

Supporting Information

Rapid and Ratiometric detection of hypochlorite with real application in tap water : molecules to low cost devices (TLC sticks)

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1. General:

The chemicals and solvents were purchased from Sigma-Aldrich Chemicals Private Limited and were used without further purification. Melting points were determined on a hot-plate melting point apparatus in an open-mouth capillary and were uncorrected. ^1H -NMR and ^{13}C -NMR spectra were recorded on 300 MHz and 100 MHz instruments respectively. For NMR spectra, CDCl_3 was used as solvent with TMS as an internal standard. Chemical shifts are expressed in δ unit and ^1H - ^1H Hz. Fluorescence experiment was done using PTI fluorescence spectrophotometer with a fluorescence cell of 10 mm path.

2. General method of fluorescence titrations:

By fluorescence method:

For fluorescence titrations, stock solution of the sensor was prepared ($c = 2 \times 10^{-5} \text{ ML}^{-1}$) in $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ (6:4, v/v). The solution of the guest anion was prepared ($2 \times 10^{-5} \text{ ML}^{-1}$) in $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ (6:4, v/v) at pH 7.4 by using 10 mM HEPES buffer. The original volume of the receptor solution is 2 ml. Solutions of the sensor of various concentrations and increasing concentrations of cations, anions and amine containing compounds were prepared separately. The spectra of these solutions were recorded by means of fluorescence methods.

3. Method for the preparation of TLC plate sticks:

It was easily prepared by immersing a TLC plate into the solution of DPNO ($2 \times 10^{-3} \text{ M}$) in CH_3CN and then exposing it to air to evaporate the solvent. The detection of hypochlorite was carried out by inserting the TLC plate to the solution of various concentrations of NaOCl (from $2 \times 10^{-5} \text{ M}$ to 2×10^{-2}) in water and evaporating solvent to dryness. Finally, under UV light the fluorescence was checked.

4. Experimental Procedure:

Synthesis of receptor 1-(2,3-dihydro-1H-perimidin-2-yl)naphthalen-2-ol (DPNO): Under an atmosphere of dry nitrogen, 1,8- diamionaphthalene (320 mg, 2.02 mmol) and 2-hydroxynaphthalene aldehyde (350 mg, 2.03 mmol) are refluxed overnight to produce the receptor, DPNO in absolute ethanol (20 mL). Then, the resultant mixture was cooled to room temperature and the solvent was removed under reduced pressure. The resultant residue was

purified by silica gel column chromatography using dichloromethane as eluent to afford the product as a reddish-yellow solid (300 mg, 46%).

¹H NMR (CDCl₃, 300 MHz) δ (ppm): 9.708 (s, 1H), 7.873 (dd, 2H, J = 19.2 Hz), 7.487 (t, 2H, J = 5.7 Hz), 7.359 (m, 4H), 6.657 (dd, 2H, J = 1.3 Hz), 6.482 (s, 1H), 4.773 (s, 1H), 3.253 (s, 1H).

¹³C NMR (CDCl₃, 100 MHz) δ (ppm): 157.67, 140.22, 134.48, 130.00, 128.93, 127.50, 122.33, 120.04, 118.33, 113.71, 112.11, 108.12, 65.08.

MS (ESI MS): (m/z, %): 313.12 [(DPNO+H⁺), 100 %]

Elemental analysis: C= 80.74%, H= 5.18%, N= 8.94%. (calculated value : C= 80.75%, H= 5.16%, N= 8.97%)

Synthesis 1-(1H-perimidin-2-yl) naphthalene-2-ol (HPNO): DPNO is mixed with two equivalents of NaOCl solution at room temperature for 10 minutes to give a colorless solution. On removing the solvent a solid product was obtained which was used for ¹H-NMR, Elemental analysis and MASS spectroscopy.

¹H NMR (CDCl₃, 300 MHz) δ (ppm): 9.822 (s, 1H), 8.161 (d, 1H, J = 9.9 Hz), 8.087 (t, 2H, J = 3.7 Hz), 7.838 (t, 2H, J = 4.2 Hz), 7.395 (t, 2H, J = 5.5 Hz), 7.328 (s, 1H), 7.007 (d, 2H, J = 1.2 Hz), 6.702 (d, 1H, J = 1.5 Hz), 5.105 (s, 1H).

¹³C NMR (CDCl₃, 100 MHz) δ (ppm): 159.11, 156.77, 144.52, 137.21, 135.58, 132.50, 128.93, 127.50, 122.33, 120.04, 118.33, 114.71, 113.11, 110.11.

MS (ESI MS): (m/z, %): 311.14 [(HPNO+H⁺), 100 %]

Elemental analysis: C= 81.2335%, H= 4.53%, N= 9.07%. (calculated value : C= 81.27%, H= 4.55%, N= 9.03%).

5. Determination of fluorescence quantum yield:

Here, the quantum yield φ was measured by using the following equation,

$$\phi_x = \phi_s (F_x / F_s)(A_s / A_x)(n_x^2 / n_s^2)$$

Where,

X & S indicate the unknown and standard solution respectively, φ = quantum yield,

F = area under the emission curve, A = absorbance at the excitation wave length,

n = index of refraction of the solvent. Here φ measurements were performed using anthracene in ethanol as standard [φ = 0.27] (error ~ 10%).

The quantum yield of **DPNO** itself is 0.01 which changes into 0.35.

6. Calculation of the detection limit:

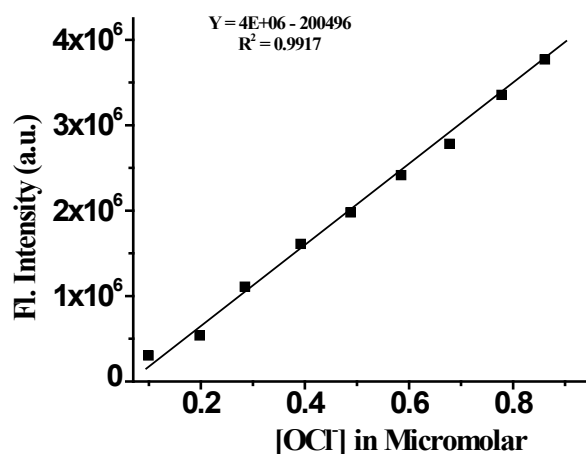


Figure S1: Fl. Intensity Vs. Conc. of OCl⁻ at 430 nm.

The detection limit DL of **DPNO** for OCl⁻ was determined from the following equation³:

$$DL = K * Sb1/S$$

Where K = 2 or 3 (we take 2 in this case); Sb1 is the standard deviation of the blank solution; S is the slope of the calibration curve.

From the graph we get slope = 4E + 06, and Sb1 value is 113650.3003.

Thus using the formula we get the Detection Limit = 0.056 μM i.e. DPNO can detect OCl⁻ in this ppm level.

7. Calculation of rate constant:

From the time vs. Fl. Intensity vs. time (sec.) plot at fixed wavelength (413nm) using first order rate equation (Figure S5), we get rate constant $K = \text{slope} \times 2.303 = 0.0142 \times 2.303 = 3.2 \times 10^{-2} \text{ sec}^{-1}$

