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Highly Selective "Turn-On" Fluorescent and Colorimetric Sensing of Fluoride Ion Using 2-(2-Hydroxyphenyl)-2,3-dihydroquinolin-4(1*H*)-one based on Excited-State Proton Transfer

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Abstract: A simple, highly selective and sensitive colorimetric system for the detection of fluoride ion in an aqueous medium has been developed using 2-(2-hydroxyphenyl)-2,3-dihydroquinolin-4(1*H*)-one. This system allows selective "turn-on" fluorescence detection of fluoride ion, which is found to be dependent upon guest basicity. An excited-state proton transfer is proposed to be the signaling mechanism, which is rationalized by DFT and TD-DFT calculations. The present sensor can also be applied to detect fluoride levels in real water samples.

Keywords: chemosensors · excited-state proton transfer · fluoride ions · fluorescence · sensors

Introduction

Inspired by nature's fundamental biological processes involving enzyme–substrate or receptor–guest interactions, which are regulated by light, ions, or small molecules, the development of chemical sensors for recognizing and sensing of analytes has attracted growing attention in recent years.[1] Accordingly, the design and synthesis of highly sensitive and selective chemosensors capable of binding biologically important cations, anions, and neutral analytes continues to be an active area in supramolecular chemistry.[2] Particularly, anions are ubiquitous in both the organic and mineral worlds and play important roles in biology, medicine, catalysis, and in the environment, and are used as fertilizers and industrial raw materials.[3] Generally, anions have an isoelectric nature, display a high energy of hydration, display tautomerism, and possess a low surface-charge density; these features make the binding of anions less effective.[4] In this context, considerable efforts have been made regarding the design and synthesis of abiotic receptors for anionic species in the past two decades, which makes anion recognition one of the fastest growing disciplines and emerging research area in the field of supramolecular chemistry.

The nature of the interaction between anions and charge-neutral organic receptors is primarily based on hydrogen-bonding. Usually, the nature of the anion sensing process is controlled by several factors including the acidity of the receptor, the basicity of the anion, and the stability of the conjugate base, all of which are solvent dependent.[5] The recognition studies are preferably carried out in aprotic media (e.g., DMSO, acetonitrile, $CHCl_3$, etc.) to avoid competition by the solvent (e.g., water or alcohol) as a hydrogen-bonding donor.[6] Many of these processes are recognized by color changes that can occur upon deprotonation. Relatively few sensors exist that are highly selective and reliable and that function in aqueous media without interference from endogenous substrates such as other anions and protic solvents. Consequently, selective and reliable sensing of anions is generally difficult to accomplish.

Of particular interest concerning anion sensing is the fluoride ion, which is one of the smallest anions with a high charge density, is a strong hydrogen-bond acceptor, and exhibits strong solvation in polar and/or hydrogen bond-donating solvents.[7] It is an attractive target for sensor design as it is one of the most toxic anions and harmful to the environment and human health, particularly in dental care (fluorosis), osteosarcoma (deficiency, poor dental health),[7b] osteoporosis, and in many pathological events.[8] A large number of receptor molecules have been reported for fluoride ion sensing in organic media;[9] only few of them function in complex aqueous media and are readily adaptable to practical applications.[10] This is mainly because of issues such as solubility, polarity, H-bonding, and ionic strength that arise under aqueous conditions, which in turn resulting in high detection limits for the fluoride ion. Colorimetric receptors that are easy and safe to handle have received significant attention due to their ability to achieve high selectivity and sensitivity. Recently, numerous colorimetric receptors have been reported for the detection of fluoride ions.[11] Furthermore, the use of chemodosimeters for the chromo/fluorogenic detection of fluoride anions has also been explored.[12] These chemodosimeters are usually employed for the detection of reactions induced by the target anion coupled with

