Naked-eye detection of fluoride ion in water: a remarkably selective easy-to-prepare test paper†

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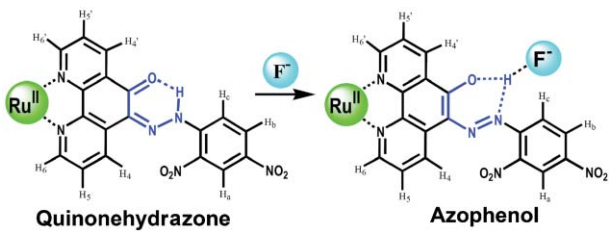
A test paper for high-selectivity detecting fluoride ion in natural aqueous environments without any spectroscopic instrumentation was achieved by using Ru-bipy based quinonehydrazone as a chromo- and fluorogenic hybrid chemosensor.

The design of an artificial receptor capable of selective interactions with simple water-soluble anions remains the basis of many important subdisciplines of supramolecular chemistry, which investigate a variety of functions, including recognition, sensing, catalysis, *etc*.[1,2] In particular, the sensing of fluoride ion has attracted growing attention,[3] because of its great potential for biological and industrial applications,[4] and fluoride's unique properties compared to its congeners as a result of relative size and electronegativity. While a number of compounds that are able to bind fluoride ions with high affinity and selectivity have been reported,[5] the challenges of detecting and amplifying the fluoride ion binding event to produce a measurable output still remain. Of particular interest in this regard are colorimetric anion sensors, species that would allow the naked-eye detection of fluoride without resorting to any spectroscopic instrumentation.[6] Here, we report a remarkable selective Ru-based fluoride chromo- and fluorogenic hybrid chemosensor **1** of a Schiff-base compound HL, 1,10-phenanthroline-5,6-dione 2,4-dinitrophenylhydrazone.[7] It contains a quinonehydrazone group that can be transformed to azophenol form in the presence of fluoride ion (Scheme 1),[8] from which significant changes in absorption spectra and color of the solution can be expected. Furthermore, the existence of a photoactive $Ru(bipy)_3$ moiety (bipy = 2,2′-bipyridine) not only enhances the affinity through electrostatic interactions, but also provides fluorogenic as well as chromogenic sensing.[9]



Scheme 1 Proposed mode of anion binding of **1**.

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† Electronic supplementary information (ESI) available: ESI-MS spectra (Fig. S1), UV-vis spectra in the presence of anions (Fig. S2) and UV/vis–pH titrations upon addition of F^- and OH^- (Fig. S3) of compound **1**. See DOI: 10.1039/b514337c

Compound **1** was prepared by reaction of 2,4-dinitrophenylhydrazine with bis(2,2′-bipyridine)(1,10-phenanthroline-5,6-dione) Ru^{II} in the presence of H_3PO_4 and crystallized as PF_6^-salt.‡ Elemental analyses and spectroscopic measurements suggested the formation of $[Ru(bipy)_2(HL)](PF_6)_2$. ESI-MS of the complex **1** in methanol solution showed two strong peaks at m/z = 803.1 and 948.9 (Fig. S1)†, which were assigned to $[Ru(bipy)_2L]^+$ and $[Ru(bipy)_2(HL)(PF_6)]^+$, respectively, indicating that complex **1** was stable in solution. The UV-vis spectrum exhibited a strong absorption band at about 475 nm with a shoulder at about 450 nm, which was assigned to the 2,4-dinitrophenylhydrazone-centered charge transfer (CT) and the metal-to-ligands charge transfer (MLCT) of the $Ru(bipy)_2$ moiety,[9] respectively. Addition of F^- to the solution of **1** caused a dramatic change in color from orange to blue-violet, which was accompanied by a new intense absorption band centered at about 580 nm in the UV-vis spectrum. We ascribed this new band to the ligand(HL)-based charge transfer (CT) of the azophenol tautomer, which was induced by an incipient proton-transfer from the quinonehydrazone tautomer to fluoride ion.[8] The presence of two sharp isosbestic points at 390 nm and 500 nm indicated that only **1** and $\mathbf{1}\cdot F^-$ adducts coexist. The titration profile at 580 nm (insert in Fig. 1) supported the formation of 1: 1 stoichiometry adduct with an association constant log$K$ being 6.23 $\pm$ 0.03 (calculated through nonlinear least-squares fitting).

