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1
2 Selective interactions of 5-(hydroxyimino)quinolin-8-one with tetrabutylammonium fluoride and
3 zinc(II) ions

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7 **Abstract:**

8 5-(hydroxyimino)quinolin-8-one (**HL**) selectively interacts with tetrabutylammonium fluoride to
9 form supramolecular adduct. Formation of supramolecular adduct in solution causes drastic
10 color change or causes quenching of fluorescence emission of **HL** enabling its distinction from
11 other tetrabutylammonium halides. Among different metal ions, addition of zinc ions to solution
12 of **HL** causes selective color change or well distinguishable fluorescence emission intensity
13 enhancement from other cations. Selective colouration of **HL** due to increase in absorption at
14 ~640 nm in acidic condition in a similar way upon addition of zinc or fluoride ions is attributed
15 to their ability to deprotonate **HL**. Di-aqua-bis(5-nitroso-8-oxyquinolinato)zinc(II) is
16 structurally characterized. It shows strong visible absorption at 718 nm, which differs from the
17 absorption of species formed in acidic condition by zinc causing visual color change.

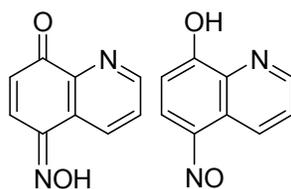
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19 **Introduction:**

20

21 Conventionally fluoride sensors are based on two principles, namely guest displacement of a
22 chromogenic receptor by fluoride ions or by specific reactions between chromogenic hosts with
23 fluoride ions to cause color changes.¹ Chelation induced optical properties of a metal complex
24 can help to design as receptors for fluoride ions.^{1c} These leave scopes to develop simple
25 chromogenic or fluorogenic metal complexes for detection and estimation of fluoride ions.¹
26 Structurally simple oxy-quinolate metal complexes are in use to detect fluoride ions.² Uses of
27 such complexes would reduce complicity involved in multi step syntheses of sensor molecules
28 for fluoride ions.³ On the other hand, hydroxyquinoline derivatives form zinc complexes
29 selectively which have potential application in biology.⁴ Utility of zinc oxyquinolate
30 complexes are not demonstrated for fluoride detection.⁵ With such a background, we explore the

31 ability of 5-(hydroxyimino)quinolin-8-one (**HL**) for selective anion and cation binding.
32 Compound **HL** is chosen as it may adopt keto and enol form (Figure 1); of which latter
33 represents a hydroxyquinoline skeleton. On the other hand, oximes have ability to senses fluoride
34 ions⁶ and fluoride ions can deprotonate hydroxy group⁷. Hence these effects are anticipated to be
35 operative with **HL** to cause changes in optical properties. On the other hand ability to coordinate
36 to zinc ions overall effect may be either cooperative or counterproductive in fluoride detection.
37 To understand such facts, we studied interactions and optical properties changes on **HL** and its
38 zinc complex on interaction with fluoride ions.

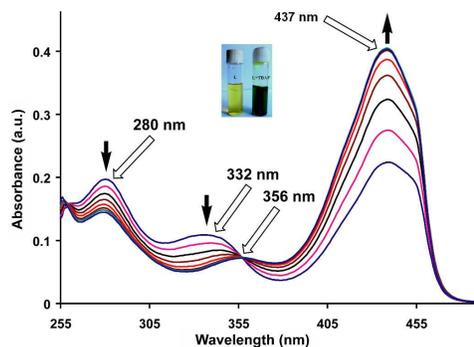


39
40 Figure 1: Keto and enol forms of 5-(hydroxyimino)quinolin-8-one.

