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Full Paper

Novel Chromogenic Chemosensors for Fluoride Anion Based on 8-Hydroxyquinoline Azo Derivatives

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A series of 8-hydroxyquinoline azo derivatives with diverse conjugated structures were synthesized and studied to chromogenically detect anions. All the dyes allowed selective detection for fluoride anion in CH_3CN via instant deprotonation of the compounds, which was affirmed by UV-Vis absorption and ^1H NMR spectra. The chromogenically responding ability increases as the substituent changes from phenyl to naphthyl or anthryl. This result is likely to be related to the enhancement of intramolecular charge transfer (ICT) induced by extension of conjugated structure.

Keywords 8-hydroxyquinoline, azo derivative, anion, chromogenic sensor

Introduction

Design and synthesis of new chemosensors for inorganic anions are an important subject in supramolecular chemistry due to the fundamental role of anions in biological, environmental and chemical processes.[1] Some different ways have been recently reported to specifically detect a given anion in the presence of other anionic analytes. As the smallest anion, fluoride ion has unique biological and chemical properties, and its recognition and detection are of growing interest because it is associated with dental care[2] and the treatment of osteoporosis.[3] Among the sensors for fluoride anion, either the specific Lewis acid-base interaction or designed hydrogen bonding is mostly adopted.[4] The detection of fluoride anion is usually performed by spectroscopic or electrochemical signals upon binding of anions to the receptor.[5] To develop simple-to-use, naked-eye diagnostic tools, a great effort has been made for the design and synthesis of selective chromogenic sensors for fluoride anion.[6]

Azophenol is one type of important chromogenic sensors for anions. In the presence of some special anions (such as fluoride anion), the strong phenol-anion interaction causes the absorption band of azophenol to red-shift in ultraviolet-visible light region.[7] To make the absorption band of azophenol more red-shifted, a strong electron-withdrawing group (such as NO_2 or CN) is usually introduced into azophenol. However, in some case, the presence of strong electron-withdrawing group may reduce the selectivity of azophenol to recognize various anions.[8] Therefore, 2,6-dialkyl azophenol derivatives with the steric hindrance were used to improve the selectivity to anion.[9] As an alternative to 2,6-dialkyl azophenol derivatives, 8-hydroxyquinoline was used as the receptor of anion in this paper. Herein, 2-methyl-5-phenylazo-8-hydroxyquinoline (**1**, Scheme 1) was synthesized to recognize the fluoride anion. Moreover, as an alternative of strong electron-withdrawing group, naphthyl and anthryl groups were introduced into **1** to generate **2** and **3**, respectively, and two new compounds: 2-methyl-5-(*α*-naphthylazo)-8-hydroxyquinoline (**2**) and 2-methyl-5-(2-anthrylazo)-8-hydroxyquinoline (**3**) were synthesized to improve the chromogenically responding ability of azo derivatives. In the presence of fluoride anion, the strong interaction between 8-hydroxyquinoline and fluoride anion resulted in the instant deprotonation, thereby causing a dramatic change in the photophysical properties, especially the UV-Vis absorption spectra.

Experimental

Instruments and reagents

All starting materials (aniline, *α*-naphthylamine and 2-aminoanthracene) were obtained from Aldrich and used as received. 2-Methyl-8-hydroxyquinoline (**4**) was obtained from commercial supply. All the anion sources in experiments were introduced by the means of their tetra-*n*-butylammonium salts except tetra-*n*-octyl ammonium bromide. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker DMX-500. MS (EI) data were recorded with an MA1212 mass spectroscope. UV-Vis spectra were recorded with a UV-Vis 2550 spectroscope (Shimadzu). The compounds studied here can be dissolved in CH_3CN very well. All spectroscopic and

