Supporting Information

Phenolic oxime based receptors for selective detection of fluoride

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A. Instrumentation and reagents:

Melting points were recorded on a JSCW melting point apparatus. Infrared spectra were recorded with a Nicolet Impact I-410 FT-IR spectrometer as KBr diluted discs. Elemental analysis was done by using Perkin Elmer PR 2400 series analyzer. The $^1$H NMR spectra (400 MHz) and $^{13}$C NMR spectra (100 MHz) were recorded on a ‘JEOL’ NMR spectrophotometer in DMSO-$d_6$ at room temperature. In NMR spectra, chemical shifts are reported in parts per million (ppm) downfield of Me$_4$Si (TMS) as internal standard. $^1$H NMR spectroscopy based titration studies were carried out on a Bruker Avance-400 MHz FT NMR spectrometer in CD$_3$CN. The diffraction data was obtained with a Bruker Smart APEX- II diffractometer with Mo-K$_\alpha$ rotating anode generator, and Smart CCD detector. Structures were solved and refined using SHELXL-97 with anisotropic displacement parameters for non-H atoms. The hydrogen atoms on O and N were located from the Fourier map in all of the crystal structures. All C–H atoms were fixed geometrically. Empirical absorption correction was done using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. A check of the final CIF file using PLATONS3 did not show any missed symmetry. UV-visible data were recorded with a Shimadzu UV-2450 spectrophotometer. CV measurements were performed on an electrochemical work station Sycopel AEW2-10 with an Ag/AgCl reference electrode, a platinum wire as a counter electrode.

$^1$H NMR spectroscopy based titration studies were carried out on a Bruker Avance-400 MHz FT NMR spectrometer in acetonitrile-$d_3$.

UV-visible titrations were carried out in dimethylsulphoxide solution. All tetrabutylammonium salts for NMR and UV-visible titration were purchased from Sigma-Aldrich® and used as such. All anions were used in the form of their tetrabutyl ammonium salts (fluoride as its trihydrate). The receptor solutions were titrated by adding known quantities of concentrated solution of the anions in question. The anion solutions used to effect the titrations contained the receptor at the same concentration as the receptor solutions into which they were being titrated so as to nullify the dilution effect.

All tetrabutylammonium salts for NMR and UV-visible titration were purchased from Sigma-Aldrich® and were directly used in the titration experiment.
B. Synthesis procedure

Synthesis of H1

\[
\begin{align*}
\text{O} & \xrightarrow{\text{NH}_2\text{NH}_2\text{H}_2\text{O}} \text{H}_2\text{N} & \xrightarrow{\text{HO} \text{CHO}} & \text{OH} \text{N} \xrightarrow{\text{N} \text{OH}} \\
\end{align*}
\]

*Step 1: Synthesis of Diacetyl monoxime hydrazine*

Diacetyl monoxime (500 mg, 4.94 mmol) was dissolved in 20 mL of CH\(_3\)OH and stirred for 10 minute. To the above solution, hydrazine hydrate (275 mg, 5.49 mmol) was added drop wise with constant stirring. The reaction is highly exothermic and results a hot orange solution from which white needle shaped crystals start separated within 10 minute. The reaction mixture was left in the air for 2 h. The crystals were filtered, washed with cold ethanol and dried in vacuum.

FT-IR (KBr): \( \tilde{\nu} = 3389(\text{m}), 3307(\text{m}), 3222(\text{s}), 3008(\text{w}), 2842(\text{w}), 1639(\text{w}), 1575(\text{m}), 1432(\text{m}), 1365(\text{s}), 1127(\text{w}), 1004(\text{m}). \)

*Step 2: Synthesis of H1*

A mixture of salicylaldehyde (122 mg, 1 mmol) and diacetyl monoxime hydrazone (115 mg, 1 mmol) was taken in a round bottom flask and dissolved in 50 mL ethanol. The solution was refluxed for 4 h with continuous stirring. The resultant solution was cooled to room temperature and filtered. The yellow coloured filtrate was kept undisturbed in a beaker for crystallization at room temperature. Yellow block shaped crystals were observed after 2 days at the bottom of the beaker. The solvent was decanted and the solid was dried in air which yield 127 mg of H1 as light yellow solid.