41 **Results and discussion:**

42 An intense green coloration of a solution of **HL** in dimethylsulphoxide (DMSO) occurs on
43 addition of tetrabutylammonium fluoride (TBAF). This change is very specific to
44 tetrabutylammonium fluoride and not caused by other tetrabutylammonium salts such as
45 chloride, bromide, iodide, perchlorate, nitrate or bisulphate. Hence it enables selective visual
46 detection of fluoride ions. Similar color change of a solution of **HL** in DMSO can also be brought
47 about by other fluoride salts such as ammonium fluoride or sodium fluoride but not by other
48 halides with similar cations. Color change is prominently reflected in increase in visible
49 absorption at 437 nm of **HL** with a growth of a new absorption peak at 640 nm (Figure 2a, 2b).
50 From such changes fluoride ions can be detected in the range of 10^{-2} mol/L to 10^{-7} mol/L which
51 is comparable to the detection limit of conventional fluoride ions sensors such as zirconium-
52 oxyquinolate^{8a-b}. Enhancement of intensity of absorption at 437 nm is associated with formation
53 of an isobestic point at 356 nm, suggesting one to one transformation of **HL** to a colored species
54 in solution. Acetate ions generally interfere in detection of fluoride ions,^{1d} we also find a similar
55 interference of ammonium acetate. Similarity in visible spectra of **HL** by acetate or fluoride ions,
56 suggests a deprotonation of **HL** in solution by these ions. Color change of **HL** by fluoride ions

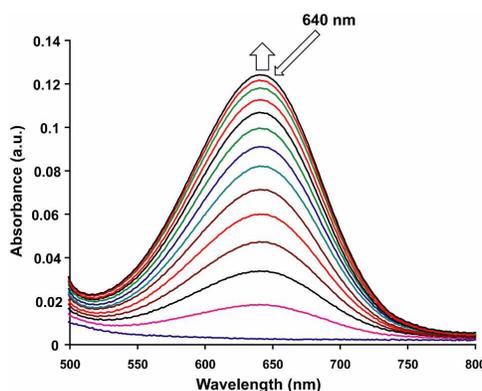
57 are effectively visible by naked eyes at pH 4 or 7, however, compound **HL** turns dark green at
 58 pH 9, which disables detection of fluoride ions (supporting figures S1-S3).



59

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(a)



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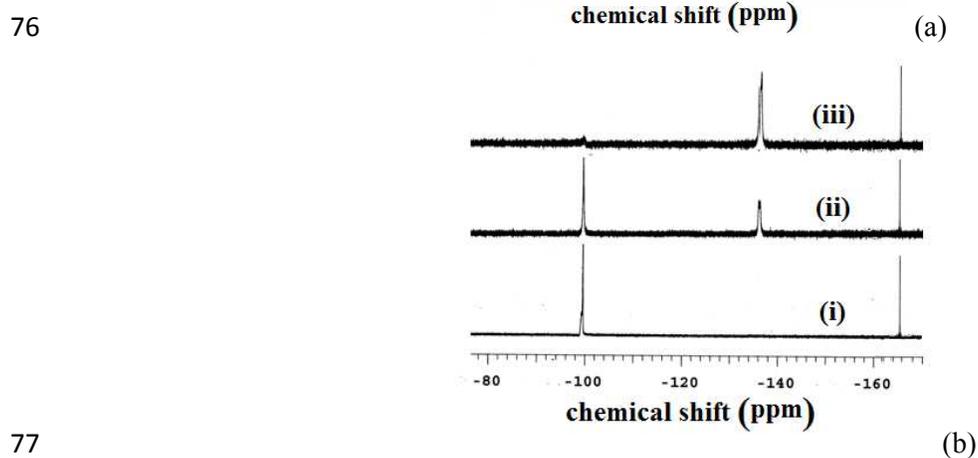
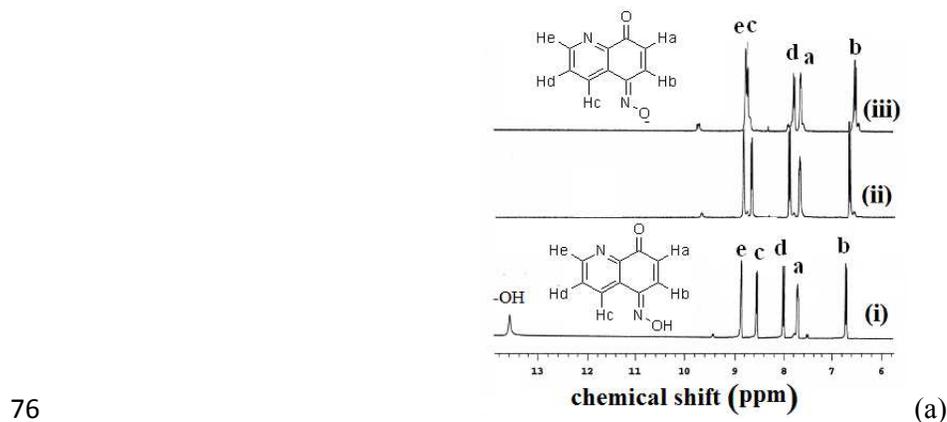
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(b)