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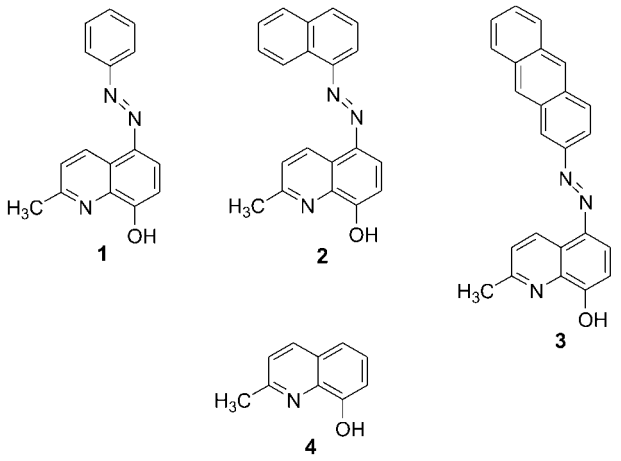
Scheme 1 Molecular structures of compounds **1**—**4**.



chromogenic measurements were carried out in CH_3CN.

Synthesis

The compounds **1**—**3** were prepared by the similar procedure reported previously.[10] Herein, only the synthesis of **1** was described in detail.

2-Methyl-5-phenylazo-8-hydroxyquinoline (**1**): Aniline (0.093 g, 1 mmol) was suspended in 30.0 mL of distilled water at the temperature of 0—5 ℃. Then 1.0 mL of 6.0 mol•L^{-1} hydrochloric acid solution was added to the mixture. After 15 min, 10.0 mL of aqueous solution of sodium nitrite (0.076 g, 1.1 mmol) was added, followed by acetonitrile solution of 2-methyl-8-hydroxyquinoline (0.159 g, 1 mmol), then pH was adjusted to 8—9 with 2.0 mol•L^{-1} NaOH solution. After stirred for 2 h, the solution was neutralized with 1.0 mol•L^{-1} HCl solution. The produced precipitate was filtered and washed with water for several times, then purified by column chromatography on silica gel with 100∶1 (*V*∶*V*) chloroform/methanol as eluent. The yellow product **1** was obtained with a yield of 76%. m.p. 101—102 ℃. ^{1}H NMR (500 MHz, DMSO-d_6, RT) δ: 10.41 (s, 1H, OH), 9.19 (d, J=9.0 Hz, 1H, QH), 7.99 (d, J=7.5 Hz, 2H, ArH), 7.92 (d, J=8.5 Hz, 1H, QH), 7.65 (d, J=8.5 Hz, 1H, QH), 7.62 (t, J=7.5 Hz, 2H, ArH), 7.56 (t, J=7.5 Hz, 1H, ArH), 7.21 (d, J=8.0 Hz, 1H, QH), 2.76 (s, 3H, CH_3); ^{13}C NMR (125 MHz, DMSO-d_6, RT) δ: 158.00, 157.16, 153.04, 139.27, 137.78, 132.24, 131.09, 129.78, 126.09, 124.37, 122.88, 114.28, 111.82, 25.13; MS (EI) *m*/*z*: 263.2 [M^+]. Anal calcd for $C_{16}H_{13}N_3O$: C 72.99, H 4.98, N 15.96; found C 72.91, H 4.96, N 16.01.

2-Methyl-5-(α-naphthylazo)-8-hydroxyquinoline (**2**): The yield of **2** is 69%. m.p. 146—148 ℃. ^{1}H NMR (500 MHz, DMSO-d_6, RT) δ: 10.45 (s, 1H, OH), 9.29 (d, J=8.5 Hz, 1H, QH), 8.96 (d, J=8.5 Hz, 1H, ArH), 8.15 (d, J=9.0 Hz, 2H, ArH), 8.09 (d, J=8.0 Hz, 1H, ArH), 8.01 (d, J=7.5 Hz, 1H, QH), 7.70—7.66 (m, 4H, 3ArH, 1QH), 7.28 (d, J=8.5 Hz, 1H, QH), 2.78 (s, 3H, CH_3); ^{13}C NMR (125 MHz, DMSO-d_6, RT) δ: 158.11, 157.40, 147.87, 140.13, 137.86, 134.47, 132.36, 131.27, 131.03, 128.51, 127.51, 127.06, 126.38, 126.29, 124.52, 123.42, 114.87, 112.29, 112.08, 25.18; MS (EI) *m*/*z*: 313.2 [M^+]. Anal calcd for $C_{20}H_{15}N_3O$: C 76.66, H 4.82, N 13.41; found C 76.64, H 4.79, N 13.46.

