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Dual chemosensing properties of new anthraquinone-based receptors toward fluoride ions

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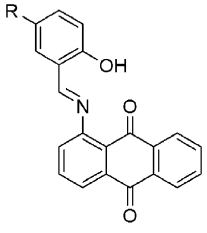
Abstract—Novel colorimetric receptors 1-[(2-hydroxy-5-bromo-benzylidene)-amino]-anthraquinone, 1-[(2-hydroxy-5-methyl-benzylidene)-amino]-anthraquinone, and 1-[(2-hydroxy-5-nitro-benzylidene)-amino]-anthraquinone have been synthesized as fluoride ion sensors. A color change was observed visually (naked-eye) upon addition of fluoride ions in organic solvents to solutions of the receptors.

The recognition[1] and sensing[2] of anionic analytes is a key research topic within supramolecular chemistry.[3] A significant amount of work has been devoted to obtain specific chemosensors that are able to change one or several macroscopic properties, upon complexation with the target guests. In response to the molecular coordination event, changes in color,[4] fluorescence[5] or absorbance[6] are the output signals used in the development of optical chemosensors. In this regard, 'colorimetric anion sensors' are species that would allow 'naked-eye' detection of anions without resort to any spectroscopic instrumentation. Such sensor systems are generally composed of two parts: one is the anion binding part (receptor), which is typically based on various combinations of pyrrole,[7] urea/thiourea,[8] amine[9] or phenol[10] moieties, and the other is a chromophore, which converts binding induced changes into an optical signal such as the appearance of color. These two parts are either directly linked[11] or intramolecularly associated.[12] Among various important analytes, fluoride ions are significant due to their role in dental care and treatment of osteoporosis.[13] According to previous studies,[14] F^- seems to interact with a hydrogen bond donor (NH_2, –OH, –C(O)NHR) of a receptor more strongly than any other anions. With reference to binding groups, only a limited number of reports are available using –OH as a binding site.[15] Hence, in continuation of our previous work,[16] we herein report chromogenic and selective fluoride chemosensors possessing a phenolic OH group able to bind fluoride via H-bond interactions, and an anthraquinone group which acts as a chromogenic signalling unit. The nature of these simple anthraquinone-based sensors is altered by incorporation of electron-withdrawing (Br^- or NO_2^-) and electron-donating (CH_3) substituents, which are able to tune the anion recognition selectivity.[17]

Receptors **1**, **2**, and **3** were synthesized by Schiff's base condensation of 1-aminoanthraquinone with 5-bromosalicylaldehyde, 5-methylsalicylaldehyde, and 5-nitrosalicylaldehyde, respectively. The products were purified by column chromatography on silica gel with hexane/chloroform (50:50 v/v) as eluent. The elemental and spectroscopic analysis results were consistent with the proposed structures of the receptors.[18]



R
1 = Br
2 = Me
3 = NO_2

Keywords: Chemosensors; Colorimetric; Fluoride; Anthraquinone; Electrochemical study.
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The ^{1}H NMR spectra of the receptors were recorded in DMSO-d_6 in the presence and absence of fluoride ions to determine their interactions. The ^{1}H NMR spectra of receptors **1**, **2**, and **3** showed an OH proton signal at δ 10.2 (**1**), 9.4 (**2**), and 11.2 (**3**), respectively, in the absence of F^-. The variations in the OH proton signal indicate the influence of the substituents. The more electron-withdrawing NO_2 group deshields the OH proton in comparison to the electron-donating CH_3 group. After the addition of fluoride ions (5 equiv), the OH proton signals disappeared. Hence, the effect on the OH proton resonances of **1**–**3** in the presence of F^- can be assigned as evidence for the occurrence of hydrogen bond interactions between OH and the fluoride ions.

The colorimetric sensing ability of receptors **1**, **2**, and **3** with halide anions (F^-, Cl^-, Br^-, and I^-) in $CHCl_3$, CH_3CN and DMSO was monitored by visual (naked-eye), optical (absorption and fluorescence) and electrochemical methods. The halide anions (F^-, Cl^-, Br^-, and I^-) were added as tetrabutylammonium salts to 5×10^{-5} M solutions of the receptors in DMSO.