Yield: 127 mg (58% based on diacetyl monoxime hydrazone); m.p.: 122-124 °C; FT-IR (KBr, cm\(^{-1}\)): 3201(br), 3052(w), 1964(w), 1612(s), 1543(w), 1492(w), 1359(m), 1267(m), 1202(m), 1147(m), 1011(m), 941(m), 796(w), 750(m), 702(m), 649(w); \(^1\)H NMR (DMSO-\(d_6\), 400 MHz, \(\delta\) in ppm): 11.92 (s, 1H), 11.28 (s, 1H), 8.71 (s, 1H) 7.64 (d, \(J=7.32\) Hz, 1H), 7.35 (t, \(J=7.76\) Hz, 1H), 6.9 (m, 2H), 2.18 (s, 3H), 2.02 (s, 3H). \(^13\)C NMR (DMSO-\(d_6\), 100 MHz, \(\delta\) in ppm): 162.16,
156.78, 155.15, 131.33, 120.33, 40.22, 40.02, 39.81, 11.70, 9.85, 164.60, 161.23, 159.25, 155.24, 133.55, 131.71, 120.07, 118.96, 116.94, 13.48, 9.89. Elemental analysis % calculated for C_{11}H_{13}N_{3}O_{2}: C = 60.27, H = 5.98, N = 19.16; Found: C = 59.93, H = 5.99, N = 15.10. UV-vis: (\lambda_{\text{max}}, \text{nm}): 294, 338.

**Synthesis of compound H2:**

\[
\begin{align*}
\text{O} & \quad \text{COOC}_{2}\text{H}_5 \quad \text{NH}_{2}\text{NH}_{2}\text{H}_2\text{O} \\
\text{OH} & \quad \text{O} \quad \text{NH}_{2} \quad \text{N-O} \\
\text{H}_2 & \quad \text{N} \quad \text{N} \quad \text{OH}
\end{align*}
\]

*Step 1: Synthesis of 2-Hydroxybenzohydrazide*

A mixture of 16.6 g (0.1 mole) ethyl salicylate and 0.2 mole (10 mL) hydrazine hydrate were refluxed in 50 mL ethanol for 15 h. The resultant mixture was concentrated, cooled and poured into crushed ice. The solid mass thus separated out was filtered, dried and purified by recrystallization from ethanol.

*Step 2: Synthesis of H2*

Diacetylmonoxime (200 mg, 2 mmol) was dissolved in 30 mL of ethanol in a 100 mL round bottom flask. To the solution, 2-hydroxybenzohydrazide (300 mg, 2 mmol) was added and the solution was refluxed overnight with continuous stirring. The resultant solution was evaporated in vacuum which yield 367 mg H2 as white solid.

Yield: 78%; m.p.: 276.0-279.4 °C; FT-IR (KBr, cm\(^{-1}\)): 3283 (w), 3104 (br), 2717(m), 2575(m), 1927(w), 1811(w), 1651(s), 1547(s), 1495(w), 1452(s), 1373(s), 1299(s), 1227(s), 1150(s), 1101(w), 1023(m), 985(w), 944(s), 828(w), 745(s), 619(s), 565(m), 503(m), 456(m), 414(w); \(^1\)H NMR (DMSO-\(d_6\), 400 MHz, \(\delta\) in ppm): 11.69(s, 1H), 11.59(s, 1H), 11.28(s, 1H), 7.94-7.92 (d, J = 7.96 Hz, 1H), 7.73(s, 1H), 7.38-7.36 (d, J = 7.16 Hz, 1H), 6.98-6.92 (m, 1H), 2.22-2.12(d, J =39.68, 3H), 2.09-1.99 (d, J = 36.52, 3H); \(^{13}\)C NMR (DMSO-\(d_6\), 100 MHz, \(\delta\) in ppm) : 162.16, 156.78, 155.15, 131.33, 120.33, 40.22, 40.02, 39.81, 11.70, 9.85; Elemental analysis % calculated for C\(_{11}\)H\(_{13}\)N\(_3\)O\(_2\): C = 59.15, H = 5.87, N = 18.83; Found: C = 56.28, H = 5.22, N =17.77; UV-Vis : (\(\lambda_{\text{max}}\), nm): 280, 375.
**Figure S1:** FTIR spectrum of compound H1

**Figure S2:** FTIR spectrum of compound H2
Figure S3: $^1$H-NMR spectrum of compound H1.
Figure S4: $^{13}$C-NMR spectrum of compound H1.
Figure S5: $^1$H-NMR spectrum of compound H2.
Figure S6: $^{13}$C-NMR spectrum of compound H2.
**Figure S7:** ORTEP diagram of H1, with the displacement ellipsoid drawn at the 35% probability level. Crystal data: C$_{11}$H$_{13}$N$_{3}$O$_{2}$, \(a = 19.7074\) (7) Å, \(b = 4.4839\) (5) Å, \(c = 12.7541\) (5) Å, \(\alpha = \gamma = 90^\circ\), \(\beta = 107.994^\circ\) (2), \(V = 1071.91\) (8), \(T = 296\) K, Monoclinic, Space group P2(1)/n, \(z = 4\). Colour code: red: O, blue: N, grey ellipsoid: C, grey sphere: H.