2-Methyl-5-(2-anthrylazo)-8-hydroxyquinoline (**3**): The yield of **3** is 65%. m.p. 205—208 ℃. ^{1}H NMR (500 MHz, DMSO-d_6, RT) δ: 10.43 (s, 1H, OH), 9.29 (d, J=8.5 Hz, 1H, QH), 8.85 (s, 1H, ArH), 8.77 (s, 1H, ArH), 8.67 (s, 1H, ArH), 8.23 (s, 2H, ArH), 8.17—8.14 (q, 2H, ArH), 8.03 (d, J=8.5 Hz, 1H, QH), 7.69 (d, J=8.5 Hz, 1H, QH), 7.61 (t, J=7.5 Hz, 2H, ArH), 7.26 (d, J=8.5 Hz, 1H, QH), 2.78 (s, 3H, CH_3); ^{13}C NMR (125 MHz, DMSO-d_6, RT) δ: 158.09, 157.18, 150.32, 139.55, 137.87, 132.67, 132.41, 132.21, 132.05, 131.61, 130.25, 129.80, 128.74, 128.65, 126.94, 126.89, 126.65, 126.19, 124.42, 116.90, 114.20, 112.01, 25.16; MS (EI) *m*/*z*: 363.3 [M^+]. Anal calcd for $C_{24}H_{17}N_3O$: C 79.32, H 4.72, N 11.56; found C 79.30, H 4.68, N 11.60.

Structure determination

Crystallographic measurements of compounds **1**—**3** were carried out using a Bruker SMART CCD diffractometer, σ scan, graphite-monochromated Mo Kα radiation (λ=0.71073 nm) under room temperature. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 values using SHELXS-97 program.[11] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were calculated in ideal geometries. For the full-matrix least-squares refinements [$I>2\sigma(I)$], the unweighted and weighted agreement factors of $R_1=\sum(F_o-F_c)/\sum F_o$ and $wR_2=[\sum w(F_o^2-F_c^2)2/\sum wF_o^4]^{1/2}$ were used. CCDC reference numbers are 295947, 296302 and 295893 for **1**, **2** and **3**, respectively.

Results and discussion

Synthesis and characterization of the azo compounds

Compounds **1**—**3** were prepared by a diazo-reaction of 2-methyl-8-hydroxyquinoline with arylamine, and further characterized by NMR spectra. The appearance of characteristic pattern of OH signals at about δ 10.4 was observed for **1**—**3** [see electronic supporting information (ESI)]. Further structure information was obtained by single-crystal X-ray diffraction studies. Molecular conformations of **1**—**3** are shown in Figure 1. The crystal data and details of the structure determinations are summarized in Table 1.

As expected, the steady structures of **1**—**3** are *trans*-form in the crystals. Compounds **1** and **2** crystallized in the monoclinic space group $P2(1)/n$ and $P2(1)/c$, whereas **3** crystallized in the triclinic space group P-1, indicating that the azo substituents affect the crystal systems of these 8-hydroxyquinoline derivatives. Interestingly, compounds **1** and **2** exhibit two independent