In the naked-eye experiments, receptors **1**, **2**, and **3** (5×10^{-5} M in DMSO) showed dramatic color changes from light pink to dark pink, brown, and golden yellow, respectively, in the presence of TBAF (2.5×10^{-4} M) (Figs. 1a–1c). All the receptors were found to be insensitive to addition of a large excess of Cl^-, Br^-, and I^- (up to 100 equiv). Color changes are most probably due to the formation of hydrogen bond interactions between the OH groups and fluoride ions. These H-bond interactions affect the electronic properties of the chromophore, resulting in a color change along with a new charge-transfer interaction between the fluoride-bound OH and the electron-deficient anthraquinone moiety.[5] Fluoride ions interact with the receptors more strongly due to their higher electronegativity and their smaller size compared to the other halides.[14]

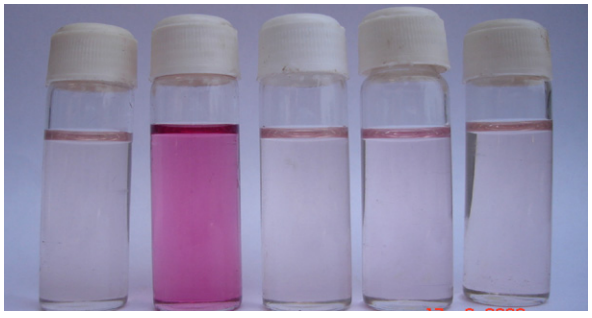

Figure 1a. Color changes of receptor (R) **1** in DMSO (5.0×10^{-5} M) before and after the addition of 2 equiv of representative anions (from the left to the right: R, R + F^-, R + Cl^-, R + Br^-, R + I^-).

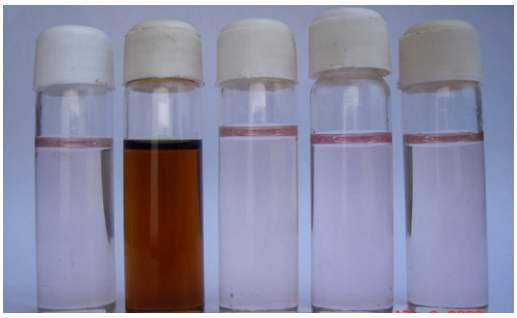

Figure 1b. Color changes of receptor (R) **2** in DMSO (5.0×10^{-5} M) before and after the addition of 2 equiv of representative anions (from the left to the right: R, R + F^-, R + Cl^-, R + Br^-, R + I^-).

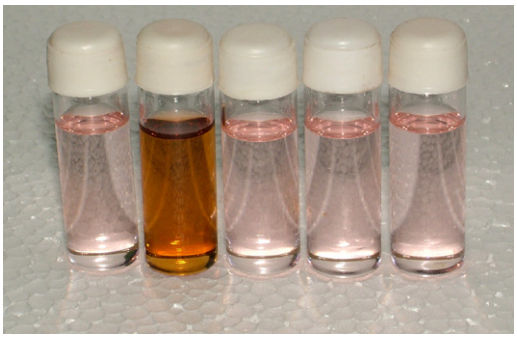

Figure 1c. Color changes of receptor (R) **3** in DMSO (5.0×10^{-5} M) before and after the addition of 2 equiv of representative anions (from the left to the right: R, R + F^-, R + Cl^-, R + Br^-, R + I^-).

Observable color changes also took place in $CHCl_3$ and CH_3CN solutions. Upon addition of fluoride ions, the pale red colored solutions (**1**–**3**) became dark red (**1** and **2**) and reddish brown (**3**) in CH_3CN and, yellow solutions (**1**–**3**) turned pink (**1**) and reddish brown (**2** and **3**) in color in $CHCl_3$. The colors of the receptors in CH_3CN and $CHCl_3$ remained the same in the presence of chloride, bromide, and iodide.