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a chromo- or fluorogenic event including fluoride-induced hydrolysis of silyl ethers. Although several sensing systems for the fluoride ion in aqueous media have been reported,[13] there are associated problems such as 1) the need for complex syntheses that involve multiple steps and/or hazardous chemicals, besides tedious work-up and purification procedures, 2) the necessity of a relatively long time (from several minutes to hours) for quantitative detection, 3) the requirement of high concentrations (mM range) of analyte for most of the systems that are based on colorimetric detection, and 4) the involvement of "turn-off" fluorescence or quenching for which the sensitivity is known to be invariably low. Taking all these factors into account, the development of simple, inexpensive, and highly selective "turn-on" fluorescent sensors that allow for the accurate determination of fluoride anions in aqueous medium/polar protic solvents is challenging and highly desirable.[14]

In our group, suitable supramolecular sensing probes for neutral analytes,[15b,16a] cations,[15a–d,16c,d] and anions[16b] have been developed and recently reported. Encouraged by the results of these studies, herein we report a simple, highly selective and sensitive detecting system for fluoride anions using 2-(2-hydroxyphenyl)-2,3-dihydroquinolin-4(1*H*)-one (probe **L1**) in aqueous medium. This system allows the selective "turn-on" fluorescence detection of the fluoride ion, and excited-state proton transfer (ESPT) is suggested to be the signaling mechanism, as rationalized by theoretical studies.

Results and Discussion

The probe **L1** (Figure 1) used in our study was readily synthesized[17] by a one-pot reaction between 2′-aminoacetophenone and 2′-hydroxybenzaldehyde in the presence of per-6-amino-β-cyclodextrin. Control molecules (**L2** and **L3**) have also been synthesized, and all the probes were fully characterized (see the Supporting Information). Probe **L1** was chosen as the acidities of phenolic OH and amino NH protons are drastically enhanced upon photoexcitation and therefore an ESPT channel can be opened upon anion binding; in addition, our choice was based on the fact that probe **L1** is weakly fluorescent whereas the anion-bound form is expected to be highly fluorescent.[18–21] Consequently, the selective recognition of **L1** towards fluoride ions in an aqueous medium has been demonstrated using UV/Vis absorption and fluorescence spectroscopies and was further supported by ^{1}H NMR spectroscopy, ESI mass spectrometry, and theoretical calculations.

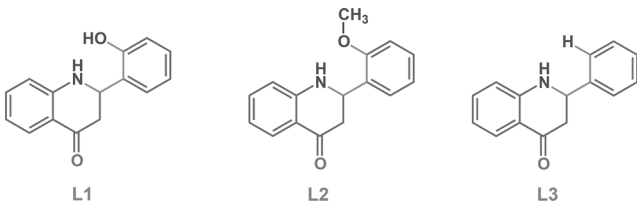


Figure 1. Structures of sensor probe **L1** and control compounds **L2** and **L3**.

Sensing Response of Probe L1 in the Presence of Various Anions

To explore the selectivity of probe **L1** towards various anions, UV/Vis measurements and fluorescence titrations were carried out against seventeen anions, that is, F^-, Cl^-, Br^-, I^-, NO_3^-, CH_3COO^-, CNS^-, ClO_4^-, HSO_4^-, PF_6^-, $H_2PO_4^-$, SH^-, CN^-, HCO_3^-, S^{2-}, HPO_4^{2-}, and SO_4^{2-} (added as their tetrabutylammonium/sodium salts) in water by adding equimolar concentrations of anions to a fixed amount of **L1** (50 μM). Remarkably, among these ions tested, only the fluoride ion led to a significant (11-fold) enhancement in fluorescence emission concomitant with a considerable red shift (from 426 nm to 566 nm, $\Delta\lambda_{em} = 140$ nm), whereas all other anions exhibited a relatively negligible change in fluorescence emission (Figure 2B). In other words, besides observing a higher, red-shifted turn-on fluorescence activating the ESPT process, **L1** was found to be insensitive to the presence of other anions. Similarly, the absorption spectra of probe **L1** remained unchanged upon addition of the various other anions (Figure 2A). Upon addition of fluoride or other anions beyond one equivalent, no significant increase in emission or absorbance was noticed. Upon addition of fluoride ion to probe **L1**, the solution turned from colorless to yellow with a new absorption maximum appearing at 360 nm. Figure S20 in the Supporting Information shows the selective binding ability of probe **L1** towards the fluoride ion in an aqueous medium.