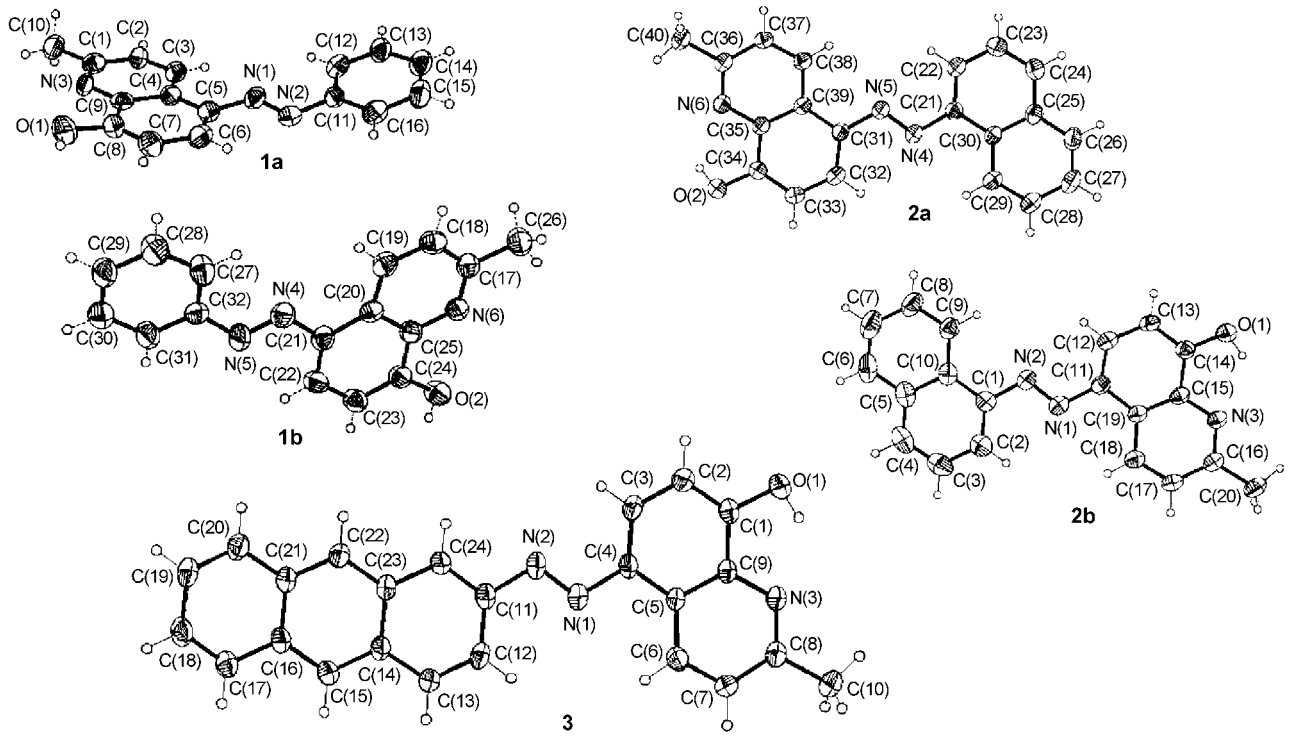


Figure 1 Molecular conformations of **1**—**3**.

Table 1 Crystal data collection and structure refinement parameters for **1**—**3**

	1	**2**	**3**
Empirical formula	$C_{32}H_{26}N_6O_2$	$C_{40}H_{30}N_6O_2$	$C_{24}H_{17}N_3O$
M_r	526.59	626.70	363.41
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	*P*2(1)/*n*	*P*2(1)/*c*	*P*-1
Crystal size/mm^3	0.05×0.03×0.02	0.20×0.10×0.05	0.12×0.05×0.03
a/nm	57.74 (1)	118.24(2)	73.65(2)
b/nm	212.26(4)	170.86(3)	99.04(2)
c/nm	218.25(4)	155.38(3)	128.47(3)
α/(°)	90	90	75.43(3)
β/(°)	95.28(3)	94.73(3)	82.65(3)
γ/(°)	90	90	79.54(3)
V/nm^3	2.66(3)	3.12(9)	0.88(8)
Z	4	4	2
ρ_{calcd}/(g•cm^{-3})	1.313	1.331	1.358
μ/mm^{-1}	0.085	0.085	0.085
F(000)	1104	1312	380
R_1 [$I>2\sigma(I)$]	0.0652	0.0560	0.0669
wR_2 [$I>2\sigma(I)$]	0.1312	0.1450	0.1457
GOF	0.666	0.974	0.917