63 Figure 2: (a) Changes in UV-visible spectra of compound **HL** (10^{-5} mol/L in DMSO) on addition
 64 of TBAF 250 nm - 500 nm region (0.1 equiv. from TBAF 10^{-4} mol/L stock solution to 1 equiv.
 65 of **HL** in aliquots) and inset is photographs of a solution of **HL** in absence and presence of
 66 TBAF) and (b) Changes in absorption in 500 nm - 800 nm region of **HL** (10^{-4} mol/L in DMSO)
 67 on addition of TBAF.

68 This is reflected in the ^1H -NMR spectroscopic titration of **HL** with TBAF. A comparison of
 69 signals appearing in ^1H -NMR spectrum at aromatic region from solution of **HL** with or without
 70 TBAF is shown in figure 3a. Signals appearing in aliphatic region (1-3 ppm) from $-\text{CH}_2-$ and $-\text{CH}_3$
 71 groups of tetrabutylammonium cations remain invariant. $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of **HL**
 72 shows a carbonyl peak at 183.4 ppm supports a keto form. ^1H -NMR signal of OH at 13.4 ppm
 73 disappears on addition of TBAF, which suggests deprotonation of **HL**. The peak designated at

74 H_c is in close proximity of the -ve charge of oximate, hence it is affected and chemical shift
 75 moves downfield.



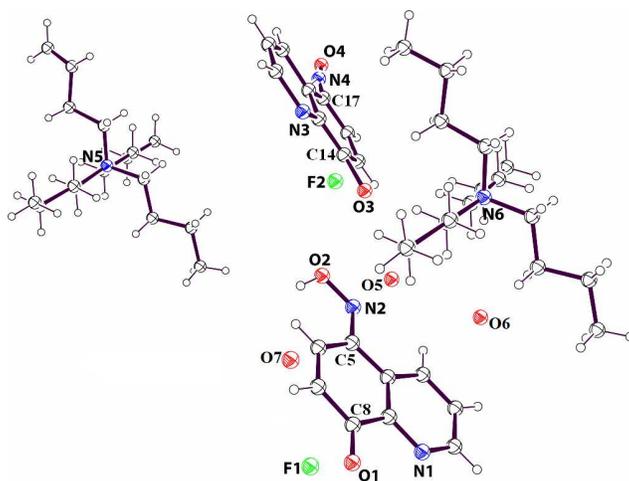
78 Figure 3: (a) ¹H-NMR spectra in region of 6 ppm to 14 ppm obtained during titration of **HL**
 79 (DMSO-d₆) with TBAF: (i) **HL**, (ii) **HL** with 0.25-equivalent of TBAF and (iii) **HL** with 0.5
 80 equivalent of TBAF. (b) ¹⁹F-NMR spectra in region of -80 ppm to -170 ppm of a solution of (i)
 81 TBAF (DMSO-d₆) and (ii-iii) TBAF by adding 0.5-equivalent and 1-equivalent of **HL** (reference
 82 C₆F₆ at -164.9 ppm).