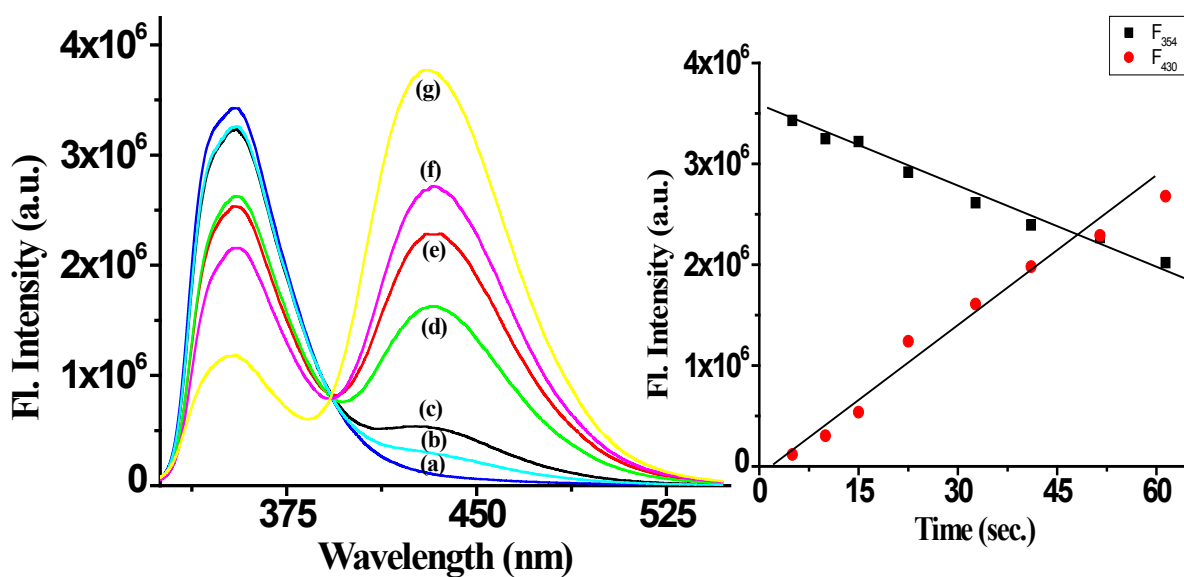


Figure S2: The time vs. fluorescence intensity spectra of (a) DPNO ($c = 2.0 \times 10^{-5}$ M) in presence of 1 equiv. OCl^- ($c = 2.0 \times 10^{-5}$ M) at pH 7.1 in $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ (6:4, V/V) at different time [(b) 10 (c) 20 (d) 30 (e) 40 (f) 50 (g) 60 sec].

8. Fluorescence responses of DPNO to OCl^- + various metal ions and anions:

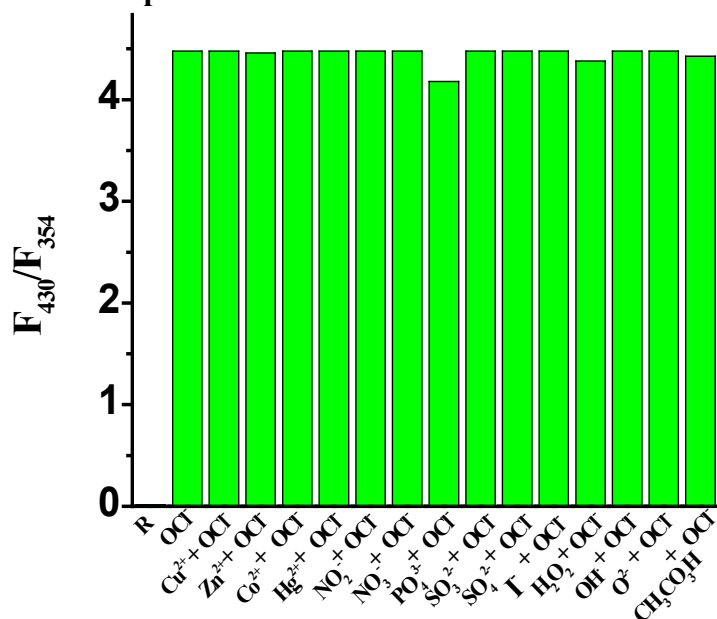
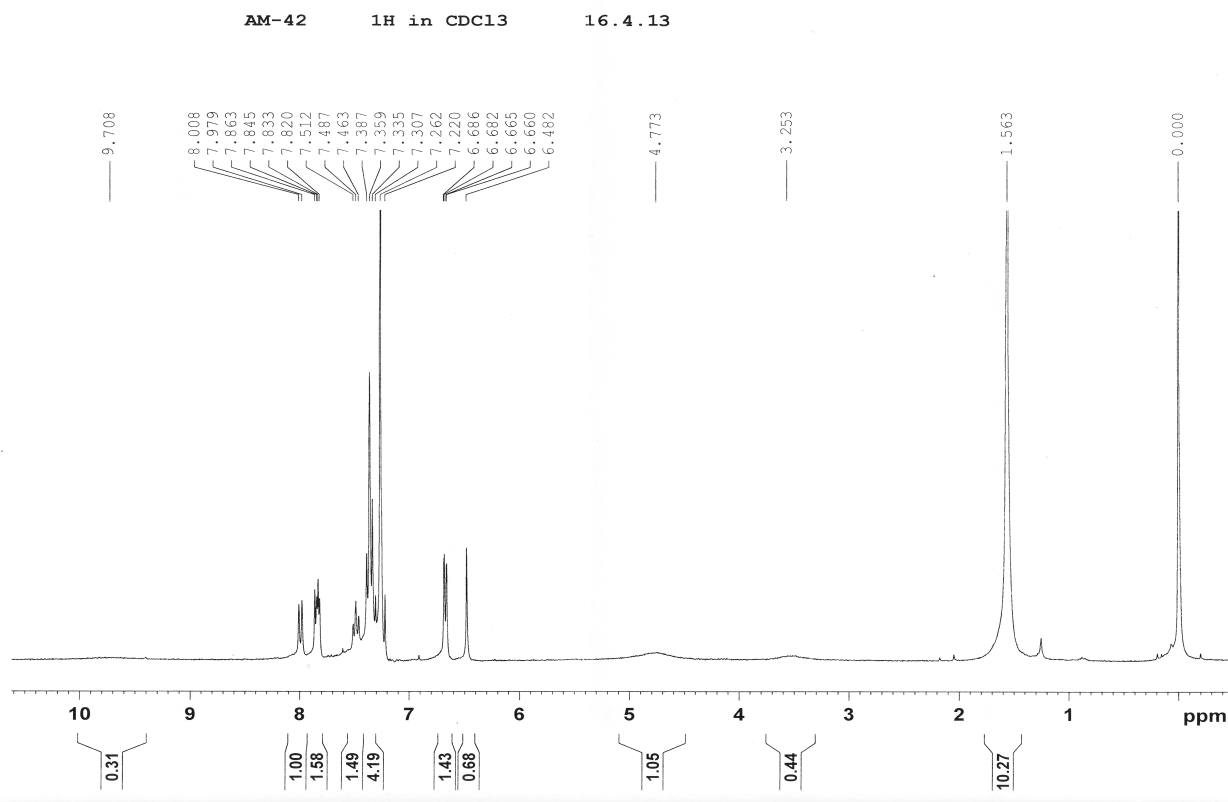
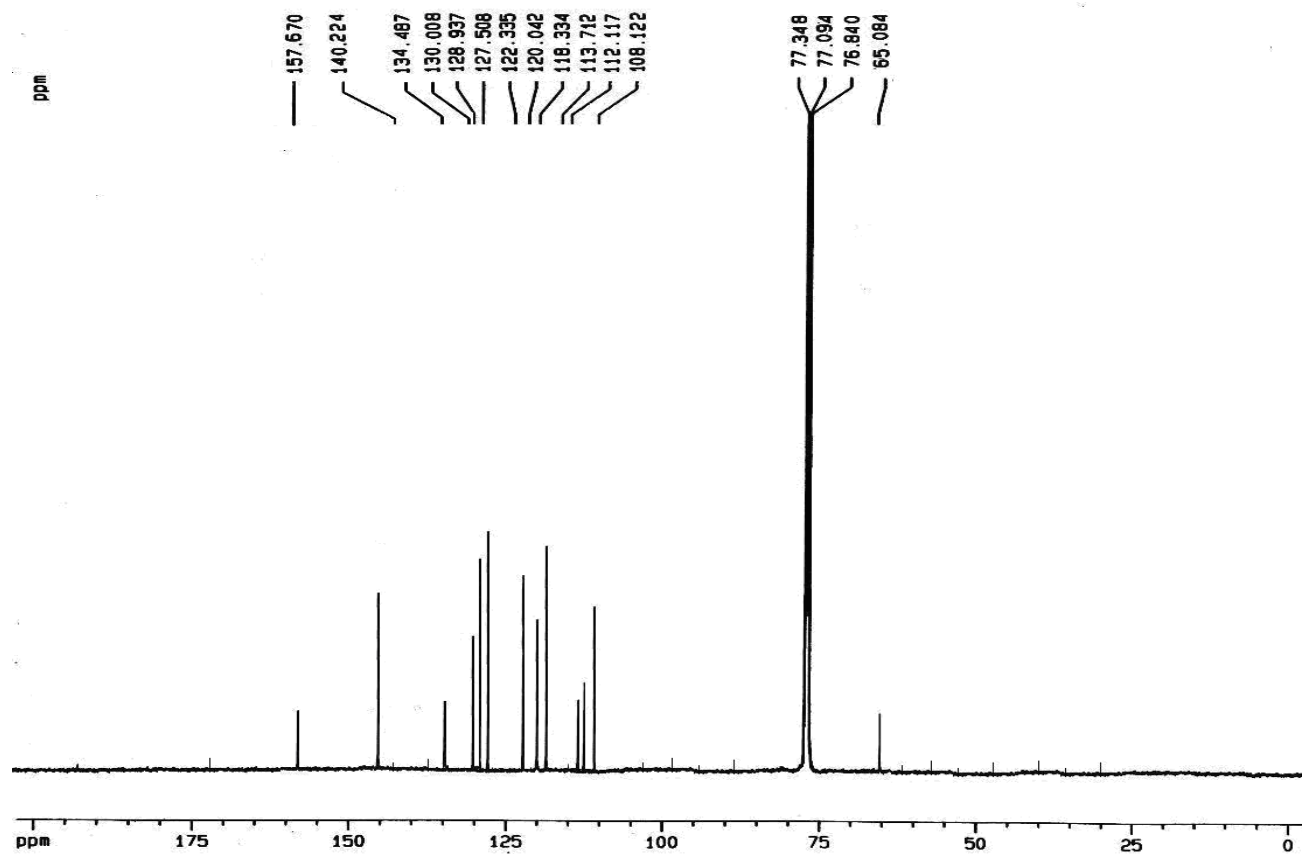