molecules with different bond length, bond angle and dihedral angle in the asymmetric unit cell in contrast to only one molecule for **3** (Figure 1).

Photophysical properties

The UV-Vis absorption spectra of **1**—**4** were measured in CH_3CN (2.0×10^{-5} mol•L^{-1}) and the corresponding data are shown in Table 2. The maximal absorption wavelengths (λ_{max}) of **1**—**3** in CH_3CN are 380, 401 and 402 nm, respectively. Compared with the absorption spectrum of **4** (λ_{max}=303 nm), the maximal absorption wavelengths of **1**—**3** are red-shifted obvi-

Table 2 Photophysical properties of **1**—**4**

Compd	λ_{max}[a]/nm	ε/(mol^{-1}•L•cm^{-1})	λ_{max}[b]/nm	$\Delta\lambda_{max}$[c]/nm	K_a/(mol^{-1}•L)		
					F^-	AcO^-	$H_2PO_4^-$
1	380	2.3×10^4	518	139	2.7×10^4	1.1×10^4	2.8×10^3
2	401	2.3×10^4	546	145	3.0×10^4	9.5×10^3	3.3×10^3
3	402	2.7×10^4	554	152	9.1×10^4	2.4×10^4	2.8×10^3
4	303	1.0×10^4	—	—	—	—	—

[a] In CH_3CN solution. [b] Upon addition of F^- to CH_3CN solution. [c] $\Delta\lambda_{max}=\lambda_{max}{}^b-\lambda_{max}{}^a$.

ously, indicating that the introduction of —N=N— system improves the chromogenic characteristics of the 8-hydroxyquinoline derivatives. Furthermore, the maximum absorption wavelengths of **2** and **3** are red-shifted (*ca*. 20 nm) as reference to that of **1** in CH_3CN, which may be attributed to the more extension of the conjugation for **2** with naphthyl group and **3** with anthryl group. Moreover, the absorption band intensities of **1**—**3** are similar in the same solvent. The molar absorption coefficients of **1**—**4** are 2.3×10^4, 2.3×10^4, 2.7×10^4 and 1.0×10^4 mol^{-1}•L•cm^{-1}, respectively, revealing **1**—**3** have stronger ability of absorbing light than **4**.

Titration experiments

The complexation abilities of **1**—**3** with fluoride ion were investigated by the UV-Vis absorption technique. In our present experiments, tetra-*n*-butylammonium fluoride (TBAF) as a fluoride source was gradually added to a CH_3CN solution of **1**—**3**. The changes of their photophysical properties are summarized in Table 2. As an example, Figure 2 shows UV-Vis absorption spectra of **1** and **3** in CH_3CN solution upon addition of various concentrations of F^- anion. Notably, for compound **1** (Figure 2a), upon complexation with F^-, the characteristic strong absorption band at 380 nm decreased obviously, and a new band centered at 518 nm appeared and increased, corresponding to a λ_{max}(abs) red-shift of 139 nm. Moreover, a clear isosbestic point at 415 nm was observed, indicating the formation of a new compound. At the same time, upon addition of F^-, an apparent color change from yellow to red in ambient light could be observed by 'naked eye' for **1** in CH_3CN (Figure 3). The similar experimental phenomena were observed when F^- was added into the CH_3CN solution of **2** and **3**. It was noted that upon addition of F^- to CH_3CN solution, the characteristic strong absorption bands of **2** and **3** were red-shifted by 145 and 152 nm, respectively, accompanying an apparent color change from yellow to purple, which is more obvious than that from yellow to red of **1** (Figure 3). These facts indicated that phenolic anions of these compounds were formed via instant deprotonation.[6d,9,12] Then the formation of phenolic anions increased electron donating ability of the donors of **1**—**3**, which increased the intramolecular charge transfer and contributed to the red-shift of absorption band of **1**—**3**. On the basis of nonlinear least-square analysis,[13] the binding constants (K) of **1**, **2** and **3** with fluoride anion were calculated from the absorption-titration curves to be 2.7×10^4, 3.0×10^4 and 9.1×10^4 mol^{-1}•L at 20 ℃ in CH_3CN, respectively (Table 2). However, no apparent color change occurred for **4** in CH_3CN solution upon addition of F^-. Therefore, the extent of the conjugated system of these compounds is very important for this kind of anion detection.[14]