83
 84 A ¹H-NMR titration was performed by adding triethylamine to a solution of **HL** in DMSO-d₆;
 85 which also showed disappearance OH signal at 13.4 ppm (Figure S4). Since identical color
 86 change caused by fluoride ions to a solution of **HL** was also observed by adding triethylamine or
 87 a base to a solution of **HL**, hence interactions of these ions with **HL** is similar. In ¹⁹F-NMR
 88 TBAF showed a signal at -98.1 ppm, this signal disappeared on addition of **HL** and a new peak
 89 at -134.6 ppm appeared (Figure 3b). On the other hand, reported ¹⁹F-NMR chemical shift for

90 hydrofluoric acid in different solvents were different.¹¹ Hence, the signal observed at -134.6 ppm
 91 is attributed to hydrogen fluoride formed in situ.

92 A solution of **HL** shows a fluorescence emission peak at 556 nm ($\lambda_{\text{ex}} = 475$ nm). Fluoride ions
 93 cause quenching of this fluorescence emission of **HL** but other anions donot cause such
 94 quenching (Figure S5-S9). The fluorescence quenching is due to internal charge transfer between
 95 fluoride and the ligand, which commonly causes by fluoride ions.^{1b} Binding constant of fluoride
 96 ion with **HL** is calculated as $2.66 \times 10^5 \text{ mol}^{-1}\text{L}$ by Benesi-Hildebrand equation from absorption
 97 changes caused by TBAF.

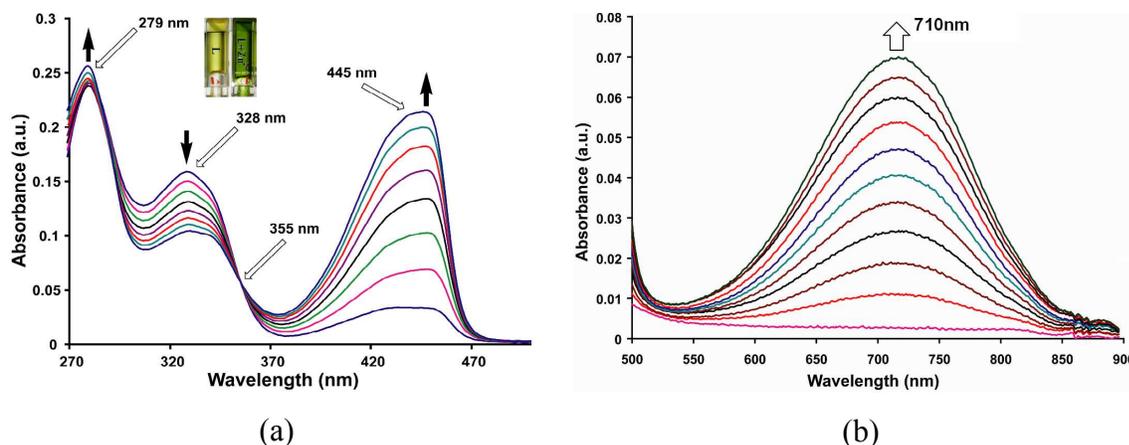
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99

100 Figure 4: Structure of supramolecular adduct **HL.TBAF.1.5H₂O** (Drawn with 35% thermal
 101 ellipsoid). Some relevant bond lengths are O1-C8 = 1.24 Å, C5-N2 = 1.35 Å, O2-N2 = 1.28 Å,
 102 O3-C14 = 1.38 Å, C17-N4 = 1.38 Å, N4-O4 = 1.20 Å.