Figure S3: Fluorescence responses of DPNO ($c = 2.0 \times 10^{-5}$ M) to OCl^- (1 equiv) containing 10 equiv of various metal ions and anions ($\lambda_{\text{exc}} = 305$ nm).

9. ^1H NMR, ^{13}C NMR and ESI MS spectra of DPNO and HPNO: ^1H NMR spectrum of Receptor i.e. DPNO:



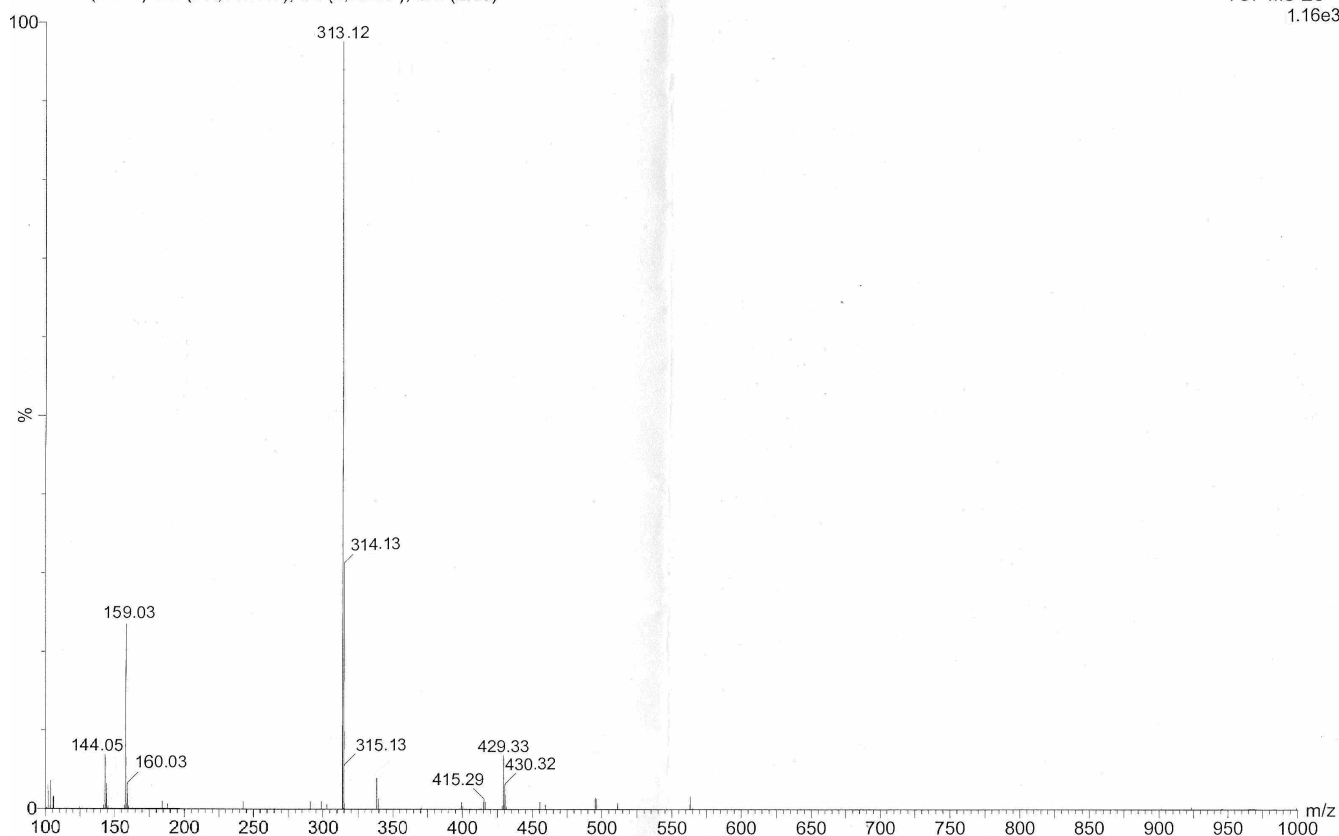
^{13}C NMR spectrum of Receptor i.e. DPNO:



ESI MS Mass Spectra of DPNO:

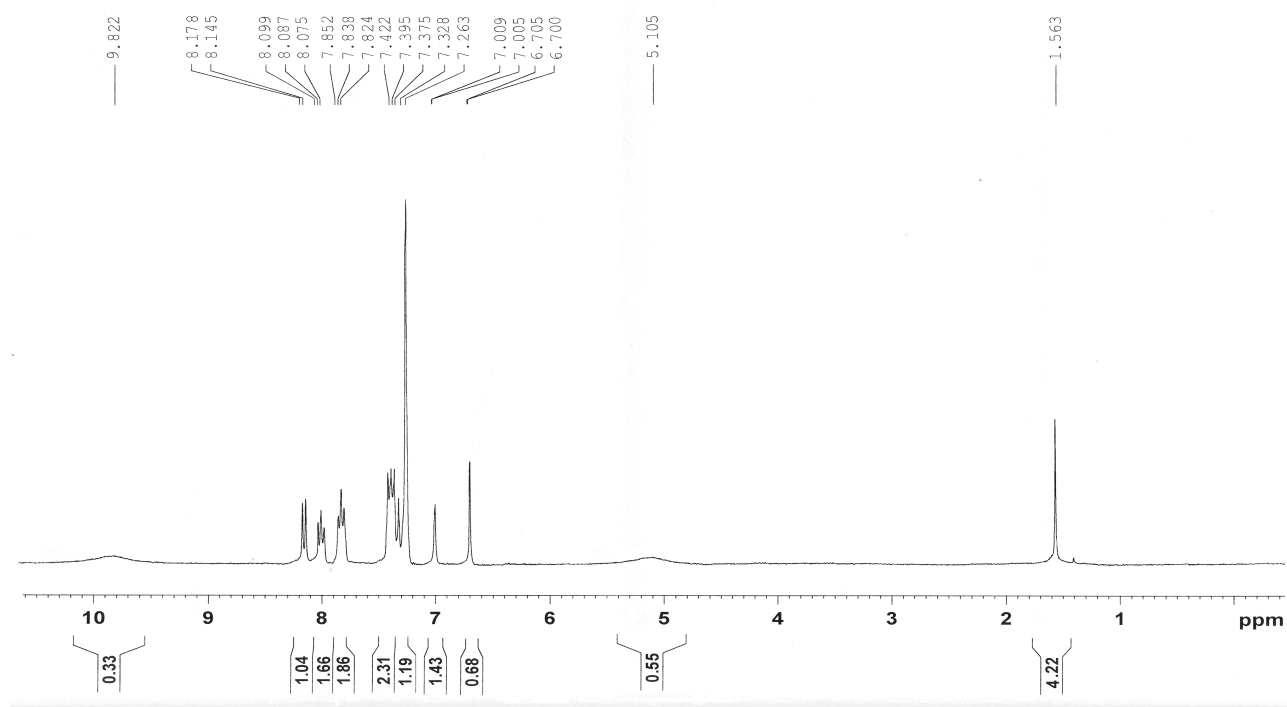
3ESU5 7 (0.073) Sm (Mn, 2x1.00); Sb (2,70.00); Cm (2:16)

