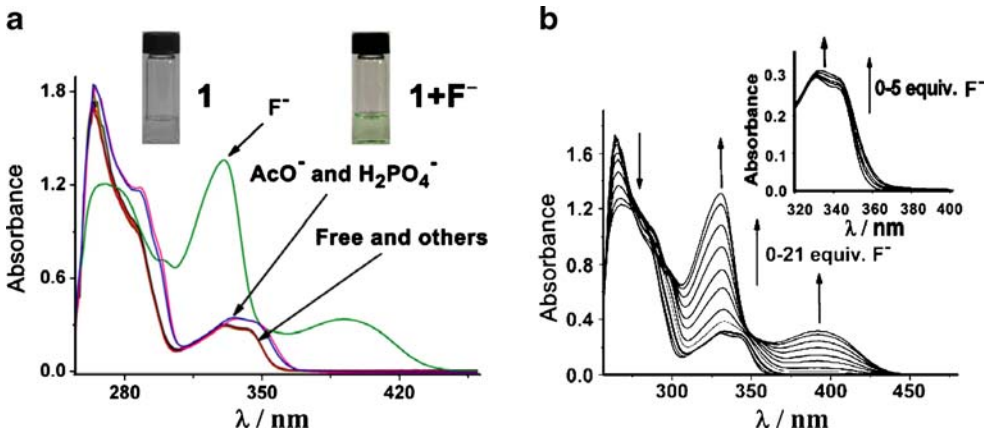

Fig. 1 Absorption spectra of **1** (5×10^{-5} M in DMSO) after addition of (**a**) 20 equiv. of representative anions (F^-, Cl^-, Br^-, I^-, AcO^-, NO_3^-, $H_2PO_4^-$, HSO_4^-, ClO_4^- as Bu_4N^+ salts) and (**b**) 0, 1, 2, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21 equiv. of F^-. Inset: (**a**) F^- induced color changes and (**b**) enlarged spectra as 0–5 equiv. of F^- were added

The aforementioned results suggest that the sensor–fluoride interaction was a two-step process: 1) at lower fluoride concentration (0–5 equiv.) the F···H–N hydrogen bonding occurred; and 2) with increasing fluoride concentration (5–20 equiv.), excess fluoride interacted with the sensor-fluoride complex and led to the deprotonation of the sensor [7, 19].

The influence of other anions on the deprotonation process induced by F^- ion was also examined. In the presence of 10 equiv. of foreign competing anions, the sensitivity was repressed remarkably, as more F^- ion (~90 equiv.) was needed to deprotonate receptor **1** completely (Fig. S1). In a further study, 10 equiv. of each competing anion were added to the deprotonated system, and the results indicated that the protic anion HSO_4^- can inhibit the deprotonation greatly and another protic anion $H_2PO_4^-$ can also decrease the colorimetric changes slightly, while other anions did not induce remarkable changes. Hence, the protic anions HSO_4^- and $H_2PO_4^-$ should be the repressive factors for the deprotonation process by providing protons to the deprotonated receptor. Similarly, protic solvent such as water can also reverse these colorimetric changes (Fig. S3; vide infra).

During the deprotonation process, color changes from colorless to yellow-green and "OFF-ON" emission colour changes from dark purple to bright blue were observed which allowed the fluoride ion to be detected by naked eyes (Figs. 1, 2 and S4, S5).

Fluorescence titration

A fluorescence titration was subsequently performed in a solution of **1** in DMSO (1×10^{-5} M). As shown in Fig. 2a, the sensor **1** exhibits a weak intrinsic emission band at λ_{max} 368 nm. Upon addition of 0–9 equiv. of F^-, the band decreased slightly, which was induced by the enhanced PET (photoinduced electron transfer) quenching as the hydrogen-bonded complex $[\mathbf{1}\cdot F]^-$ formed. Notably, the deprotonation process had started, though not in dominance, after more than 1 equiv. of F^- was added, which was reflected by the appearance of a new band at 474 nm which pertains to the ICT induced emission of the deprotonated sensor. As more F^- was added, the deprotonation process was in dominance, leading to sharper quenching of the band at 368 nm and enhancement at 474 nm (Fig. 2b). After about 30 equiv. of F^- were added, the deprotonation process was completed. However, only 20 equiv. of F^- were needed to finish this process in the UV-vis titration when a 5×10^{-5} M solution of **1** was used, indicating that the deprotonation efficiency by F^- can be decreased as the concentration of **1** decreased. This may be attributed to the fact that the water contained in the solvent DMSO (0.2%) can somewhat reverse the deprotonation process and thus reduce the deprotonation efficiency of fluoride ion, which is more significant at low concentrations.