Sensing Response of Probe L1 with Fluoride Ions

To prove that the fluoride ion binds to **L1**, absorption and emission titrations were carried out separately in water. It was found that, whereas **L1** displayed only a short-wavelength fluorescence at 426 nm ($\lambda_{exc} = 330$ nm) in water with a very low intensity, a new and substantially red-shifted emission band appeared at 566 nm ($\lambda_{exc} = 360$ nm) upon addition of fluoride ions, and the intensity of the band increased with increasing the fluoride concentration (Figure 3B). Meanwhile, the absorption spectrum of **L1** underwent a systematic variation when titrated by fluoride ions (Figure 3A), and the color of the solution turned from colorless to yellow (Figure 2C). It was also noted that three new peaks appeared at 361, 312, and 238 nm, respectively, with increasing fluoride concentration.

To examine the selectivity of probe **L1** towards fluoride over other anions, competitive titrations were carried out in the presence of equimolar amounts of fluoride and other anions. No significant change in the fluorescence intensity of a sample containing **L1** and $F^-$was observed in the presence

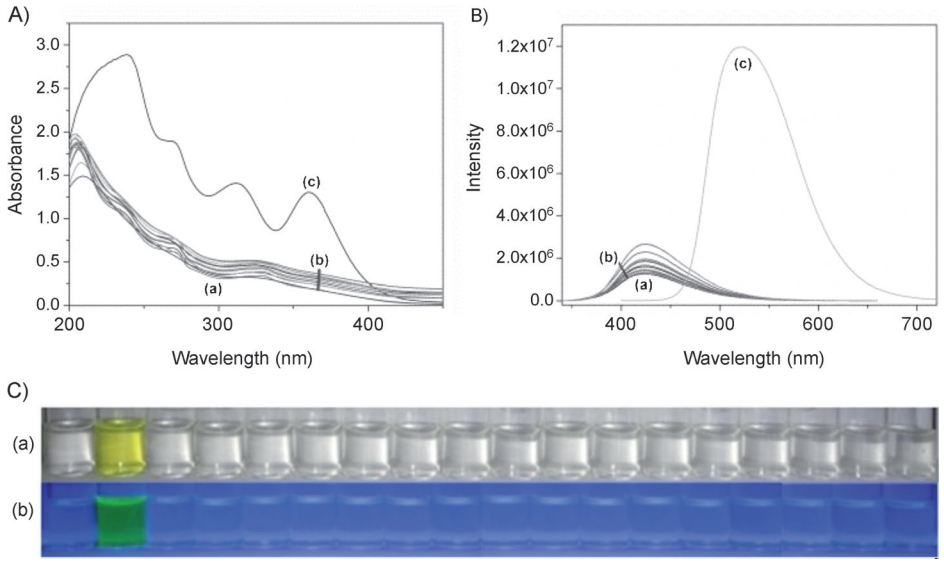


Figure 2. (A) Absorption spectra of probe **L1** (50 μM) in the absence (a) and presence (b,c) of TBA salts of various anions (50 μM): Cl^-, Br^-, I^-, NO_3^-, CH_3COO^-, CNS^-, ClO_4^-, HSO_4^-, PF_6^-, $H_2PO_4^-$, SH^-, CN^-, HCO_3^-, S^{2-}, HPO_4^{2-}, and SO_4^{2-}, respectively (curves b) and F^- (curve c). B) Fluorescence spectra of probe **L1** (50 μM) in the absence (a) and presence (b,c) of TBA salts of various anions (50 μM): Cl^-, Br^-, I^-, NO_3^-, CH_3COO^-, CNS^-, ClO_4^-, HSO_4^-, PF_6^-, $H_2PO_4^-$, SH^-, CN^-, HCO_3^-, S^{2-}, HPO_4^{2-}, and SO_4^{2-}, respectively (curves b) and F^- (curve c). $\lambda_{exc}=360$ nm. C) Color change of probe **L1** upon addition of various anions under (a) day light and (b) illumination by a UV lamp (365 nm). From left to right: control (**L1** alone), F^-, Cl^-, Br^-, I^-, NO_3^-, CH_3COO^-, CNS^-, ClO_4^-, HSO_4^-, PF_6^-, $H_2PO_4^-$, SH^-, CN^-, HCO_3^-, S^{2-}, HPO_4^{2-}, and SO_4^{2-}.