The recognition behavior of receptors **1**, **2**, and **3** toward halide anions was also investigated by absorption, emission, and electrochemical methods. Electronic spectra of the receptors showed four transitions in $CHCl_3$, CH_3CN, and DMSO and the data are given in Table 1. UV–vis titrations were carried out in DMSO at a concentration level of 5.0×10^{-5} M upon addition of tetrabutylammonium fluoride and the spectra are shown in Figures 2a–2c. The first two bands (250–280 nm) were assigned to the excitation of the π electrons of the aromatic system. The third band (around 320 nm) is due to the transition between the π orbital localized on the azomethine group (C=N). The absence of a band in the region (320–400 nm), which can occur due to intra-

Table 1. UV–visible data for **1**–**3**

Solvent	λ_{max} (nm)		
	1	**2**	**3**
$CHCl_3$	469, 335, 277, 252	460, 322, 255, 235	483, 309, 279, 243
CH_3CN	487, 311, 272, 243	498, 313, 273, 245	495, 317, 279, 258
DMSO	500, 315, 277, 258	508, 316, 277, 258	496, 316, 275, 257

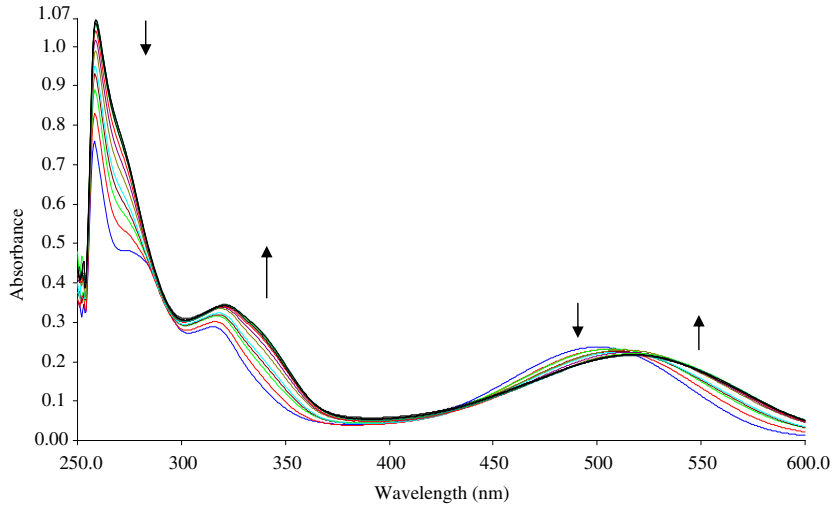

Figure 2a. Absorption spectra of receptor **1** recorded in DMSO (5.0×10^{-5} M) after addition of 0–10 equiv of tetrabutylammonium fluoride.

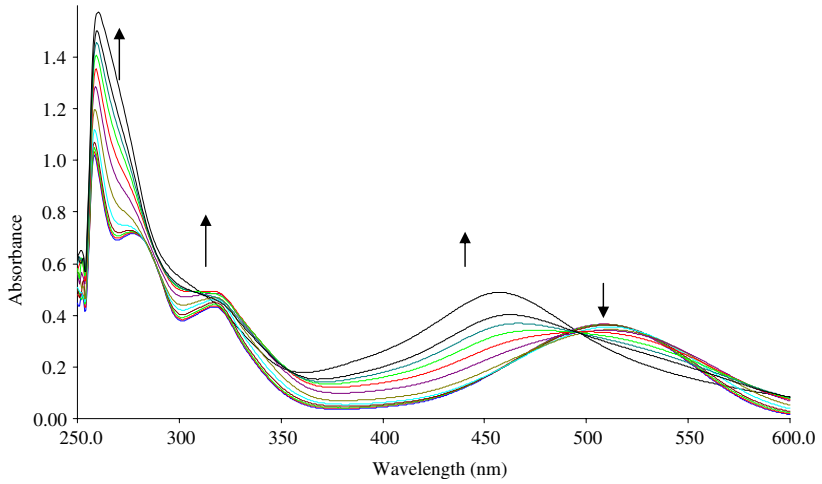

Figure 2b. Absorption spectra of receptor **2** recorded in DMSO (5.0×10^{-5} M) after addition of 0–10 equiv of tetrabutylammonium fluoride.