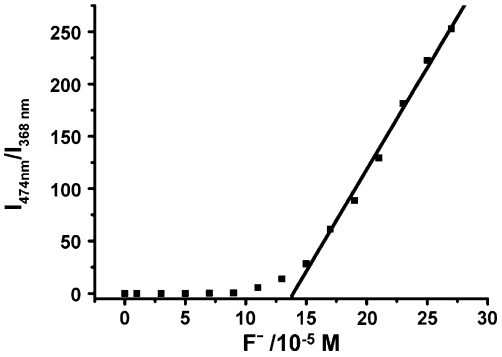

Fig. 3 Ratiometric plot of I_{474}/I_{368} versus the concentration of fluoride

This PET and ICT modulated dual channel emission provides an opportunity for elaborating **1** as a ratiometric chemosensor for F^-. Fig. 3 shows the variation of the fluorescence intensity ratio $R(I_{474}/I_{368})$ *vs* the concentration of F^-. Although the bands at 474 nm and 368 nm started to increase and decrease, respectively, upon addition of F^-, the value of R was small and only slightly enhanced before 9

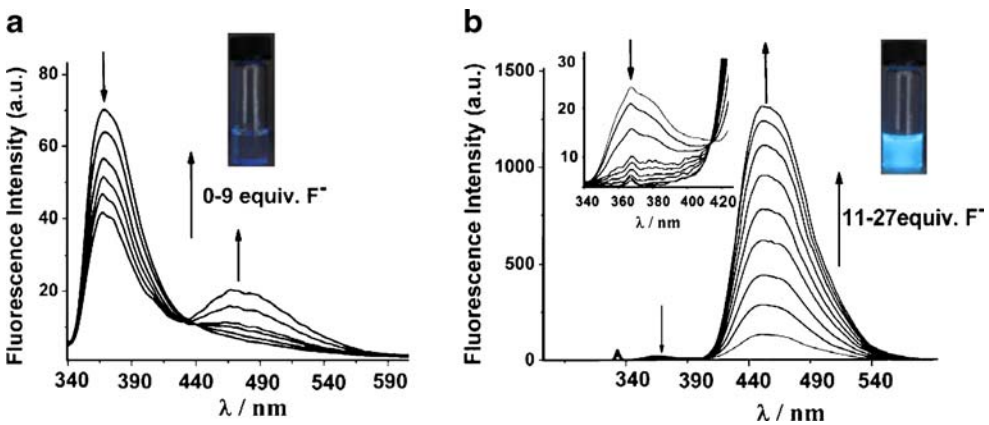

Fig. 2 Fluorescence spectra of **1** (1×10^{-5} M in DMSO) upon the addition of (a) 0, 1, 3, 5, 7, 9; (b) 11, 13, 15, 17, 19, 21, 23, 25, and 27 equivalents of F^-. Inset: F^- induced emission color changes and enlarged spectra between 340–420 nm