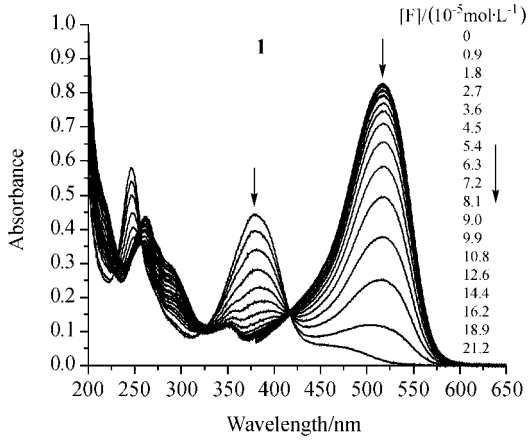


Figure 2 UV-Vis absorption spectra of **1** in CH_3CN ($c=2.0\times10^{-5}$ mol•L^{-1}) upon addition of different concentrations of F^-.

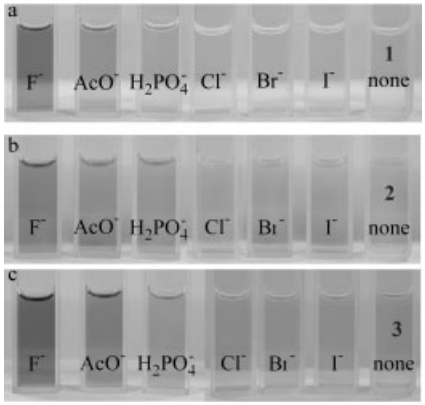


Figure 3 Color changes observed upon addition of 2.0 equivalents of anions to the CH_3CN solutions of **1**—**3** ($c=2.0\times10^{-5}$ mol•L^{-1}).

Selectivity

For an excellent chemosensor, high selectivity is a matter of necessity. The experimental results suggest

that these compounds show high selectivity as chromogenic sensors to fluoride anion. Compared to the response of **1**—**3** to F^-, relatively weak color changes were observed when AcO^- and $H_2PO_4^-$ were added to the CH_3CN solution of **1**—**3**. No color change was observed upon addition of Cl^-, Br^- or I^- (Figure 3), indicating that **1**—**3** show scarcely any response to other halide anions.

Figure 4 showed the titration profile of **1** ($c=2.0\times10^{-5}$ mol•L^{-1}) on the band at 518 nm with representative anions. Analysis of UV-Vis absorption spectra of **1** with all anions yielded binding constants in the following order: $F^- > AcO^- > H_2PO_4^- >> Cl^-$, Br^-, I^- in CH_3CN. The selectivity trends of **2** and **3** are similar with that of **1** and the stability constants of all compounds to diverse anions are shown in Table 2. For example, Figure 5 showed the UV-Vis absorption spectra of compound **3** upon addition of 2.0 equivalents of different anions. Upon addition of 2.0 equivalents of F^-, the peak intensities at 375 and 402 nm decreased obviously with the appearance of a new peak at 554 nm. In the case of 2.0 equivalents of AcO^- or $H_2PO_4^-$, smaller change was observed. Almost no spectral change was observed for **3** upon addition of 2.0 equivalents of Cl^-, Br^- or I^-. The highly selective recognition of all three azo compounds for F^- may be attributed to high charge density, small size and extreme basicity in organic solvent of F^-, which enable F^- to be strong acceptor to interact with these compounds and deprotonate these compounds at the OH position.[6d,9,12] The spectral change upon addition of AcO^- and $H_2PO_4^-$ is similar to that of F^- because AcO^- and $H_2PO_4^-$ are also basic anions.