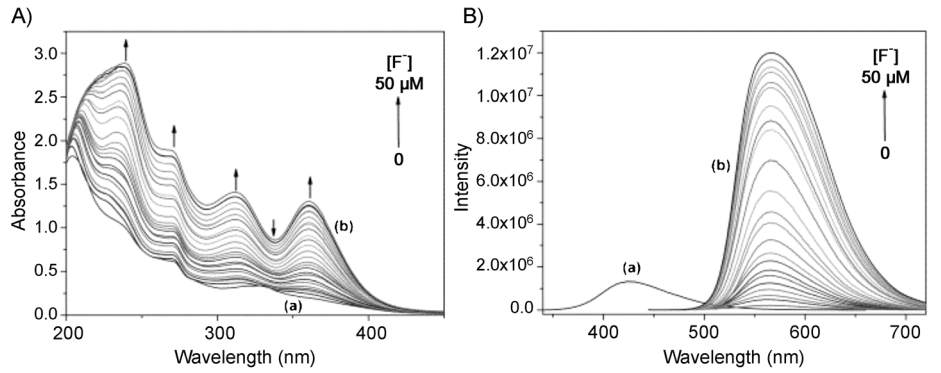


Figure 3. A) Absorption and B) fluorescence spectra of probe **L1** (50 μM, curve a) upon titration by fluoride (0–50 μM, curves b) in water.

of these competitive ions (Figure 4(a)), thus indicating that the selected other anions did not interfere with fluoride ion binding to the probe.

The precision of the method was evaluated by investigating its reproducibility at a constant **L1**-to-F^- ratio of 1:1. The limit of detection (LOD) for fluoride ion was determined using fluorescence titration and was found to be 5×10^{-11} M with a relative standard deviation (RSD) of 2.3% for three independent measurements. The speed of the sensing response of probe **L1** for the fluoride ion was found to be <1 second. Since the limit for F^- in drinking water has been set as 2 ppb by the US Environmental Protection Agency (EPA), a sample with this concentration of fluoride was analyzed by fluorescence measurements. An enhancement of 11 ± 2% in the fluorescence intensity was found at this concentration. As indicated in Figure 4b, the fluorescence intensity of probe **L1** (50 μM) increased with increasing the concentration of F^- ions. A linear correlation ($R^2=0.993$) between the emission intensity and the concentration of F^- ions was observed. Owing to its water solubility and biocompatibility as well as its constant sensitivity towards fluoride ions in a wide pH range (pH 4–9.5, Figure S27 in the Supporting Information), **L1** could find numerous applications including analysis of environmental and biological samples..

UV/Vis absorption titrations were carried out in an aqueous medium to evaluate the relative binding affinities of the various anions towards **L1**; the respective binding constants of the other anions were found to be much lower (Table S1, Supporting Information) compared to that of the fluoride ion ($7587\ M^{-1}$) at 25°C. The fact that **L1** shows a higher binding affinity to and a more efficient fluorescence enhancement by the fluoride ion than other anions is actually not surprising because of its high charge density and small size, which enables it to be a strong hydrogen-bonding acceptor that shows binding interaction with phenol or cyclic amine derivatives containing hydrogen-bonding donor groups. Job's plots based on absorption titrations (Figure S24, Supporting Information) suggested the formation of a 1:1 complex between **L1** and the fluoride ion. This conclusion was further confirmed by ESI-MS analysis. The molecular ion peaks (*m*/*z* found: 240.1092, calcd for $C_{15}H_{13}NO_2$ $[M+H]^+$: 240.1025; *m*/*z* found (negative ion mode): 258.0972, calcd for $C_{15}H_{13}FNO_2$, $[\mathbf{L1}+F^-]$, $[M]^-$: 258.0930 and *m*/*z* found (positive ion mode): 259.1021, calcd for $C_{15}H_{14}FNO_2$, $[\mathbf{L1}+F^-]$, $[M+H]^+$: 259.0978) correspond to **L1** and the **L1**:F^- complex, respectively (see the Supporting Information, Figures S3, S25, and S26).