TOF MS ES+
1.16e3

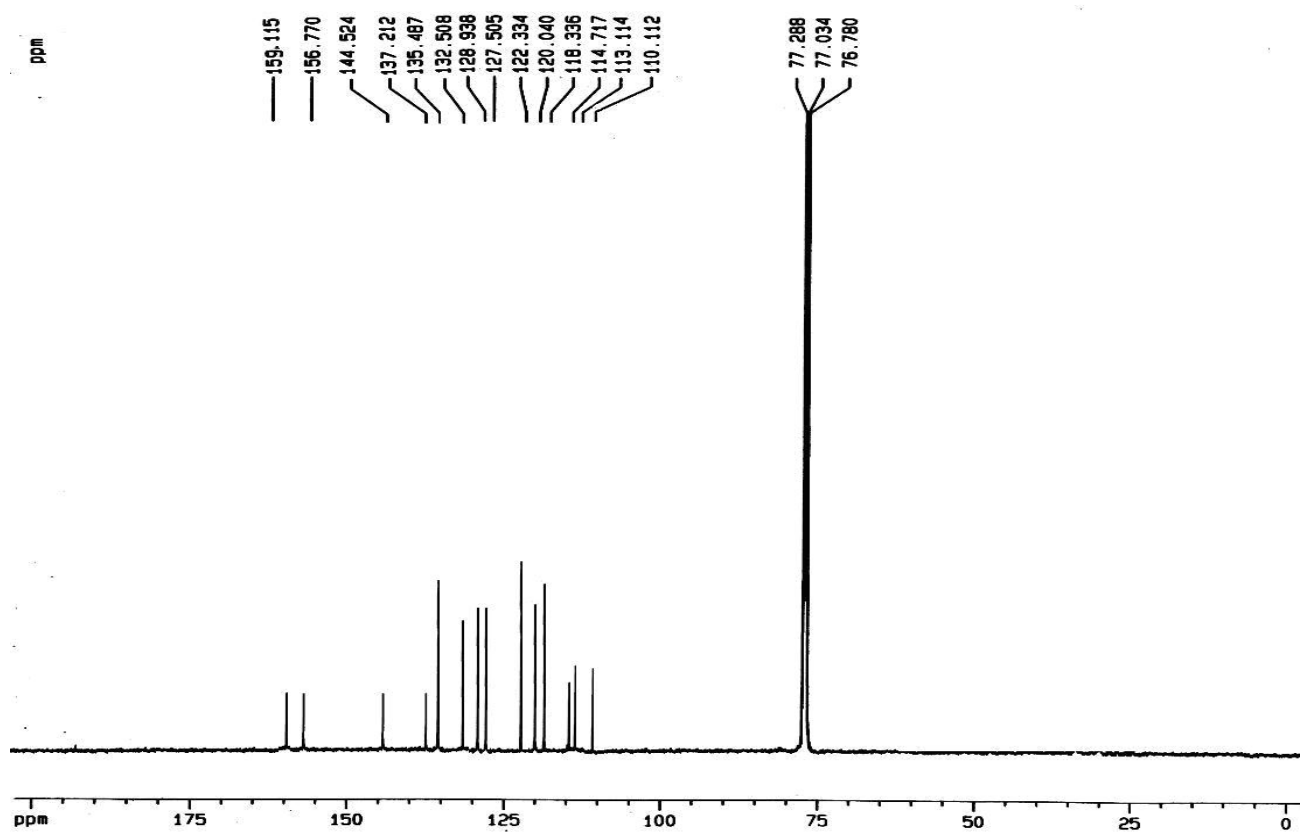


¹H NMR spectrum of HPNO:

AM-43 1H in CDCl₃ 16.4.13



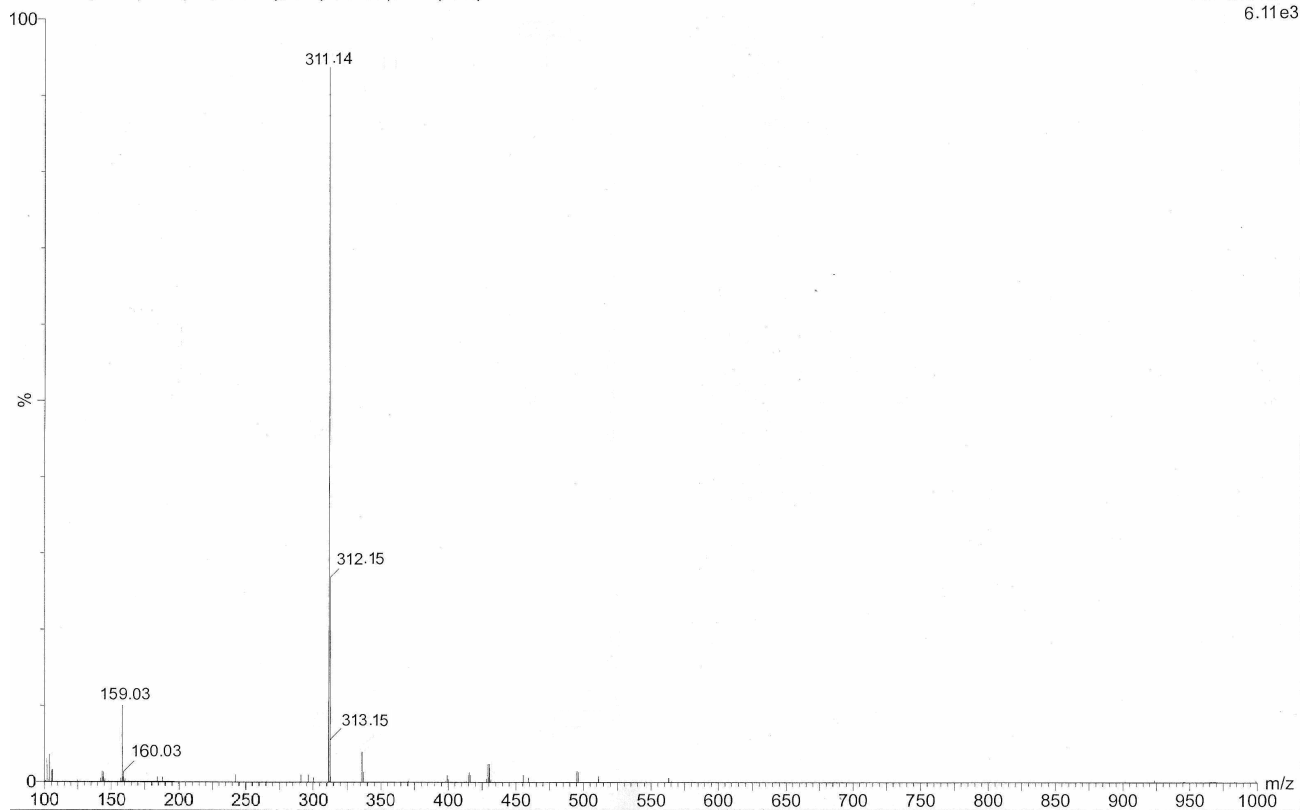
^{13}C NMR spectrum of HPNO:



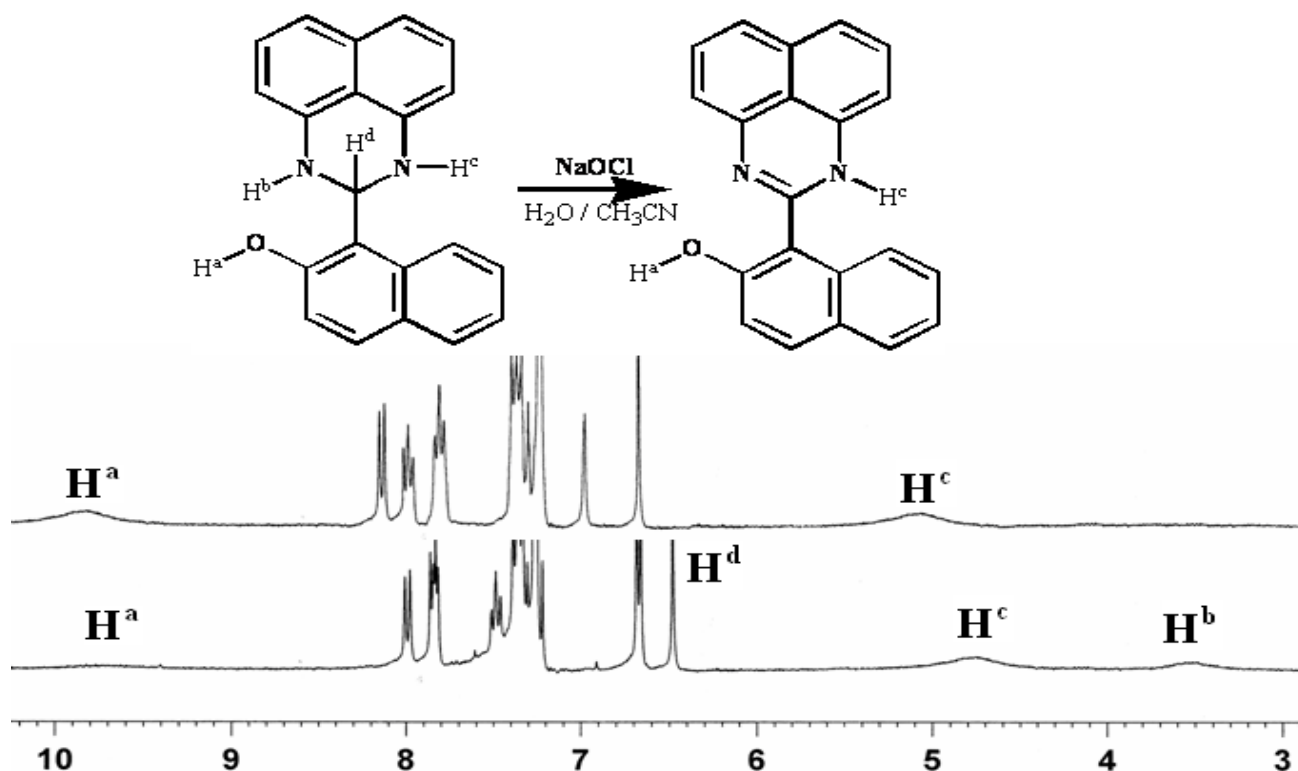
ESI MS Spectra of HPNO:

3ESU167 (0.016) Sm (Mn, 2x1.00); Sb (2,70.00); Cm (2:16)