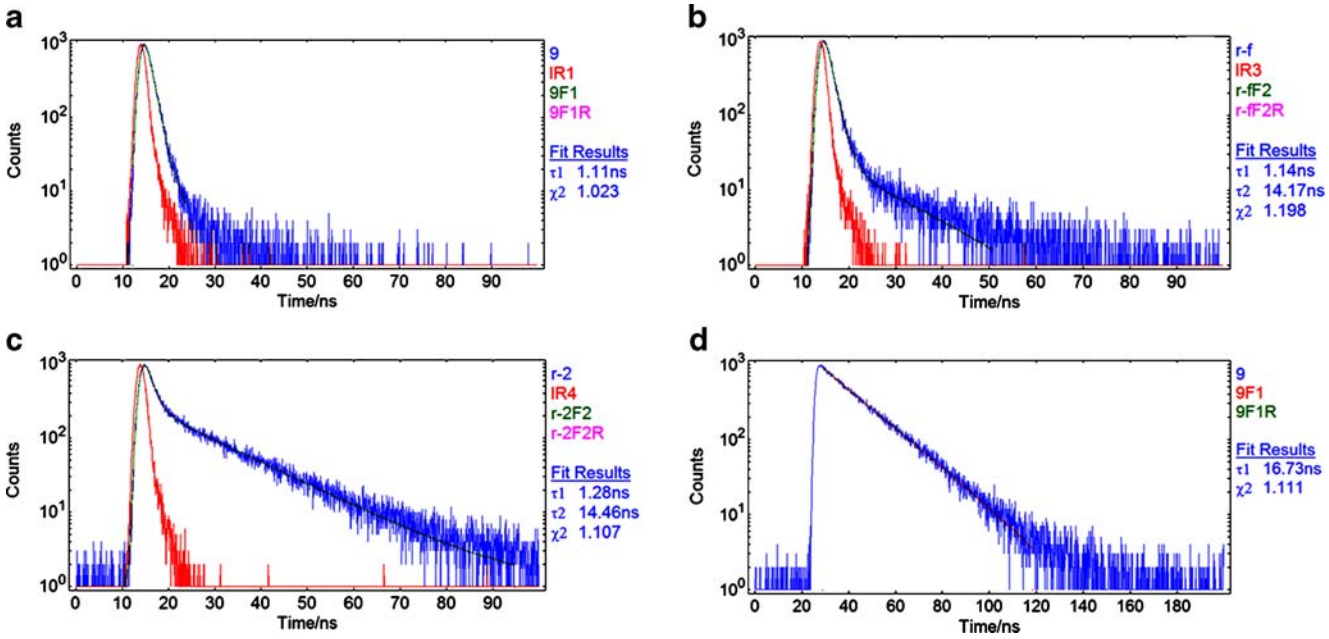

Fig. 4 Fluorescence decay profiles of **1** (10 μM) at different fluoride concentrations in DMSO. (**a**) Receptor **1** alone; (**b**, **c**, **d**) with 5, 10, and 30 equiv. of F^- (blue: **1**; red: laser profiles). λ_{ex}=330 nm; a and b, λ_{em}=368 nm; c and d, λ_{em}=474 nm