Binding of the fluoride ion with probe **L1** was also confirmed by NMR titration studies. It was found that the NH proton resonance of the cyclic amine was broadened and un-

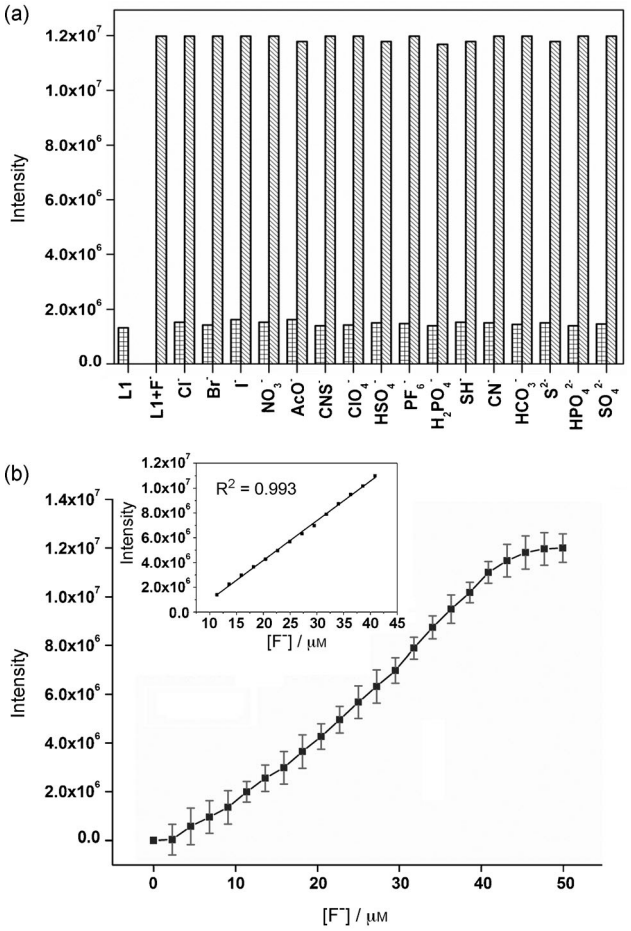


Figure 4. (a) Fluorescence response of probe **L1** (50 μM) towards the fluoride ion in the presence of other anions in water. The boxed bars represent the fluorescence intensity of probe **L1** in the presence of one equivalent of the other anions (λ_{exc} = 330 nm; λ_{em} = 426 nm). The hatched bars represent the fluorescence intensity after subsequent addition of one equivalent of fluoride ion (λ_{exc} = 360 nm; λ_{em} = 566 nm). (b) Plot of the fluorescence intensity of probe **L1** at 566 nm as a function of fluoride ion concentration. Data represent the mean values ± standard deviation of three independent measurements. Inset: Linear fit of the obtained data in the concentration range of about 12–42 μM.

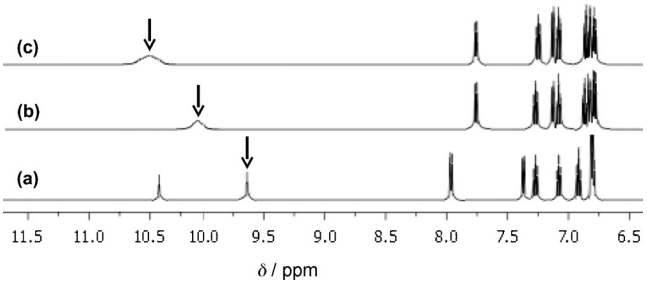


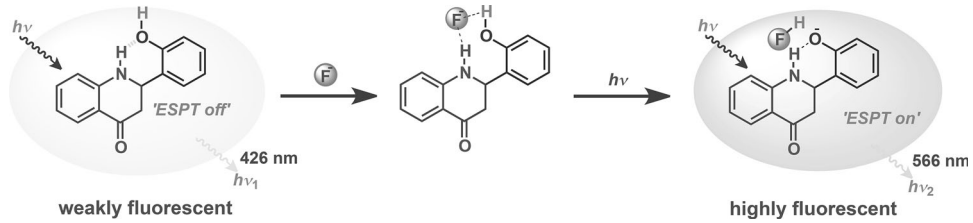
Figure 5. ^{1}H NMR (400 MHz) spectra of probe **L1** in CD_3CN containing 5% $[D_6]$DMSO in the presence of (a) 0, (b) 0.5, and (c) 1.0 equivalent of tetrabutylammonium fluoride. Arrows mark the NH proton signal. Complete ^{1}H NMR spectra are provided in Figures S13–S15 in the Supporting Information.