**Figure S8:** POV ray picture of Hydrogen bonding pattern of H1 in solid state.
**Figure S9:** POV ray picture of packing pattern of H1 in solid state showing Herringbone packing pattern.

**Figure S10:** Two-dimensional fingerprint plots of H1 for Hirshfeld surfaces.
**Figure S11:** Naked eye view of the colour change while addition of different anions as its tetrabutyl ammonium salt to the solution of H1 in dimethyl sulphoxide.

**Figure S12:** UV-visible absorption spectra of H1 in dry DMSO (20 μM) after addition of 10 equiv. of different anions in the form of TBA salts.
**Figure S13:** UV-visible absorption spectra of H1 in dry DMSO (20 μM) after addition of 10 equiv. of different anions in the form of TBA salt solution in water.

**Figure S14:** UV-visible absorption spectra of H1 with sequential addition of different anions in the form of their tetra butyl ammonium salt; blue: H1 in DMSO, Pink: CN⁻ in H1 combined with other anions Green: F⁻ in H1 combined with other anions including CN⁻.
Figure S15: UV-visible absorption spectra of H1:F⁻ in dry DMSO with addition of different anions in the form of their tetra butyl ammonium salt; Black: H1 red: H1:F; Other spectra: H1:F⁻ in presence of other anions.

Figure S16: Evolution of UV-visible spectra of H1 (20 μM) in DMSO upon gradual addition of TBAF solution (14 mmol) in DMSO.
Figure S17: Intensity of the new 445 nm peak of H1 after addition of 10 equiv. of different anions in the form of their TBA salt.

Figure S18: UV-visible spectra of H2 (20 μM) in DMSO after addition of 10 equiv. of different anions in the form of TBA salt solution.
Figure S19: $^1$H NMR titration plot of H1 vs. tetrabutyl ammonium salt of different anions in CDCl$_3$. 
Figure S20: $^1$H NMR titration plot of H1 vs. tetrabutyl ammonium fluoride in DMSO-$d_6$.

Figure S21: Expanded view of $^1$H NMR titration plot of H1 vs. tetrabutyl ammonium fluoride in DMSO-$d_6$.

Figure S22: $^1$H NMR titration plot of H1 vs. tetrabutyl ammonium fluoride in acetonitrile-$d_3$. 
Figure S23: $^1$H NMR titration plot of H2 vs. tetrabutyl ammonium fluoride in DMSO-$d_6$. 
Figure S24: Expanded view of $^1$H NMR titration plot of H2 vs. tetrabutyl ammonium fluoride in DMSO-$d_6$.

Figure S24: Change in $^1$H NMR spectra of H2 after addition of TBAOH in DMSO-$d_6$.

Figure S25: CVs recorded in $n$-Bu$_4$NCIO$_4$/DMSO. Green: H1 with TBACIO$_4$ as electrolyte; Pink: H1 with TBAF as electrolyte; blue: H1.F$^-$ with TBACIO$_4$ as electrolyte.
Figure S26: CVs recorded in $n$-Bu$_4$NCIO$_4$/DMSO. Green: H$_2$ with TBACIO$_4$ as electrolyte; Pink: H$_2$ with TBAF as electrolyte; blue: H$_2$.F$^-$ with TBACIO$_4$ as electrolyte.
**Figure S27:** UV-visible spectra of H1 (20 μM) in DMSO (green) and UV-visible spectra of H2 after addition of TBAOH solution in methanol.

**Figure S28:** UV-visible spectra of H2 (20 μM) in DMSO (green) and UV-visible spectra of H2 after addition of TBAOH solution in methanol.

**Tab1 1:** Crystal data and refinement parameters of H1.

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<tr>
<th>Empirical formula</th>
<th>C_{11}H_{13}N_{3}O_{2}</th>
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<td>b = 4.4839(2) Å</td>
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<td></td>
<td>c = 12.7541(5) Å</td>
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Density (calculated)/Mgm$^{-3}$ 1.359
Absorption coefficient/mm$^{-1}$ none
F(000) 464
Crystal size/mm$^3$ 0.18 × 0.14 × 0.11
Theta range for data collection/º 1.09 to 26.18º
Index ranges -22 ≤ h ≤ 24, -5 ≤ k ≤ 5, -15 ≤ l ≤ 15
Reflections collected 14556
Independent reflections 2139 [ R(int) = 0.0536]
Completeness to θ = 26.18º 99.5%
Absorption correction none
Refinement method Full-matrix least-squares on F$^2$
Data/restraints/parameters 2139 / 0 / 156
Goodness-of-fit on F$^2$ 1.099
Final R indices [I > 2σ(I)] R$_1$ = 0.0606, wR$_2$ = 0.1784
R indices (all data) R$_1$ = 0.0734, wR$_2$ = 0.2028
Largest diff. Peak and hole /e Å$^{-3}$ 0.606 and -0.498