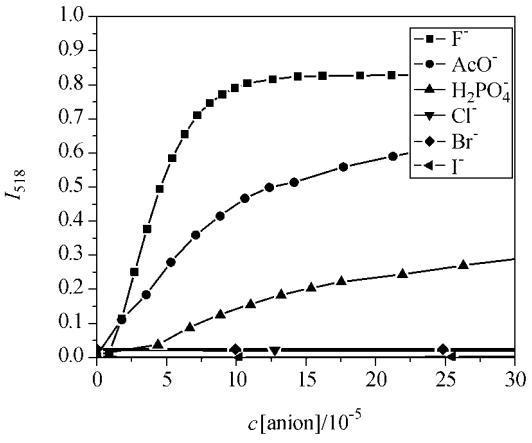


Figure 4 Titration profile of **1** ($c=2.0\times10^{-5}$ mol•L^{-1}) on the band at 518 nm with representative anions.

Competition experiments were also performed in 10.0 equiv. of F^- mixed with 10.0 equiv. of background metal cations associated with AcO^-, $H_2PO_4^-$, Cl^-, Br^-, and I^-, as shown by Figure 6. The ΔI [I_{max}(cation)—I_{max}(blank)] containing both background and F^- showed similar variation compared with that only containing F^-.

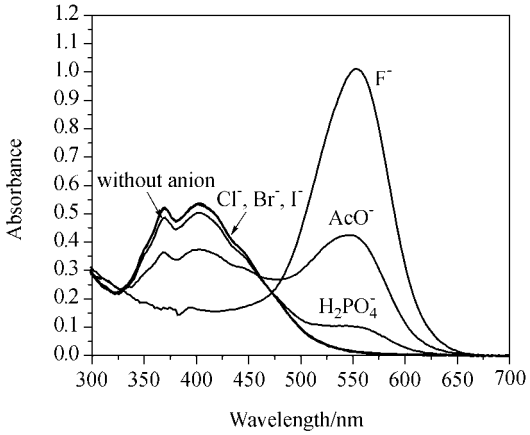


Figure 5 UV-Vis absorption spectra of **3** in CH_3CN ($c=2.0\times10^{-5}$ mol•L^{-1}) after addition of 2.0 equivalents of representative anions (F^-, AcO^-, $H_2PO_4^-$, Cl^-, Br^- and I^-).

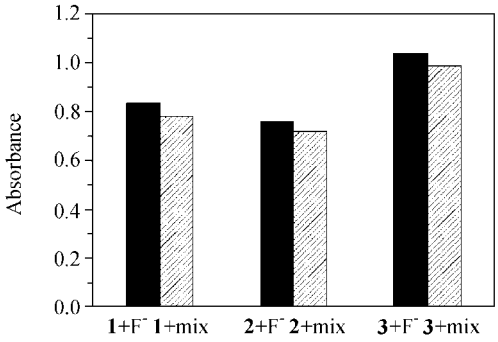


Figure 6 Responses of **1**—**3** in CH_3CN ($c=2.0\times10^{-5}$ mol•L^{-1}) to 10.0 equiv. of F^- and 10.0 equiv. of F^- mixed with 10.0 equiv. of background metal cations associated with AcO^-, $H_2PO_4^-$, Cl^-, Br^- and I^-.