derwent a continuous downfield shift from 9.645 to 10.063 to 10.489 ppm with increasing fluoride ion concentration (0, 0.5, and 1.0 equiv), whereas the phenolic −OH proton resonance (10.459 ppm) could not be similarly followed as it had completely disappeared upon addition of 0.5 equivalents of fluoride ion (Figure 5 and Figures S13–S15 in the Supporting Information). These observations clearly supported the existence of significant hydrogen-bonding interactions between **L1** and the fluoride ion involving the cyclic amine −NH and phenolic −OH protons. The sensing behavior of probe **L1** to other types of fluoride salts, such as NaF, KF, and LiF was also explored. Probe **L1** displayed a similar fluorescence response irrespective of the fluoride salt used (Figure S21, Supporting Information).

The calculated pK_a values of probe **L1** are 9.59 ± 0.35 and 1.73 ± 0.40.[22] The observed results of fluoride ion binding with probe **L1**, such as enhanced emission, indeed indicate a dramatic enhancement of the acidity in the excited state. To rationalize this result, two control molecules, **L2** and **L3** (Figure 1), in which the hydroxy group was replaced with a methoxy group and hydrogen, respectively, were also synthesized and studied. For **L2** (Figure S22, Supporting Information), with a binding constant of 521 M^{-1}, negligible variation in the absorption and relatively small changes in the fluorescence spectra upon addition of fluoride ions were observed. Upon addition of fluoride ions to **L3**, also no discernible spectral changes could be observed (binding constant 112 M^{-1}, see Figure S23, Supporting Information). It is therefore obvious that proton transfer occurs between the hydroxy group of the sensor and anions in the excited state, while both cyclic amine -NH and phenolic −OH moieties in **L1** play an important role in the binding of **L1** to the fluoride ion. A distinguishable color change of **L1** was observed only in the presence of fluoride ions (Figure S19, Supporting Information), both under visible and UV light.

Proposed Mechanism

A plausible mechanism (involving a "turn-on" ESPT process) for this efficient fluoride ion sensing is given in Scheme 1. In an aqueous solution, the fluorescence emission of probe **L1** is weak, and the spectrum is dominated by a normal emission band appearing at 426 nm, which presumably originates from the H-bonded rotamer (Scheme S1, Supporting Information) that cannot undergo ESPT.[9,23–25] Upon addition of F^- ions, a new absorption band appears at 360 nm and the solution turns from colorless to yellow (deprotonation of the phenolic OH group, see Figure S17 in the Supporting Information); the emission intensity is increased and red-shifted to 566 nm (Figure S18, Supporting Information) due to F^- ion binding to both cyclic NH and phenolic −OH protons. The acidities of these protons are drastically enhanced upon photoexcitation and therefore an ESPT channel is opened upon F^- ion binding. Subsequent proton removal from the −OH group by the fluoride ion generates a phenoxide anion that is stabilized by intramolecular hy-



Scheme 1. Proposed mechanism of fluoride ion sensing by 2-(2-hydroxyphenyl)-2,3-dihydroquinolin-4(1*H*)-one (probe **L1**) in water.

drogen bonding to the NH group facilitating a "turn-on" fluorescence signal. In order to evaluate the role of the possible deprotonation process, titration of probe **L1** with [OH^-] was performed. Upon addition of hydroxide up to 2 equivalents, only very minor changes in the absorption and emission spectra were observed. This indicates that fluoride ion complexation is essential and responsible for its detection reported in the present study.