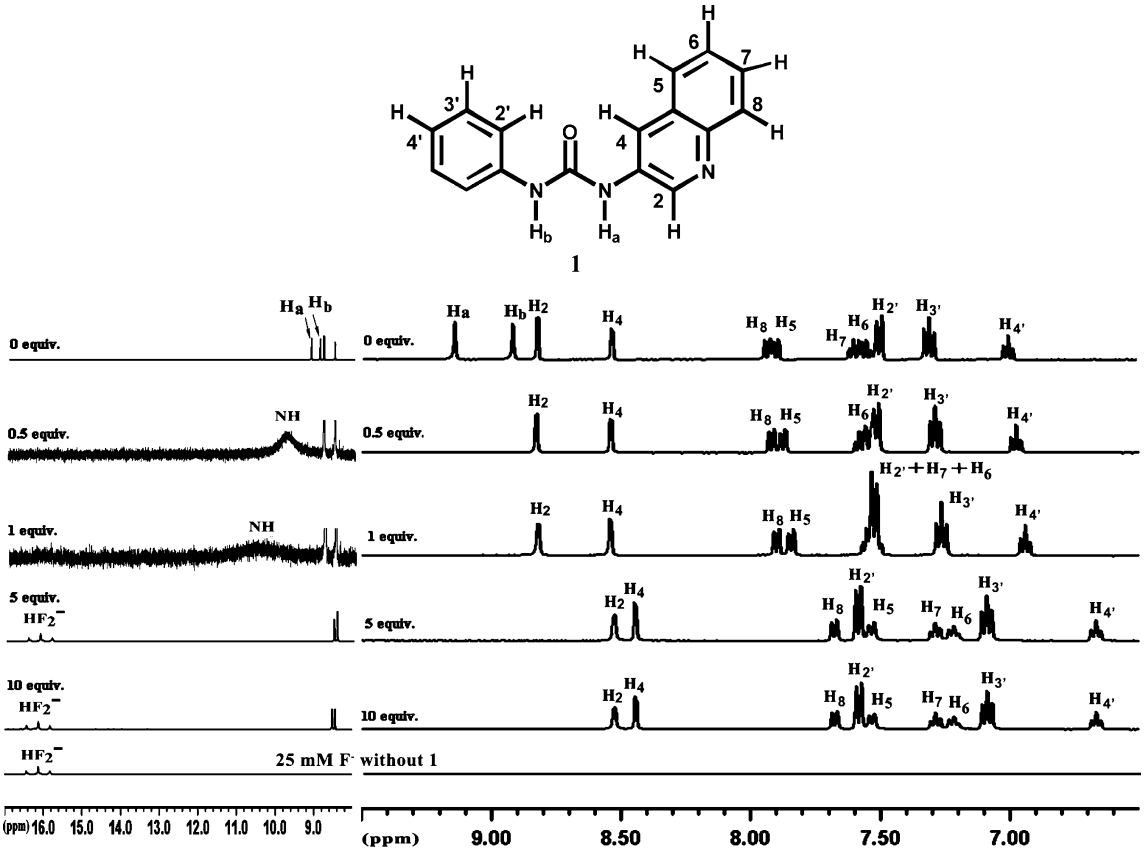

Fig. 5 Stack plot of the ^{1}H NMR spectra of **1** with F^- (as Bu_4N^+ salt) and F^- alone (*bottom*) (DMSO-d_6, 400 MHz)

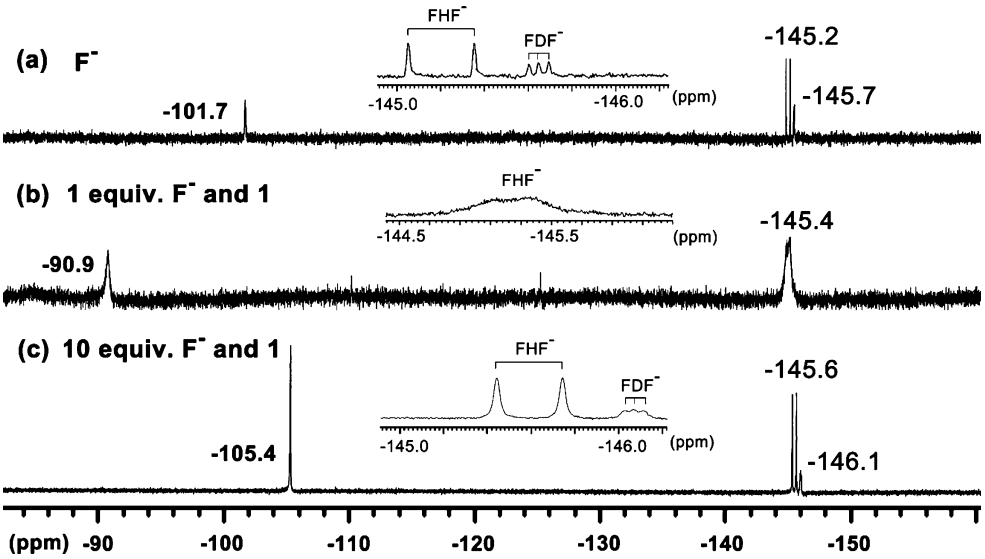

Fig. 6 Stack plot of the ^{19}F NMR spectra of (**a**) 5 mM F^- (as Bu_4N^+ salt); (**b**) 5 mM F^- and 5 mM compound **1**; (**c**) 50 mM F^- and 5 mM compound **1** (DMSO-d_6, 376.5 MHz)

equiv. of F^- (90 μM) were added. As more F^- were added to the solution of **1**, the *R* value increased significantly and reached the limit value when 27 equiv. of F^- (270 μM) were added. A nearly linear plot of *R vs* the concentration of F^- resulted in $R=19[F^-]-270$, $r=0.996$, $n=7$) (Fig. 3). Therefore, sensor **1** can be used for ratiometric estimation of fluoride ions between 150–270 μM. The ratio of the limiting value in the absence and excess of anions, R_r (R_{max}/R_{min}), which reflects the limiting dynamic range and resolution for concentration measurements, is decisive. In this work the sensor gave a much larger R_r value (up to 2620) than other ratiometric fluorescent fluoride sensors reported so far (≤ 548) [19].