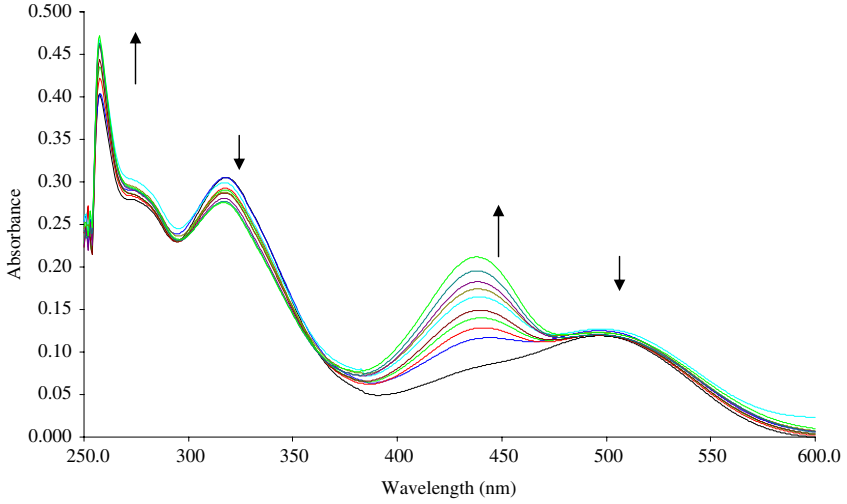

Figure 2c. Absorption spectra of receptor **3** recorded in DMSO (5.0×10^{-5} M) after addition of 0–9 equiv of tetrabutylammonium fluoride.

molecular charge-transfer transitions within the whole of the Schiff base, indicates that there is no intramolecular hydrogen bond between the OH group and the –HC=N nitrogen.[19] In the case of **1**, the intensity of the peak at 500 nm decreased, while a new peak at 518 nm appeared with an isobestic point at 510 nm after addition of F^-. Simultaneously, the intensity of the peak at 320 nm decreased. As seen in Figure 2a, a significant bathochromic shift was observed upon complexation with F^-, presumably due to a charge-transfer interaction between the fluoride-bound –OH and the electron-deficient anthraquinone moieties.[5] Addition of F^- also caused hypsochromic band shifts from 518 nm to 457 nm with an isobestic point at 490 nm, while increasing intensities of the absorbance at 310 nm were observed for receptor **2**. The intensity of the peak at 495 nm decreased with the addition of fluoride, whereas the peak at 439 nm increased with an isobestic point at 480 nm in the case of **3**. The intensity of the peak at 320 nm also decreased. Exposure to chloride, bromide and iodide anions did not result in any spectral changes in the above receptors.

Fluorescence titration experiments carried out with receptors **1**–**3** in DMSO (5×10^{-5} M) solution showed emission maxima at 598, 620, and 610 nm, respectively. Representative fluorescence spectra (Fig. 3) show the changes in the intensities of the fluorescence emission maxima of receptor **1** in the absence and presence of fluoride. Successive addition of F^- (2.5×10^{-4} M in DMSO solution) to DMSO solutions of **1**–**3** resulted in a decrease of their intensities with marginal changes in the emission maxima. The binding constants for the receptor–fluoride complex were obtained from the variation in the fluorescence intensity at an appropriate wavelength using the reported method.[20] The binding constants (K_a) for **1**, **2**, and **3** with fluoride were calculated to be 9.2×10^3, 5.785×10^3 and 1.90×10^4 M^{-1}, respectively. Receptor **3** (nitro substituent) shows a higher binding constant than the others. This may be due to the presence of the electron-withdrawing group, which results in strong hydrogen bond interactions with fluoride.