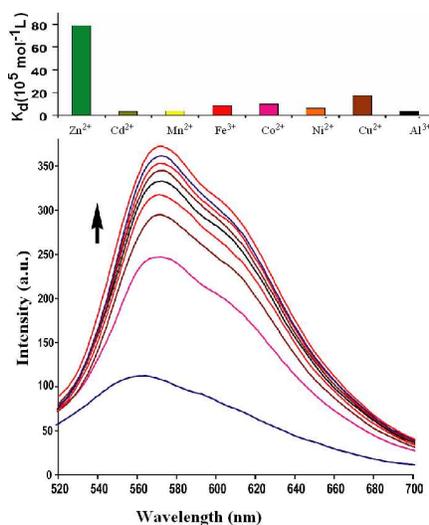
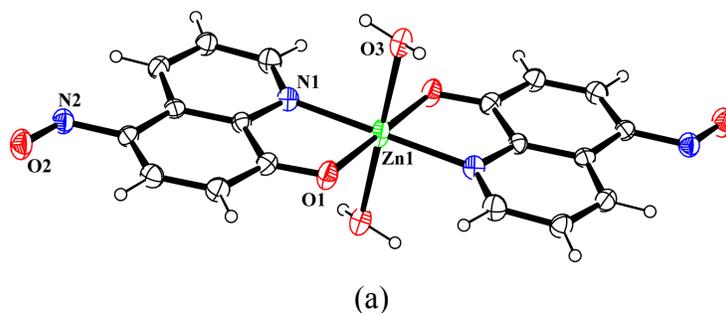
103 A supramolecular 1:1 adduct of **HL** with TBAF in ratio, and having a water molecule as solvent
 104 of crystallization is structurally characterized (Figure 4). Asymmetric unit of the supramolecular
 105 adduct has two molecules each of **HL** and TBAF which are symmetry independent. Both the
 106 symmetry independent **HL** molecules are in keto-forms. One of the **HL** is crystallographically
 107 disordered. The C8-O1 bond distance is 1.24Å, it suggest it to be a C=O bond, supporting a keto
 108 form. On the other hand, C5-N2 bond distance is 1.35 Å which is supportive of a conjugated
 109 C=N bond. Comparing the structure with the reported structure of 5-(hydroxyimino)quinolin-8-
 110 one^{9a} and its salts^{9b} it is found to be consistent with a keto-form.



111 Figure 5: (a) Changes in the UV-visible absorption spectra of **HL** (10^{-5} mol/L in methanol) on
 112 addition of Zn^{2+} in 0.1 equiv to 0.7 equiv (10^{-4} mol/L in methanol). Inset is the photographs of a
 113 methanol solution containing **HL** and a solution of zinc ions and **HL**. (b) Increase in absorbance
 114 at 710 nm on addition of zinc chloride (10^{-3} mol/L in methanol, 10 μ l in each aliquot) to a
 115 solution of **HL** (10^{-4} mol/L in methanol).

116 When zinc chloride was added to a solution of **HL** in methanol, intensity of absorptions
 117 at 445 nm increases (Figure 5a) and a new visible absorption at 710 nm is observed (Figure 5b).
 118 Other metal chloride salts such as Mn^{2+} , Cd^{2+} , Fe^{2+} , Cu^{2+} , Ni^{2+} , Al^{3+} etc. cause insignificant
 119 changes in visible spectra of **HL** (Figures S10-S14). Job's plot shows formation of a zinc
 120 complex with 1 : 2 metal to ligand ratio (Figure S15). Complex formed in solution crystallizes
 121 as di-aqua-bis(5-nitroso-8-oxyquinolino)zinc(II) is characterized by determining crystal
 122 structure (Figure 6a). Complex has a distorted octahedral geometry with two apical positions
 123 occupied by two aqua ligands. Irrespective of metal to ligand ratio used in the reaction this zinc
 124 complex could be obtained, however this complex redissolved in DMSO solution dissociates
 125 giving double the number of peaks of parent ligand in 1H -NMR spectra. Observation of isobestic
 126 point in visible spectroscopic titration of zinc ions with **HL** showing increase in absorbance at
 127 710 nm suggests this complex to be a contributing factor to color change. However, the
 128 absorbance observed at pH = 4 by addition of zinc chloride to a solution of **HL** shows
 129 absorption increase at ~ 620 nm which is similar to the change caused by fluoride ions at this pH
 130 (Figure S16). But such an absorption is not observed at pH = 7. It may be mentioned that the
 131 acetate ions at pH = 4 causes very small change in coloration at 620 nm, hence these results
 132 indicate the fluoride and zinc to be special to deprotonate **HL** at mild acidic pH. It may be noted