Theoretical Calculations

The proposed mechanism is strongly supported by theoretical calculations. To gain insight into the optical response of sensor probe **L1** to fluoride anions, the sensor and the corresponding **L1**+F^- complex were examined by density function theory (DFT) and time-dependent density function theory (TD-DFT) calculations at the B3LYP/6-31G(d) level using the Gaussian 03 program (Figures S28–S33, Supporting Information). For **L1**, both the HOMO and LUMO are distributed at the quinolinone scaffold with $E_{HOMO} = -5.37$ eV and $E_{LUMO} = -1.23$ eV, respectively, and the energy difference is $\Delta E = 4.14$ eV (Figure 6). For the probe **L1**+F^- complex, the HOMO and LUMO are distributed at the 2-aryl and quinolinone scaffolds with $E_{HOMO} = -6.24$ eV and $E_{LUMO} = -4.56$ eV, respectively, and the energy difference is $\Delta E = 1.68$ eV (Figure 6). This indicates that probe **L1** binds with F^- ion by turning on the ESPT channel, which simultaneously allows electron clouds to be transferred from the 2-aryl moiety to the quinolinone unit, consistent with the design strategy. Furthermore, the energy gap between the HOMO and LUMO of the probe **L1**+F^- complex is much smaller than that of sensing probe **L1**, which is in good agreement with the red shift in the absorption observed upon addition of fluoride ions to sensing probe **L1**.

The DFT calculations were performed for the optimized structures of probe **L1** and its F^- complex using the Gaussian 03 program. As shown in Figure 6, the dihedral angle between the quinolinone and 2-aryl moieties changed from 123.82° in **L1** to 115.76° in its F^- complex, which increases the planarity between these two moieties. Consequently, the bond lengths of N–H and O–H bonds increases and that of the C–O bond decreases upon binding with the F^- ion. Interestingly, the F–H distance in F···H–O is 1.58 Å and in F···H–N is 1.16 Å. In addition, we have performed TD-DFT calculations for both the probe **L1** and the **L1**+F^- complex. For the latter, TD-DFT calculations provide a calculated absorption band that is consistent with the absorption band at 456 nm obtained experimentally.

The present study establishes clearly a very selective and specific sensing of fluoride ions.

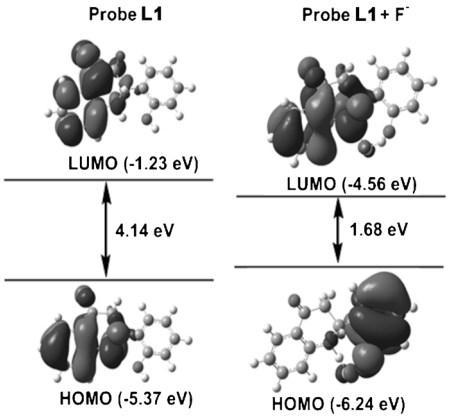


Figure 6. HOMO–LUMO energy levels and the interfacial plots of the orbitals for sensor probe **L1** and the probe **L1**+F^- complex.

The selectivity over other anions is attributed to the increase in acidity upon excitation and the basicity of the fluoride ion. The observed results are substantiated from the obtained binding constant values as well as DFT and TD-DFT studies. The hydrogen-bonding interactions ensure simultaneously proton abstraction from the phenolic -OH moiety by fluoride ion and from the –NH group by $-O^-$, which may have contributed to the highly selective sensing of fluoride ions. Increases in the intensity of fluorescence emission and UV/Vis absorption lend additional support to the above conclusions.

Determination of Fluoride Levels in Real Water Samples

To investigate the potential utility and practical applicability of the sensing probe **L1** to real samples, the levels of fluoride in five practical water samples, that is, drinking water, tap water, bore well water, and two river water samples were examined. All collected water samples were filtered three times through qualitative filter paper before use and the initial levels of fluoride ions were examined. The standard addition method was used to determine the concentration of fluoride by the addition of 20, 40, and 60 μM of fluoride ions to the above water samples. The obtained results show that probe **L1** allows for the measurement of spiked fluoride ion concentrations with good recovery (Table 1).

Table 1. Analytical results for the detection of fluoride ions in five practical samples.