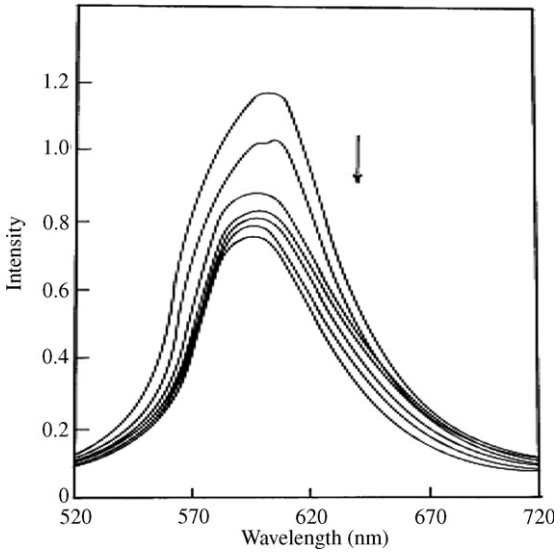

Figure 3. The changes in the fluorescence emission spectra of receptor **1** (5.0×10^{-5} M) upon titration with solutions of tetrabutylammonium fluoride in DMSO.

The anion sensing abilities of the receptors toward halide anions were also monitored by electrochemical techniques. Representative cyclic voltammograms (DMSO, 0.1 M TBAP, where the addition of TBAP to the receptor solutions did not cause any color change) of receptor **1** in the absence and presence of fluoride are shown in Figure 4. Receptors **1**, **2**, and **3** showed two irreversible reduction waves; the first reduction wave in the region −0.73 to −0.79 V, and the second reduction wave in the region −1.0 to −1.06 V. The formation of two reduction waves was assigned to the respective formation of radical anions and dianions of the anthraquinone moiety.[21]

The appearance of a sharp negative stripping peak at about −0.2 V corresponds to the electroreductive desorption of ion pairs adsorbed on the electrode surface in the oxidation step.[22] This stripping peak, however, disappeared on addition of further fluoride ions. This observation provides further evidence for F^- binding to the receptor.

Addition of successive amounts of F^- results in a reduction of the peak current along with a cathodic shift of the peak potential for receptors **1**, **2**, and **3**. The cathodic peak current of the waves decreases with cathodic shift upon addition of successive amounts of F^-. This decreasing peak current of the peak for all the receptors in the presence of F^- showed strong and perhaps electro-inactive complex formation between the receptor and F^-.[6]

In conclusion, receptors **1**, **2**, and **3** are easy-to-prepare and allow detection of F^- visually, optically, and electrochemically in DMSO at a concentration level of 10^{-5} M. Hence receptors **1**, **2**, and **3** can be used as fluoride ion colorimetric sensors.

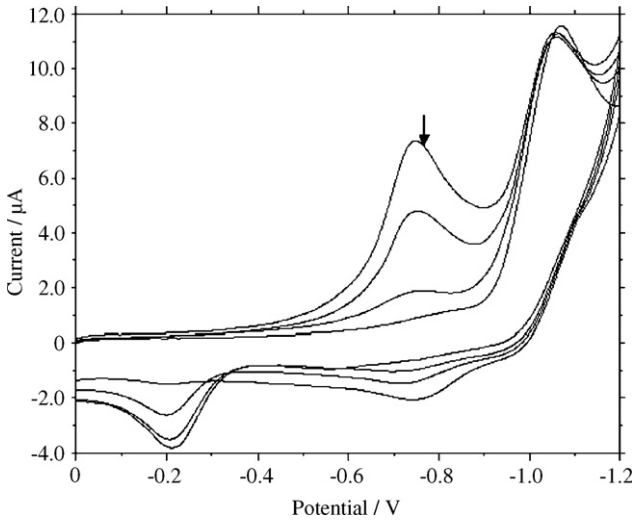

Figure 4. Changes in the redox properties of receptor **1** recorded in DMSO (5.0×10^{-5} M) upon addition of tetrabutylammonium fluoride.