133 that the reaction of 8-hydroxyquinoline with zinc chloride is highly solvent dependent, it can
 134 result in tetranuclear cluster¹⁰ or it can result in complexes of [ZnCl₄] along with zinc
 135 hydroxide^{10b}. In the present case the solution of the zinc complex in DMSO shows nine NMR
 136 signals in aromatic region in contrast to the five signals of the parent compound (Figure S17).
 137 This supports instability on redissolution in DMSO. Ligand dissociation from the complex is
 138 confirmed by ¹H-NMR titration of the complex by adding **HL** externally.
 139



140 Figure 6: (a) Structure of di-aqua-bis(5-nitroso-8-oxyquinolinato)zinc (II) (thermal ellipsoids are
 141 30% probability). Selected bond distances, Zn1-N1, 2.075(3)Å; Zn1-O1, 2.105(2)Å; Zn1-O3,
 142 2.207(3)Å and bond angles, N1-Zn1-O1, 100.07(9)°; N1-Zn1-O3, 89.71(10)°. (b) Top is a bar
 143 graph showing binding constants of **HL** with different metal ions and bottom is change in
 144 fluorescence emission of **HL** ($\lambda_{\text{ex}} = 475 \text{ nm}$; 10^{-4} mol/L in methanol) on addition of zinc chloride
 145 (in $10 \mu\text{L}$ from 10^{-3} mol/L in methanol in each aliquot).

146 Di-aqua-*bis*(5-nitroso-8-oxyquinolinato)zinc(II) complex reacts with TBAF, which
147 changes its visible absorption by shifting it from 718 nm to 676 nm through an isobestic point at
148 660 nm (Figure S18). This happens due to replacement of **L** by fluoride ions. Addition of zinc(II)
149 chloride to a solution of **HL** in presence of TBAF shifts absorption peak at 640 nm to 710 nm
150 (Figure S19) and absorption at 710 nm of a solution of **HL** with zinc chloride (Figure S20)
151 increases on addition of TBAF. Thus the zinc complex can be constructed or dislodged by
152 adequate concentration of fluoride and **HL**. Other tetrabutylammonium salt such as chloride,
153 bromide, perchlorate or nitrate does not change visible spectra of the complex at these pHs.

154 Chelation induced changes of fluorescence emission of **HL** is observed in presence of
155 various metal ions. Fluorescence titrations of **HL** with zinc(II) [figure 6b (bottom)], cadmium(II)
156 or aluminium(III) chloride in methanol show increase in fluorescence emission intensity (Figures
157 S21-S22). Whereas, addition of metal chloride of paramagnetic ions such as Mn^{2+} , Fe^{2+} , Co^{2+} ,
158 Ni^{2+} or Cu^{2+} quench fluorescence emission. Metal ions such as Na^+ , K^+ , Be^{2+} , Mg^{2+} , Ca^{2+} or In^{3+}
159 shows insignificant changes in emission spectra of **HL** (Figures S23-S27). Binding constants of
160 **HL** with metal ions are in order of $\text{Zn}^{2+} \gg \text{Cu}^{2+} > \text{Co}^{2+} > \text{Fe}^{2+} > \text{Ni}^{2+} > \text{Mn}^{2+} > \text{Cd}^{2+} > \text{Al}^{3+}$.
161 Relative binding constants are illustrated in a bar diagram shown on top of figure 6b. Zinc ions
162 have highest binding constant $78.7 \times 10^5 \text{ mol}^{-1}\text{L}$ relative to other metal ions. Among the
163 quenchers, Cu^{2+} ions are most effective and have a binding constant $17.45 \times 10^5 \text{ mol}^{-1}\text{L}$.
164 Paramagnetic Cu^{2+} ions generally causes quenching of fluorescence.¹² On the other hand, zinc
165 ions have higher binding ability to **HL** than binding ability of **HL** with fluoride ions. Despite of
166 this fact fluoride ions replace **HL** from zinc complex, this is attributed to higher electro-
167 negativity of fluoride.