The sensing of **1** for halide anions such as Cl^-, Br^-, I^-, and more complicated anions such as HSO_4^-, NO_3^- $H_2PO_4^-$ (all as tetra-*n*-butylammonium salts, TBA salts) were also studied

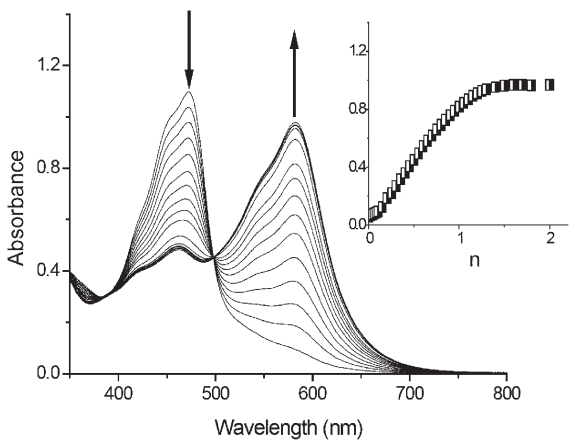

Fig. 1 UV-vis titration of **1** in MeCN (2.5×10^{-5} M) solution upon addition of fluoride ion as TBA salt. Inset: absorbance at 580 nm *vs.* number (n) of mole equivalents of F^- ion added.

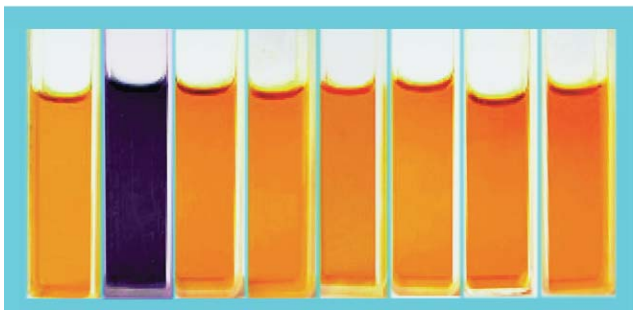

Fig. 2 Color changes observed for **1** in MeCN solution (5×10^{-5} M) upon addition of one mole equivalent of anions as TBA salts: From left to right: free **1**, F^-, Cl^-, Br^-, I^-, HSO_4^-, NO_3^- and $H_2PO_4^-$.

through UV-vis spectra in MeCN solutions (Fig. S2).† The photograph in Fig. 2 showed the color changes after addition of equimolar amounts of these anions to the MeCN solution of **1**. The color changes occurred only when fluoride anion was added, other anions failed to cause any significant color change.

Furthermore, the presence of F^- also induced significant enhancement of the luminescence intensities of Ru-based receptor **1** at 630 nm by exciting the CH_3CN solution of **1** at 465 nm (Fig. 3). The titration curve of F^- was consistent with a proposed 1 : 1 host–guest binding stoichiometry with the association constant log$K$ being 6.43 $\pm$ 0.05. Upon addition of anions such as Cl^-, Br^-, I^-, HSO_4^- and NO_3^-, no detectable changes were observed. Considering the high selectivity for F^- over other anions and the convenience without resorting to any spectrometer, the compound **1** provided a great advantage for detecting fluoride ion. It is suggested that the high selectivity might be attributed to the

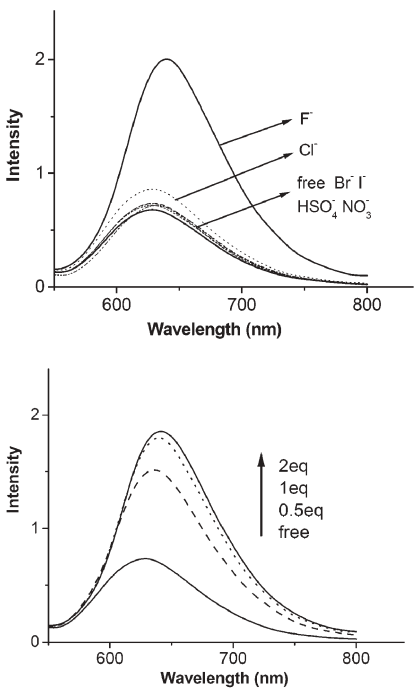

Fig. 3 Luminescence spectra of **1** in MeCN solution (2.5×10^{-5} M) after the addition of **1** equivalent of representative anions (top). Luminescence spectra of **1** in MeCN solution (2.5×10^{-5} M) and in the presence of F^- with different concentration (bottom).

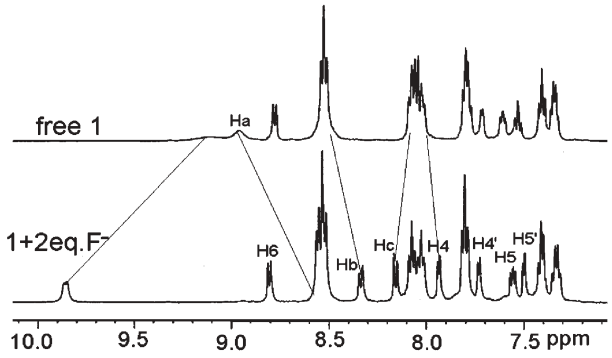

Fig. 4 ^{1}H NMR spectra of **1** in acetonitrile-d_3 (5×10^{-2} M) with the presence of 2 equivalent molar ratio of fluoride anion.

strong intramolecular N-H···O hydrogen bonding of **1**, from which the hydrogen atom was fastened, and only the anion showing the most electronegative property had the potential to form additional hydrogen bonding.[11]