Sample	Determined [fluoride] [μM][a]	Added [fluoride] [μM]	Expected [fluoride] [μM]	Found [fluoride] [μM][a]	Recovery [%]
Drinking water	5±0.2	20	25	25.0±0.7	100.0
		40	45	44.2±0.3	98.2
		60	65	65.1±0.5	100.2
Tap water	10±0.6	20	30	31.2±0.6	104.0
		40	50	49.0±0.3	98.0
		60	70	72.5±0.8	103.6
Bore well water	14±0.2	20	34	33.6±1.2	98.8
		40	54	55.3±0.9	102.4
		60	74	74.1±1.5	100.1
River water #1	76±1.3	20	96	96.0±1.8	100.0
		40	116	114.7±0.4	98.9
		60	136	134.5±1.6	98.9
River water #2	57±1.1	20	77	78.4±1.1	101.8
		40	97	96.2±0.4	99.2
		60	117	117.1±0.9	100.1

[a] Mean ± standard deviation ($n=4$).

These results clearly indicate that probe **L1** can potentially be used for fluoride detection in natural water samples.

Conclusions

In summary, herein we report a simple, highly selective and sensitive "turn-on" chemosensor for the fluoride ion using 2-(2-hydroxyphenyl)-2,3-dihydroquinolin-4(1*H*)-one (probe **L1**) as a colorimetric as well as fluorescent probe in an aqueous medium. **L1** selectively senses the F^- ion against the other thirteen anions of biological and ecological importance examined by exhibiting an up to 11±2-fold fluorescence enhancement in water. The probe **L1** forms a 1:1 complex with fluoride ion, as assessed by Job's plot and ESI-MS analysis. ESPT is suggested to be the signaling mechanism, which is rationalized by DFT and TD-DFT calculations. This sensor system has a detection limit as low as 5×10^{-11} M with an RSD of 2.3% ($n=3$) and was found to be applicable to detect fluoride ions in real water samples.

Experimental Section

The anions F^-, Cl^-, Br^-, I^-, NO_3^-, CH_3COO^-, CNS^-, ClO_4^-, HSO_4^-, PF_6^-, $H_2PO_4^-$, CN^-, HCO_3^- and SO_4^{2-} were added as tetrabutylammonium (TBA) salts, while S^{2-} and HPO_4^{2-} were added as sodium salts ($Na_2S\cdot9H_2O$, Na_2HPO_4); all salts were obtained from Sigma–Aldrich and Merck and used as received without further purification. Doubly distilled water and HPLC grade solvents were used for all spectral measurements. All other chemicals and solvents were purchased from Aldrich or Merck and used as received without further purification.

^1H and ^{13}C NMR spectra were acquired on Bruker DRX-300 and Bruker Avance-II (300 MHz and 400 MHz) instruments using TMS as an internal standard. Data for ^1H NMR are recorded as follows: chemical shift (δ, ppm, parts per million), multiplicity (s=singlet, d=doublet, t=triplet, m=multiplet or unresolved, dd=doublet of doublet, brs=broad singlet, coupling constant(s) in Hertz (Hz), integration). Data for ^{13}C NMR spectra are reported in terms of chemical shift (δ, ppm). Binding constants were calculated by non-linear regression using the Prism software (trial version). All absorption spectra were recorded with a JASCO V-550 double beam spectrophotometer equipped with a PMT detector. The emission spectra were recorded with a FLUOROMAX-4 spectrofluorometer (HORIBA JOBIN YVON) with the excitation slit set at 2.0 nm band pass and the emission at 5.0 nm band pass in quartz cell of 1 cm path length. FTIR spectra were recorded with a JASCO FT/IR-410 spectrometer. Electrospray ionization mass spectrometry (ESI-MS) data were recorded with a LCQ Fleet instrument (Thermo Fisher Instruments Limited, USA).

All calculations on sensing probe **L1** and the probe **L1**+F^- complex were carried out with the Gaussian 03 program package by using density functional theory (DFT) and time-dependent DFT (TD-DFT): Becke's three-parameter functional combined with Lee, Yang, and Parr's correlation functional[26] (B3LYP), along with the LANL2DZ (d) basis set were used. All geometries and electronic properties were calculated by assuming **L1** and the **L1**+F^- complex to be isolated molecules.

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