168 In conclusions supramolecular adduct of 5-(hydroxyimino)quinolin-8-one with fluoride ion and
169 a mononuclear complexes of zinc are isolated and characterized. Fluoride ions could be visually
170 distinguished from numbers of anions at slightly acidic pH. Fluoride as well as acetate ions
171 quench fluorescence emission of **HL** which distinguishes them from other common neutral
172 anions. Several cations can enhance intensity of fluorescence emission of **HL** independently but
173 zinc ions are special to show sharp enhancement of fluorescence intensity. Several metal ions
174 bring about quenching of fluorescence which enables zinc ions to be distinguished from other

175 cations. Similarity between fluoride ions and zinc ions in showing color change in acidic
176 condition makes **HL** it an unique example.

177 **Experimental:**

178 Infrared spectra (KBr pellets) of solid samples were recorded in the region 4000-400 cm^{-1} on a
179 Perkin-Elmer Spectrum-One FT-IR spectrophotometer. UV-visible spectra were recorded on a
180 Perkin-Elmer-Lambda 750 UV-visible spectrometer at room temperature. Mass spectra were
181 recorded on a micro mass Q-TOF (waters) mass spectrometer by using an acetonitrile / formic
182 acid matrix. Fluorescence emission spectra were recorded on a Perkin-Elmer LS-55
183 spectrofluorimeter by taking definite amount of each sample and exciting at required
184 wavelength.

185 5-(hydroxyimino)quinolin-8-one was prepared by slightly modifying reported procedure¹³
186 provided in supporting information.

187 Synthesis of di-aqua-bis(5-nitroso-8-oxyquinolinato)zinc (II): To a solution of 5-
188 (hydroxyimino)quinolin-8-one (0.348 g, 1mmol) in methanol, anhydrous zinc chloride (0.137 g,
189 1 mmol) was added and stirred for half an hour. A green precipitate obtained was filtered and
190 redissolved in dimethylformamide. Solution on standing for one week resulted dark green
191 crystals of the zinc complex. Isolated yield: 95 %. IR (KBr, cm^{-1}): 3204 (w), 1605 (s), 1577 (m),
192 1549 (s), 1529 (s), 1493 (m), 1444(w), 1411(w), 1375 (w), 1357 (w), 1305 (m), 1277 (s), 1244
193 (s), 1148 (s), 1106 (w) 1065 (w), 1027 (w), 819 (w), 796 (w), 741 (w), 692 (w), 502 (w), 473
194 (w). Elemental analysis calcd for $\text{C}_{18}\text{H}_{14}\text{N}_4\text{O}_6\text{Zn}$, C, 48.25 %; H, 3.15%; N, 12.51 %; Found C,
195 48.21%, H, 3.33%, N, 12.86 %. Crystallographic parameters: Crystal system, Triclinic; Space
196 group, *P*-1; Temperature, 296(2)K; Wavelength, 0.71073 Å; *a*, 7.2755(9) Å; *b*, 7.9392(9) Å; *c*,
197 8.4103(9)Å; α , 64.840(11)°; β , 74.394(10)°; γ , 87.012(10)°; V, 422.41(8) Å³; Z = 1, Density,
198 1.760 gcm^{-3} ; Abs. Coeff., 1.503 mm^{-1} ; Abs. Correction, multi-scan; F(000), 228; Total Nos. of
199 reflections, 1533; Reflections $I > 2\sigma(I)$, 1297; Max. 2θ , 50.50°; Ranges (h, k, l) $-8 \leq h \leq 8$, -8
200 $\leq k \leq 9$, $-8 \leq l \leq 10$; Completeness to 2θ , 99.8 %; Refinement method, Full-matrix least-
201 squares on F^2 ; Data/ restraints/parameters, 2304 / 0 / 199; Goof (F^2), 0.924; R indices [$I >$
202 $2\sigma(I)$], 0.0417; R indices (all data), 0.0539.