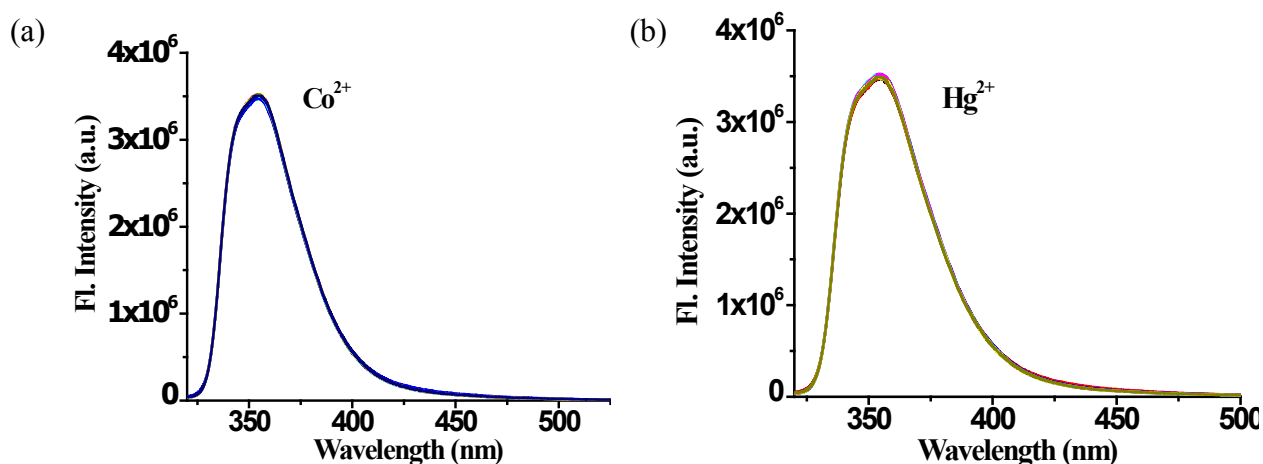
TOF MS ES+
6.11e3

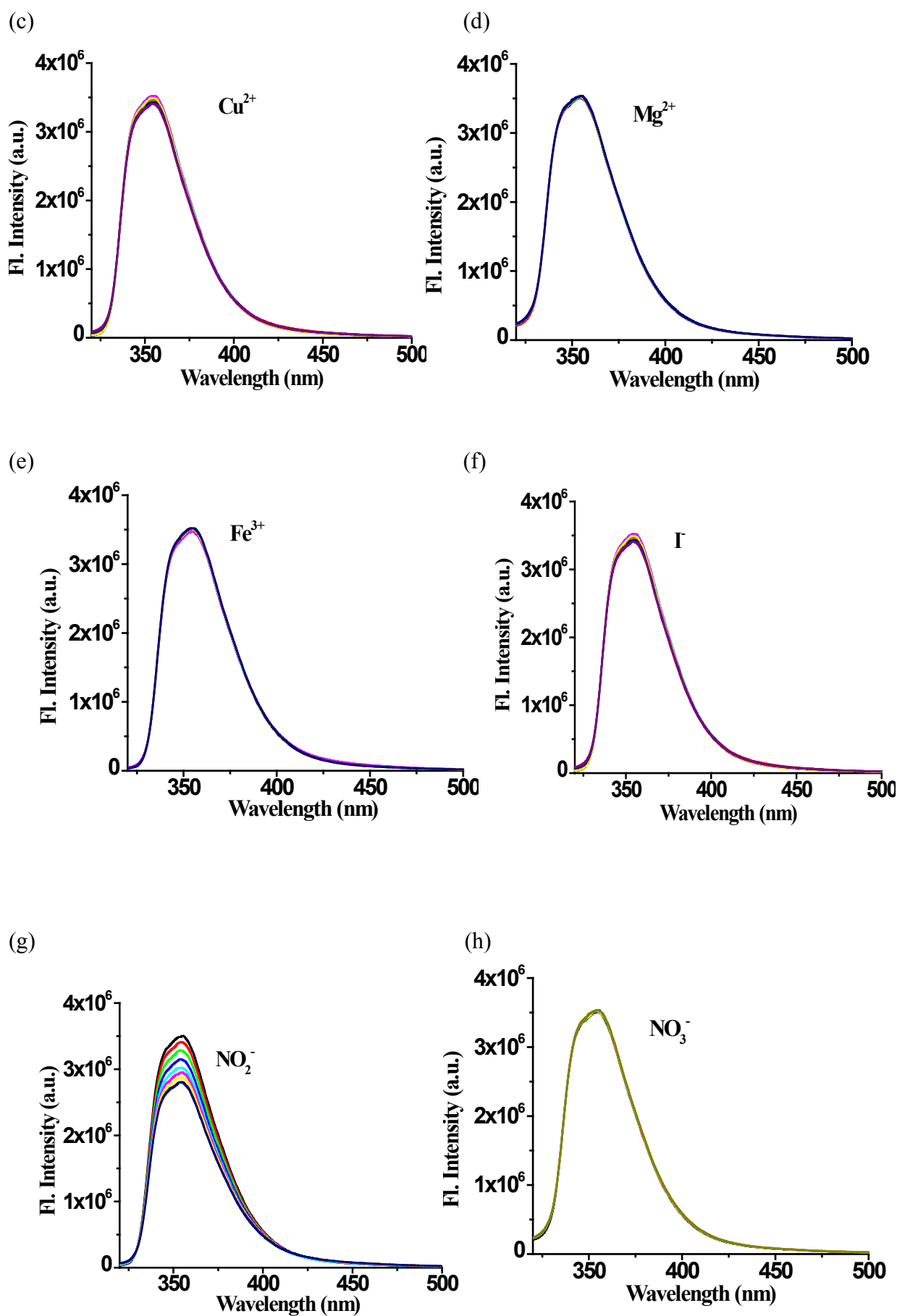


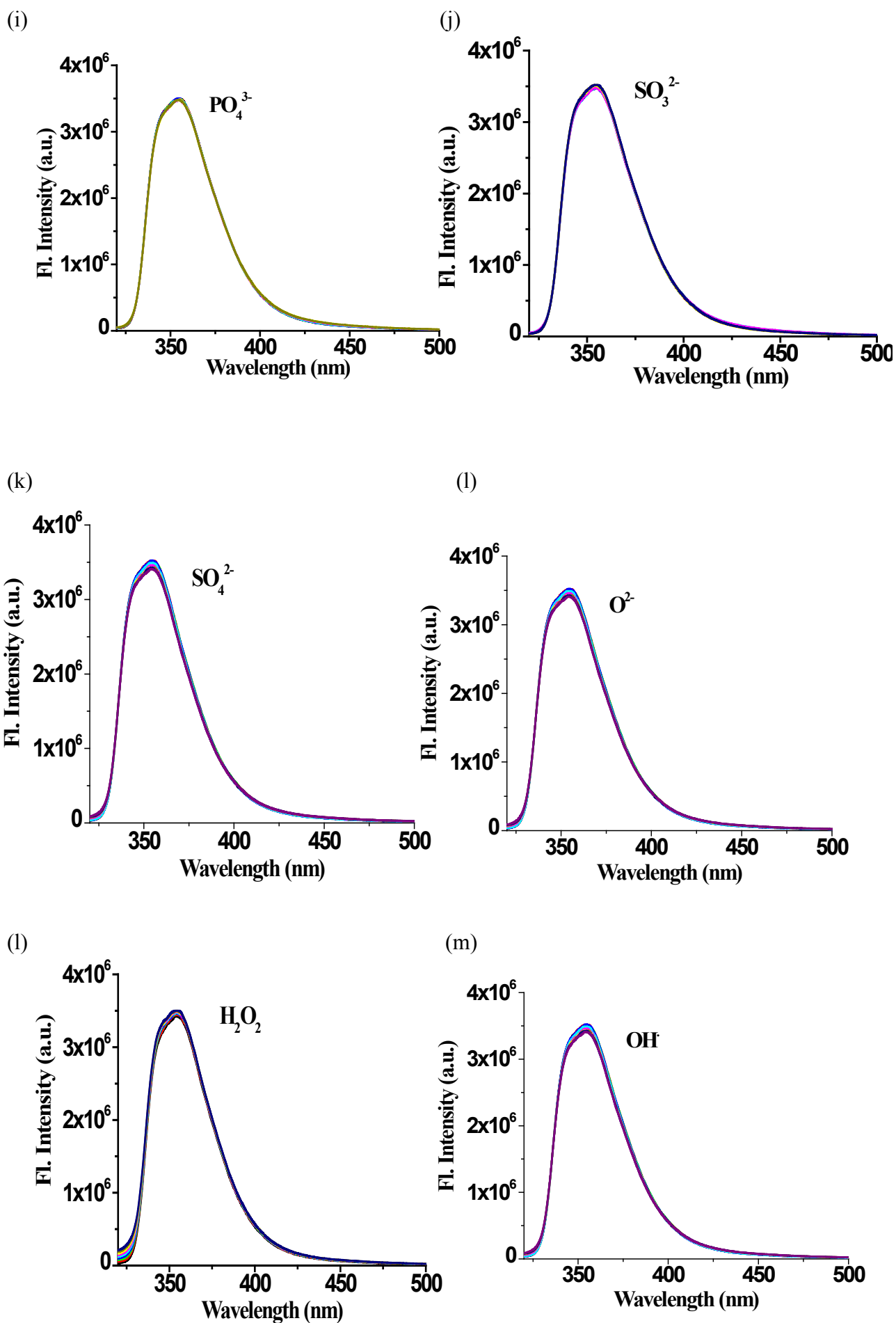
Comparative ^1H NMR spectrum of DPNO and HPNO:

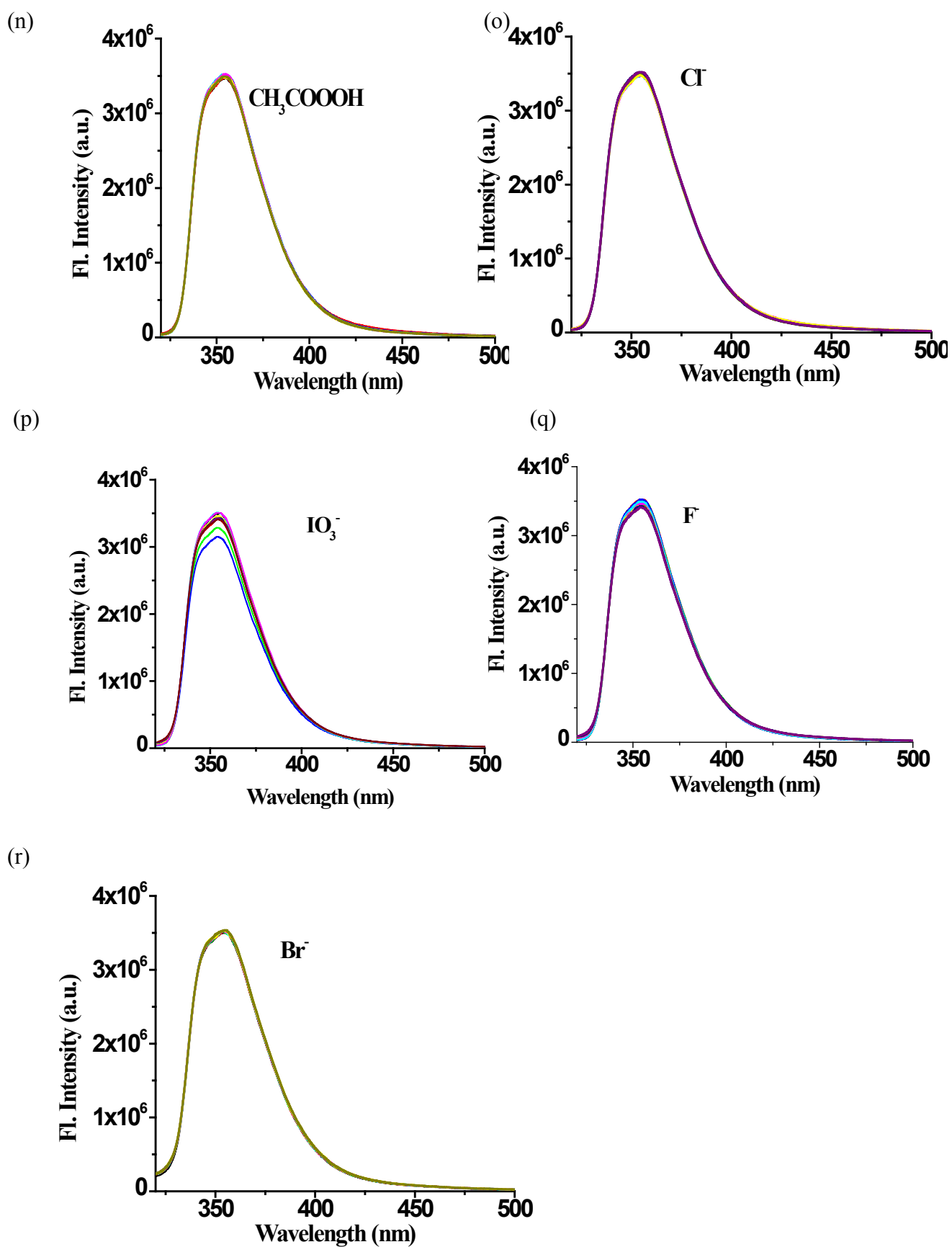


10. Fluorescence emission spectra of DPNO with different anions and oxidants as Co^{2+} , Hg^{2+} , Cu^{2+} , Mg^{2+} , Fe^{3+} , I^- , NO_2^- , NO_3^- , PO_4^{3-} , SO_3^{2-} , SO_4^{2-} , Super oxide, H_2O_2 , Hydroxyl radical, CH_3COOOH , Cl^- , IO_3^- , F^- , Br^- in $\text{CH}_3\text{CN} : \text{H}_2\text{O}$ (6:4, v/v) (The solutions of anions and oxidants were prepared from $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, HgCl_2 , $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mg}(\text{ClO}_4)_2$, FeCl_3 , KI , NaNO_2 , NaNO_3 , Na_3PO_4 , Na_2SO_3 , Na_2SO_4 , K_2O , H_2O_2 , Femton's reagent, glacial acetic acid TBACl, NaIO_3 , TBAF and TBAB respectively in $\text{CH}_3\text{CN-H}_2\text{O}$).









11. Fluorescence responses of aqueous solution DPNO to OCl⁻ :

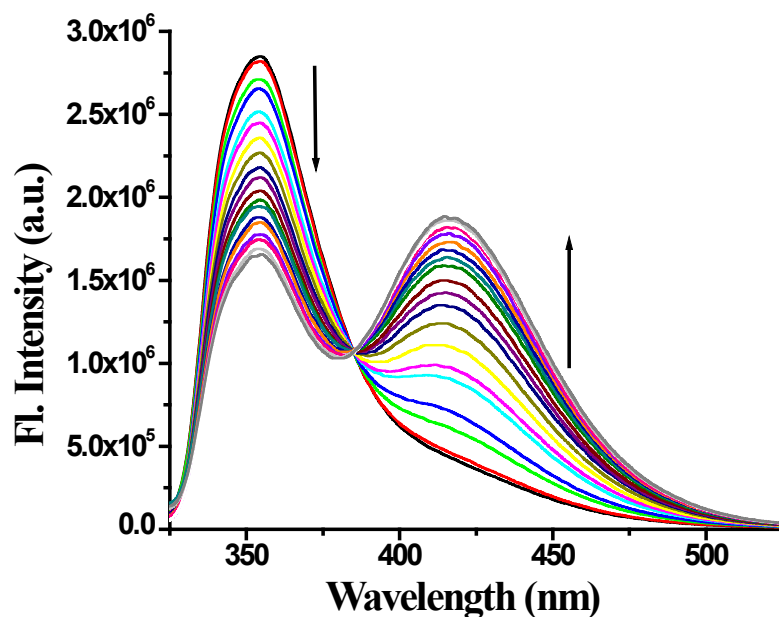



Figure S4: Fluorescence emission spectra of DPNO ($c = 2.0 \times 10^{-5}$ M) in aqueous solution i.e. CH₃CN:H₂O = 1: 9 with OCl⁻ ($c = 2.0 \times 10^{-5}$ M) at pH 7.4.

Theoretical and computational study:

 The ground state geometry of DPNO and HPNO has been fully optimized by using the DFT functionals B3LYP (a hybrid exchange-correlation functional (Becke + Slater + HF exchange and LYP + VWN5 correlations)) [S2-S4] for the 6-311+G** basis set. The Hessian analysis showed energy minimum structures on the potential-energy hyper surface as confirmed by real frequencies obtained for all normal modes of vibration.

The transition energy and the oscillator strength corresponding to 50 lowest lying singlet excited states have been calculated by time-dependent density functional (TD-DFT) method using the B3LYP functionals for the 6-311+G** basis set and the corresponding solvent-modified geometry of the molecule. All calculations have been carried out using the GAUSSIAN 09 package [S5].

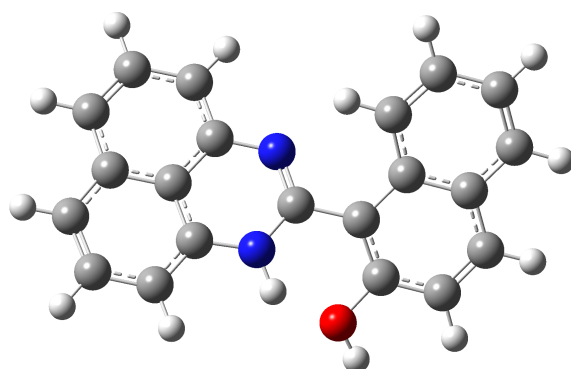


Figure S5: Optimized energy minimized structure of HPNO.

Crystallography analysis of DPNO:

Single crystal X-ray analysis was performed on Bruker APEX II Duo CCD area-detector diffractometer using Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). Data collection was performed using the *APEX2* software, whereas the cell refinement and data reduction were performed under the *SAINTE* software. The crystal structures were solved by direct method and refined against F^2 by full-matrix least-squares refinement using *SHELXTL* package. The non-hydrogen atoms were refined anisotropically, whereby the N-bound and O-bound hydrogen atoms were located in difference fourier maps and refined freely (N–H = 0.86(2) or 0.87(2) \AA and O–H = 0.79(3) \AA). The remaining H atoms were positioned geometrically and refined using a riding model, with C–H = 0.93 or 0.98 \AA and $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$. The final refinement converged well. Absorption correction was applied to the final crystal data by using the *SADABS* software. Crystallographic data are depicted in Table 1. The crystallographic information file for DPNO has been deposited in the Cambridge Crystallographic Data Base Center as CCDC 947173.

The molecular structure of DPNO, Fig. 1, features an intramolecular O1—H1O1 \cdots N2 hydrogen bond, forming an S(6) ring motif. The naphthalene ring systems are essentially

planar (r.m.s. deviation = 0.025 and 0.029 Å, respectively) and make a dihedral angle of 61.09(5) ° with each other. The six-membered (N1/N2/C1/C9-C11) ring is in envelope conformation [puckering parameters $Q = 0.4949(14)$ Å; $\theta = 55.46(16)$ ° and $\varphi = 302.7(2)^\circ$], with atom C11 at the flap. In the crystal (Fig. 2), intermolecular N2—H1N2···O1 (Table 2) hydrogen bonds result in the formation of chains propagating in [001].