As a validation of the above verdict, the binding property of the receptor **1** was studied by ^{1}H NMR spectroscopy (Fig. 4). The addition of F^- into an acetonitrile-d_3 solution of **1** resulted in significant perturbations of the most notably NH signal downfield shift from 9.11 to 9.87 ppm, and exhibited a doublet as a result of coupling with the fluoride (J = 30 Hz), and the similar ^{1}H–F coupling has been reported in a cryptand fluoride receptor.[10] This result demonstrated the potential hydrogen bonding including the fluoride anion. The signals of H_a and H_b exhibited progressive upfield shifts, whereas the signal of H_c exhibited significant downfield shift. The promotion of the downfield suggested that the complexed fluoride anion positioned near the H_c proton.[11] The evidence above was consistent with the formation of a **1**·F^- H-bonding host–guest complex. To further investigate the potential anion–receptor complexation, UV/vis–pH titrations upon addition of F^- and OH^- of the peak at about 580 nm were displayed (Fig. S3).† As can be expected, the presence of F^- and OH^- caused different titration curves from pH 6.0 to 12.0. Such a result supported the formation of a **1**·F^- H-bonding host–guest complex.

Generally, receptors for anions based solely on hydrogen-bonding interactions cannot serve as efficient sensors in aqueous media, due to the strong solvent competition. To avoid the competing solvation effect of water, we prepared a test paper of **1** for inspecting F^- in aqueous environments by putting a filter paper (3×0.5 cm^2) into the acetonitrile solution of **1** (2.0×10^{-3} M) and then drying it in the air. For detecting the fluoride anion in water, a test paper was immersed in the test aqueous fluoride-containing solution for several seconds then dried in the air. Fig. 5 exhibits the color changes of the test papers with different fluoride concentrations at pH $\approx$ 7. Clearly, the test paper can detect F^- in aqueous solution at a low limit about 10 ppm (10 mg L^{-1}). Other anions such as Cl^-, Br^-, I^-, HSO_4^- and NO_3^- did not cause any detectable changes. In fact, sensing F^- in natural aqueous environments without any spectroscopic instrumentation has been very useful in preventing fluorosis caused by the fluoride toxicity[12] in undeveloped regions. However, since many other anions such as chloride were present in most water at much higher concentrations than fluoride, it was important to know that chloride (or other

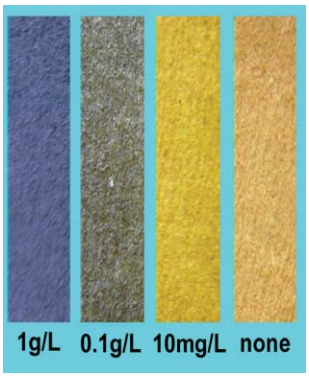

Fig. 5 The color changes of the test papers for detecting fluoride ion in neutral aqueous solution with different F^- concentrations.

common anions) did not cause color changes at concentrations normally found in water. As a complete study of the real application of fluoride detection, test papers were immersed in aqueous solutions having different fluoride concentrations in the presence of 10 g L^{-1} chloride anion (or/and other anions listed above). Similar color changes to those of solutions containing only fluoride showed the test papers provided the practical means to inspect fluoride anion concentrations in the wilderness.

In summary, we have presented here a rational strategy for the development of a new highly selective chromo-sensor to detect F^- in natural aqueous environments without any spectroscopic instrumentation. The proton transfer from the quinonehydrazone tautomer to fluoride anion induced the formation of azophenol tautomer and caused a dramatic change in color from orange to blue-violet. The easy-to-prepare fluoride test paper can detect F^- in aqueous solution at a low limit about 10 ppm (10 mg L^{-1}). This cheap sensing probe would be advantageous in the prevention of fluorosis in undeveloped regions.

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Notes and references

‡ A solution of 2,4-dinitrophenylhydrazine (0.198 g, 1 mmol) and bis(2,2′-bipyridine)(1,10-phenanthroline-5,6-dione)rutheniumbis (hexafluorophosphate) (0.9 g, 1 mmol) in mixed solvent comprised of 5 mL H_3PO_4, 25 mL MeCN and 25 mL EtOH was refluxed for 8 h under N_2. The solution was concentrated to 5 mL. An orange precipitate formed by adding the solution to a saturated aqueous solution of KPF_6 was collected and dried under vacuum. Yield 60%. Anal. calc. for $(C_{10}H_8N_2)_2Ru(C_{18}H_{10}N_6O_5)(PF_6)_2$: C, 41.7 H, 2.4 N, 12.8%. Found: C, 41.6 H, 2.5 N, 12.7%. ^1H NMR (500 MHz, CD_3CN), δ (ppm): 9.11 (br, 1H, −NH), 8.97 (br, 1H), 8.74 (d, 1H), 8.52 (m, 6H), 8.05 (m, 7H), 7.68 (m, 4H), 7.58 (t, 1H), 7.53 (t, 1H), 7.37 (m, 2H), 7.32 (m, 2H).

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