203 Supramolecular adduct of TBAF with **HL** was prepared by slow evaporation of a solution of
204 TBAF and **HL** in 1 : 1 molar ratio in dimethylsulphoxide. Few blue crystals could be obtained

205 after 3 weeks. ¹H-NMR (DMSO-d₆, ppm): 8.78 (d, *J* = 8.0 Hz, 2H), 7.82 (d, *J* = 8.4 Hz, 1H),
206 7.67(t, *J* = 4.4 Hz, 1H), 6.55 (d, *J* = 10.4 Hz, 1H), 3.16 (t, *J* = 8.4 Hz, 8H), 1.56 (m, 8H), 1.31
207 (m, 8H), 0.92 (t, *J* = 7.6 Hz, 12H). ¹³C-NMR (DMSO-d₆, ppm): 182.7, 149.7, 146.8, 143.6,
208 131.6, 130.2, 127.5, 126.22, 122.9, 57.5, 23.1, 19.2, 13.4. IR (KBr, cm⁻¹): 3442 (w), 1603 (s),
209 1573 (m), 1529 (s), 1488 (m), 1466(w), 1380 (w), 1303 (w), 1129 (m), 1277 (s), 1105 (w), 1065
210 (w), 796 (w), 737 (w). Elemental anal calcd for C₉H₆N₂O₂·C₁₆H₃₆NF·H₂O, C, 66.19; H, 9.78;
211 N, 9.26; found C, 65.98; H, 9.76; N, 9.12. Formula, C₅₀H₈₂F₂N₆O₇; Mol. Wt. 917.22; Crystal
212 system, Monoclinic; Space group, *P*2₁/*c*; Temperature, 296(2)K; Wavelength, 0.71073 Å; *a*,
213 22.5699(14)Å; *b*, 9.4519(7) Å; *c*, 26.9700(17) Å; α, 90.00°; β, 104.307(3)°; γ, 90.00°; *V*,
214 5575.0(6) Å³; *Z* = 4, Density, 1.093 gcm⁻³; Abs. Coeff., 0.077 mm⁻¹; Abs. Correction, Multi-
215 scan; F(000), 1992; Total Nos. of reflections, 9788; Reflections *I* > 2σ(*I*), 5798; Max. 2θ, 50.00°;
216 Ranges (h, k, l) -26 ≤ h ≤ 26, -11 ≤ k ≤ 11, -32 ≤ l ≤ 32; Completeness to 2θ, 99.8 %;
217 Refinement method, Full-matrix least-squares on *F*²; Data/ restraints/parameters, 9788 / 18 /
218 583; Goof (*F*²), 1.351; R indices [*I* > 2σ(*I*)], 0.0988; R indices (all data), 0.2106.

219 Measurement of absorption or emission: Respective solution of tetrabutylammonium salt or of
220 metal chloride was prepared in methanol or DMSO. These solutions were independently titrated
221 with solution of **HL** (3ml, 10⁻⁵ mol/L) taken in quartz cuvette. Titrations were done by adding
222 desired amount of solution of salts with the aid of a microliter syringe in aliquots and recording
223 the UV-visible or fluorescence emission spectra after each addition.

224 **Supporting information:**

225 Crystallographic information files of supramolecular adduct and zinc complex have CCDC Nos.
226 1024294 and 983710 respectively. Synthetic procedure of **HL**, ¹H-NMR titration of **HL** with
227 zinc salt, various fluorescence and visible spectroscopic titrations are available.

228 **Acknowledgments:**

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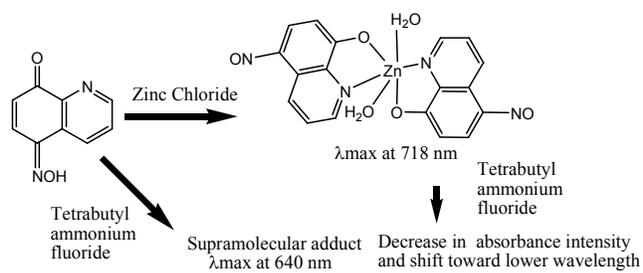
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291 Table of content entry:

292 Selective interactions of 5-(hydroxyimino)quinolin-8-one with tetrabutylammonium fluoride and
293 zinc(II) ions



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295 Zinc ions or fluoride ions can be selectively detected by 5-(hydroxyimino)quinolin-8-one at mild
296 acidic condition

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