Acknowledgements

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18. (a) *Selected data for receptor* **1**: $C_{21}H_{12}BrNO_3$: Yield: 70%. Mp: 230 °C. Elemental Anal. Calcd (%): C, 62.09; H, 2.98; N, 3.45. Found (%): C, 61.88; H, 3.21; N, 3.45. EI Mass (*m*/*z*): 407.1 $(M+2H)^+$; IR (KBr, *v* cm^{-1}): 3374, 1683, 1635. ^1H NMR (400 MHz, $(CD_3)_2SO$): δ 10.2 (s, 1H), δ 9.99 (t, 1H, $J = 9.16$ Hz), δ 8.28 (s, 1H), δ 8.14 (d, 1H, $J = 7.32$ Hz), δ 8.07 (d, 1H, $J = 7.32$ Hz), δ 7.8–7.6 (m, 2H) δ 7.59 (t, 1H, $J = 8.06$ Hz), δ 7.39 (s, 1H), δ 7.25 (d, 1H, $J = 8.28$ Hz), δ 7.2 (d, 1H, $J = 8.8$ Hz); ^{13}C NMR (100 MHz, $(CD_3)_2SO$): δ 110.11, 112.42, 115.25, 117.3, 118.58, 126.15, 126.23, 126.41, 127.17, 130.96, 132.33, 133.44, 134.02, 134.4, 135.58, 150.97, 154.70, 184.05.
(b) *Selected data for receptor* **2**: $C_{22}H_{15}NO_3$: Yield: 70%. Mp: 203 °C. Elemental Anal. Calcd (%): C, 77.41; H, 4.43; N, 4.10. Found (%): C, 77.61; H, 4.22; N, 4.03. EI Mass (*m*/*z*): 341.1 (M^+); IR (KBr, *v* cm^{-1}): 3370, 1674, 1639. ^1H NMR (400 MHz, $(CD_3)_2SO$): δ 9.9 (t, 1H, $J = 8.5$ Hz), δ 9.5 (s, 1H), δ 8.1 (s, 1H), δ 7.82–7.89 (m, 3H), 7.6 (t, 1H, $J = 8.4$ Hz), δ 7.45 (d, 1H, $J = 7.2$ Hz), δ 7.3 (d, 1H, $J =$ 8.6 Hz), δ 7.06 (s, 1H), δ 6.95 (d, 1H, $J = 8.2$ Hz), δ 6.79 (d, 1H, $J = 8$ Hz), δ 2.3 (s, 3H); ^{13}C NMR (100 MHz, $(CD_3)_2SO$): δ 43.1, 109.01, 111.22, 114.55, 115.3, 117.28, 124.32, 125.21, 125.41, 126.08, 129.52, 130.2, 132.51, 133.25, 133.44, 134.85, 149.68, 153.58, 182.80.
(c) *Selected data for receptor* **3**: $C_{21}H_{12}N_2O_5$: Yield: 72%. Mp: 220 °C. Elemental Anal. Calcd (%): C, 67.74; H, 3.25; N, 7.52. Found (%): C, 67.82; H, 3.01; N, 7.71. EI Mass (*m*/*z*): 372.1 (M^+); IR (KBr, *v* cm^{-1}): 3364, 1679, 1637. ^1H NMR (400 MHz, $(CD_3)_2SO$): δ 11.6 (s, 1H), δ 10.1 (t, 1H, $J = 8.8$ Hz),δ 8.3 (s, 1H), δ 8.19 (d, 1H, $J = 7.6$ Hz), δ 7.94 (s, 1H), δ 7.89–7.83 (m, 3H), δ 7.63 (t, 1H, $J = 7.6$ Hz), δ 7.55 (d, 1H, $J = 7.2$ Hz), δ 7.24 (d, 1H, $J =$ 8.4 Hz), δ 7.05 (d, 1H, $J = 9.2$ Hz); ^{13}C NMR (100 MHz, $(CD_3)_2SO$): δ 112.56, 115.39, 115.55, 118.47, 124.26, 125.82, 126.17, 126.35, 132.3, 133.42, 134.21, 134.27, 134.38, 135.57, 139.53, 150.88, 161.77, 184.12.
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