No significant change of the emission was observed upon addition of 30 equiv. of other anions except AcO^- and $H_2PO_4^-$, which showed obvious quenching of the band at 368 nm (Fig. S6) due to hydrogen bonding with the sensor. As expected, the addition of OH^- induced similar fluorescence changes (Fig. S7) to the case of F^-.

The interaction between F^- and receptor **1** in DMSO has also been investigated by the time-resolved fluorescence technique, and representative fluorescence decay profiles of **1** with different concentrations of F^- are shown in Fig. 4. The free receptor **1** exhibited a single-exponential lifetime (Fig. 4a, $\tau_f=1.11$ ns). As 5 or 10 equiv. of F^- were added, the fluorescence decay of **1** was biexponential (Fig. 4b, $\tau_{f1}=1.14$ ns, $\tau_{f2}=14.17$ ns; 4c, $\tau_{f1}=1.28$ ns, $\tau_{f2}=14.46$ ns), indicating that there were two distinct species coexisting in the solution (the anion-bound or deprotonated form and free **1**). The contribution of the new longer component amplitude increased as the concentration of F^- was increased and finally turned the decay to a single-exponential one (Fig. 4d, $\tau_f=16.73$ ns) when 30 equiv. of F^- were added which would deprotonate **1** completely. These results clearly support that the lifetime changes of **1** in the presence of F^- are due to the formation of new ICT states [10].

^1H NMR titration

More detailed information of the interaction of receptor **1** with F^- was provided by ^1H NMR titration experiments carried out in DMSO-d_6 (Fig. 5). In particular, a 5 mM DMSO-d_6 solution of **1** was titrated with F^- of up to 10 equiv. Within addition of 1 equiv. of F^-, continuous broadening and distinct downfield shifts of the NH signals as well as slight upfield shifts of the aromatic signals were observed, indicating the formation of hydrogen bonding interactions between F^- and the urea unit. As 5 equiv. of F^- were added, the NH signals disappeared completely and a new 1:2:1 triplet at 16.1 ppm with a coupling constant *J*=

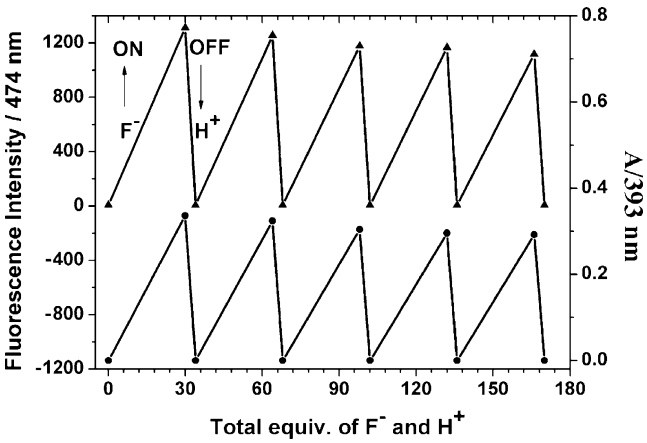

Fig. 7 Reversible sensing of F^- (as Bu_4N^+ salt in DMSO-0.2% H_2O) and recovering of the sensor by H^+ (as HCl in DMSO-0.3% H_2O) (▲ fluorescence emission at 474 nm and ● absorption band at 393 nm) in a DMSO solution of **1** (1.0×10^{-5} M in fluorescent experiments and 5.0×10^{-5} M in UV-vis experiments)