^{1}H NMR

The response properties of compounds **1**—**3** to fluoride anion were further investigated by using ^{1}H NMR experiment in DMSO-d_6. Upon addition of F^-, dramatic changes occurred in ^{1}H NMR spectra of all compounds (see ESI). Figure 7 showed the ^{1}H NMR spectra of **1** before and after various equivalents of F^- added (Here, only the range of δ 6.0—10.0 was presented because OH protons of all compounds were very lively and signals were broad). The OH proton was visible as a broad signal appearing at δ 10.41 for **1**, and it broadened and disappeared upon addition of F^- (see ESI). Meanwhile, the addition of F^- led to significant upfield shifts of proton chemical shifts of the phenyl and quinoline groups with varied degree. The phenomena of other compounds **2** and **3** before and after F^- addition are similar to that of **1**. To further confirm the interaction of OH with F^-, the complexation of **4** with fluoride anion was also investigated with ^{1}H NMR titration. Figure 8 shows ^{1}H NMR of **4** in DMSO-d_6 before and after various equivalents of F^- were added. Similarly, the OH

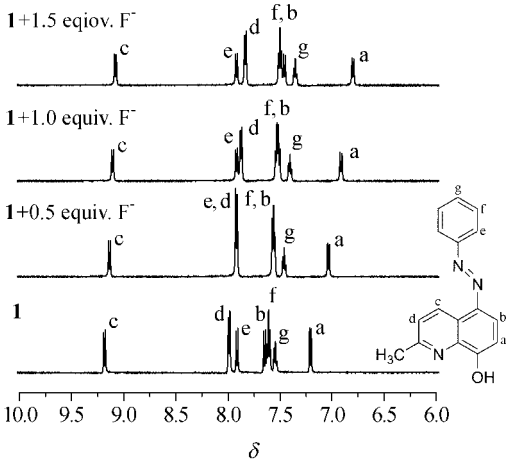


Figure 7 ^{1}H NMR of **1** in DMSO-d_6 before and after various equivalents of F^- were added.

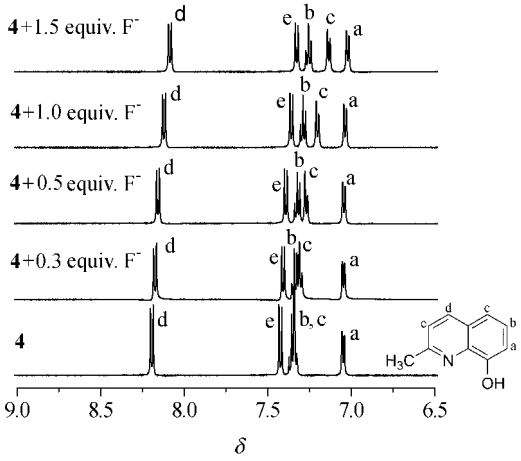


Figure 8 ^{1}H NMR of **4** in DMSO-d_6 before and after various equivalents of F^- were added.

proton signal at δ 9.40 disappeared and the obvious chemical shifts of the 8-hydroxyquinoline ring were observed (see ESI), indicating that OH group is the critical response site to anionic guests.[9,14]

Conclusion

In summary, we have presented a series of chromogenic 8-hydroxyquinoline based azo derivatives **1**—**3** with various extended π-conjugation for fluoride sensors. The presence of —N=N— group improves the chromogenically responding ability of the chemosensors. It is also evident that bathochromic effect of these derivatives occurs as substituent changes from phenyl to naphthyl or anthryl in CH_3CN solution. Importantly, these dyes can be used as sensors to detect fluoride anion over other anions including AcO^-, $H_2PO_4^-$, Cl^-, Br^- and I^-, by 'naked-eye' observation. Furthermore, ^{1}H NMR spectra reveal that OH group in various reagent molecules is an indispensable site to bind anionic species.

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