120 Hz appeared, which is due to the bi-fluoride ion (FHF^-) [33, 34]. In some recent reports [6, 19] the appearance of this new triplet has been taken as an evidence for the deprotonation of the receptor. However, in a control experiment we found that the typical signal of FHF^- also appeared in the 25 mM DMSO-d_6 solution of $(Bu_4N)F$ (Fig. 5) without the sensor, indicating that the FHF^- ion can also be generated through deprotonation of the solvent by $(Bu_4N)F$ itself [33]. The deprotonation of the urea group was supported by the fact that all CH protons showed distinct upfield (H2, 0.35; H4, 0.09; H5, 0.37; H6, ~0.31, H7, ~0.31; H8, 0.25; H3', 0.22; H4', 0.43 ppm) or downfield (H2', 0.08 ppm) shifts compared with the free sensor, arising from an overall change of the electron distribution in the chromophore when the NH moiety was deprotonated [33]. The more profound upfield shift of H2 than H2' would suggest that deprotonation occurs at the NHa fragment rather than NHb, inducing electron density delocalization onto the aromatic rings and the upfield shifts [7]. The disappearance of the NHb signal was owing to the hydrogen bonding between this proton and excess F^- (Fig. 5) [12]. Interestingly, the upfield shift of H4 was obviously less and the H2' even showed a downfield shift. This is rationalized considering the through-space polarization effect exerted by the nearby urea oxygen atom (Fig. 5) which would acquire more electron density from the negative N atom following the deprotonation [7]. The deprotonation process was completed within addition of 5 equiv. of F^- as no further changes were observed with the addition of up to 10 equiv. of fluoride.

On the other hand, excessive OH^- induced similar but more distinct upfield shifts of the corresponding signals resulted from the stronger hydrogen bonds between OH^- and NHb in the sencond step (Fig. S8). ^{19}F NMR (DMSO-d_6, Fig. 6) provides direct evidences for the sensor-fluoride hydrogen bonding interactions in the first step (1 equiv. F^- and **1**). The signal of the free fluoride at -101.7 ppm was downfield shifted to -90.9 ppm ($\Delta\delta$=10.8 ppm), a typical result of hydrogen bonding of fluoride [35]. In the second step (10 equiv. F^- and **1**), the fluoride signal was shifted to -105.4 ppm ($\Delta\delta$=–3.7 ppm compared to the free fluoride ion) which may be resulted from the increased shielding effects of the anion-characterized sensor on the fluoride ion [36, 37]. However, the signal of the expected hydrogen bound fluoride did not appear which may be a result of fast proton exchanging between the bound fluorides and the free ones [12].

Reversibility studies

Based on the deprotonation mechanism of the sensor, recovery of the deprotonated sensor should be possible. In fact, it had been discovered that protic solvents such as water (Fig. S3) and ethanol can reverse the deprotonation-induced spectra and color changes [6], while the deprotonation can hardly proceed again once much protic solvent was brought in the system. Taking H^+ (as 0.01M HCl DMSO-0.3% H_2O solution) as the "recovering reagent" can avoid this problem which only brings in small amounts of water while functions more effectively than protic solvents. As shown in Fig. 7, the fluorescent emission band as well as the absorption band can be reversibly turned "ON" and "OFF" for at least five times by alternative adding of 30 equiv. of F^- (as Bu_4N^+ salt) and 4 equiv. of H^+. There was only a slight decay of the responses, which may result from the competitive water brought in by the HCl solution [4]. These results proved H^+ to be a proper "recovering reagent" for the deprotonated sensor. In another view, the sensor can function as a fluorescent and colorimetric switch modulated by F^-/H^+. Like other molecular switches, it has the potential to be utilized in designing new molecular logic gates [38]. In further studies, we found that the compound **1** presented remarkably different colorimetric and fluorescent properties under acidic conditions from those under neutral and basic conditions, which may be induce by protonation of the nitrogen of quinoline. Additionally, in other aprotic solvents such as MeCN or $CHCl_3$, much more amounts of F^- (> 300 equiv.) were needed to deprotonate the sensor due to the weaker deprotonation ability of these solvents than DMSO [5].

Conclusions

We demonstrated a 3-quinolinyl substituted urea as a novel colorimetric and fluorescent ratiometric chemosensor for fluoride. The sensor showed the largest R_r value among the ratiometric fluorescent fluoride sensors reported so far. The colorimetric and ratiometric properties of the sensor are attributed to the anion-induced deprotonation of the urea subunit as confirmed by UV-vis, fluorescence and NMR results. Furthermore, the sensor can be reversibly "used" and "recovered" for at least five times with H^+ as the recovering reagent.

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