Table S1: X-ray crystallographic data and structure refinement

Compound	DPNO (CCDC 947173)
Formula	C ₂₁ H ₁₆ N ₂ O
Formula weight	312.36
Crystal system	Orthorhombic
Spacegroup	<i>Iba</i> 2
T, K	100
Z	8
a, Å	13.9108 (8)
b, Å	25.429 (2)
c, Å	8.8131 (5)
α, β, γ , deg	90, 90, 90
Volume, Å ³	3117.5 (4)
d_{calcd} , g/cm ³	1.331
μ , mm ⁻¹	0.08
Independent reflections	2457
Reflections with $I > 2\sigma(I)$	2320
θ range, deg	2.93-30.11
GOF (F^2)	1.03
$R_{\text{int}}, R[F^2 > 2\sigma(F^2)]$	0.039, 0.033
$wR(F^2)$	0.092

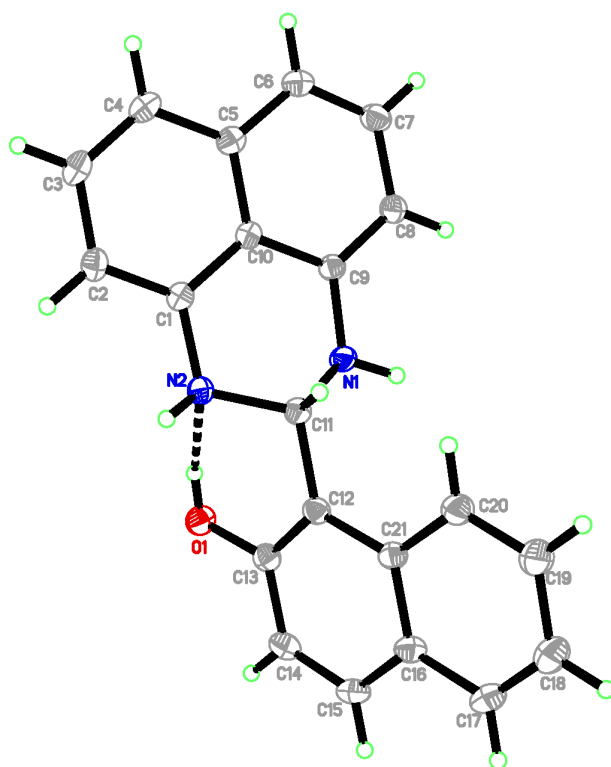


Figure S6: Molecular view of the DPNO. Intramolecular interaction is shown as dashed line.

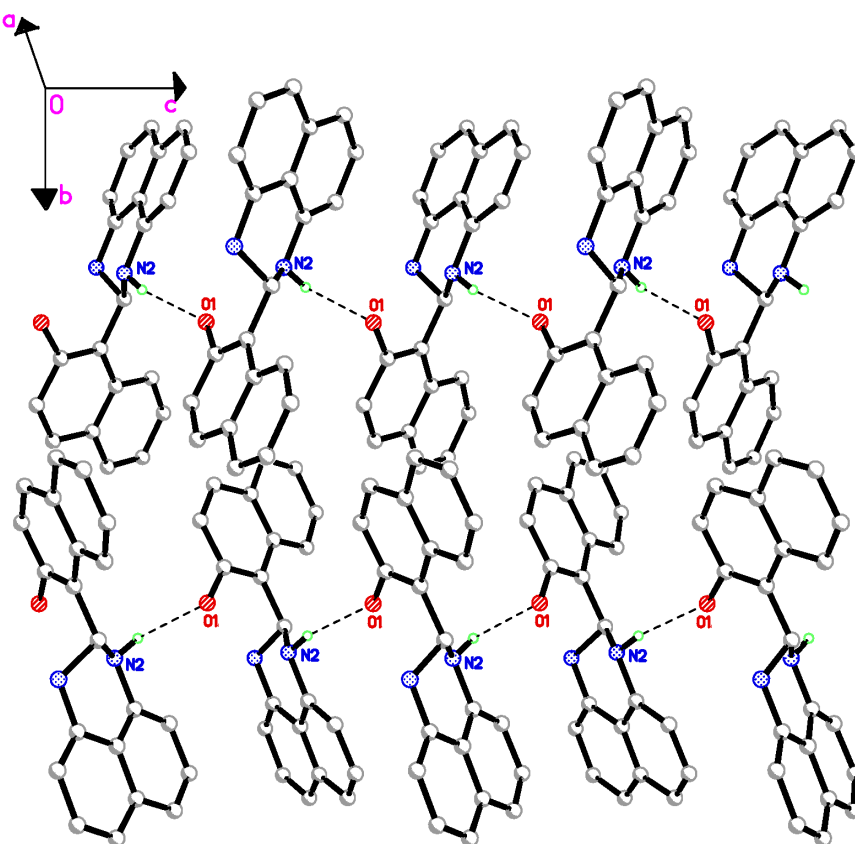


Figure S7: The crystal packing of the DPNO, viewed along *a*-axis.

Table S2: Hydrogen-bond geometry (Å, °)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N2-H1N2\cdots O1^i$	0.86 (2)	2.05 (3)	2.8663 (18)	157 (2)
Intra $O1-H1O1\cdots N2$	0.79 (3)	1.88 (3)	2.6059 (18)	151 (3)

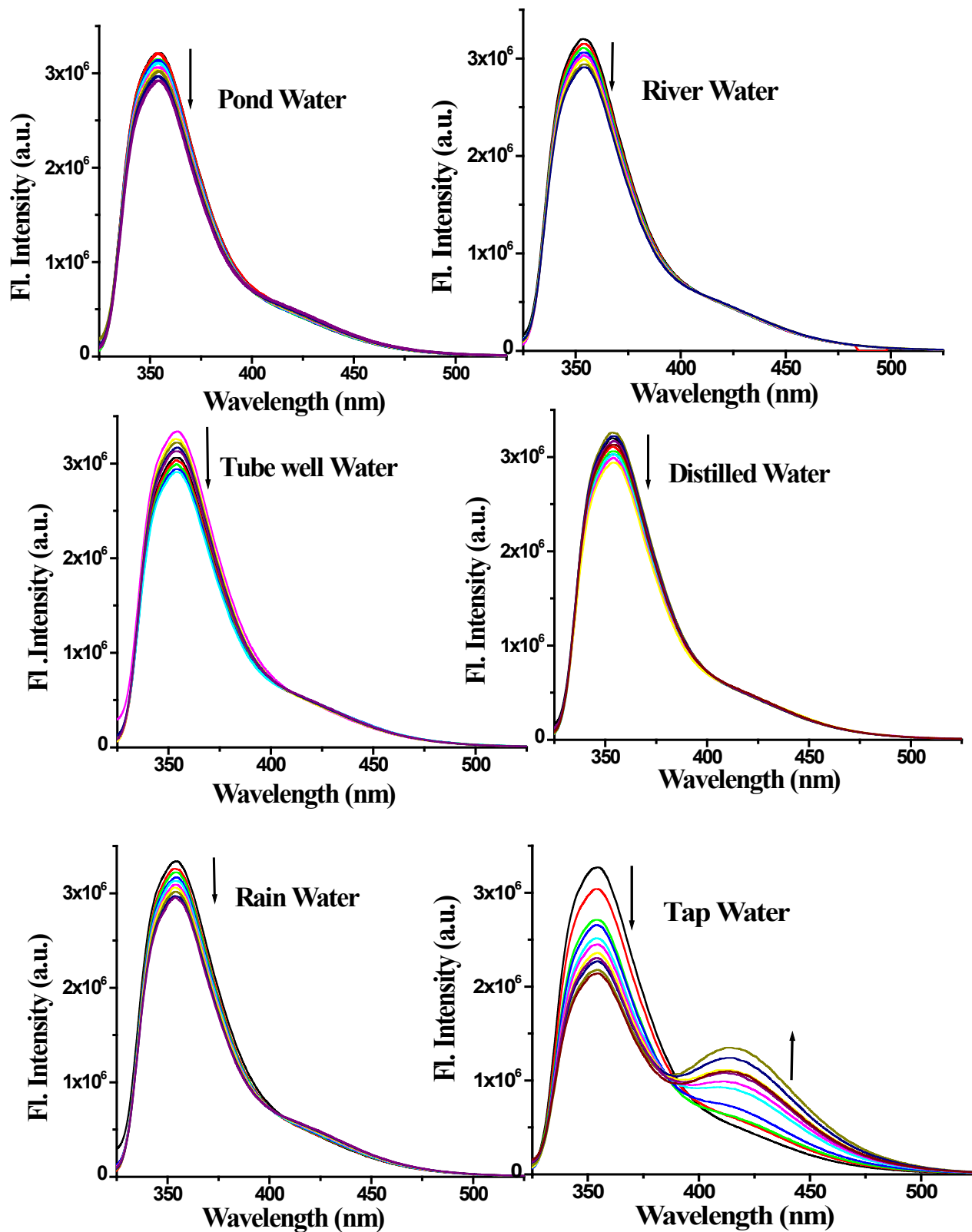
Symmetry code: (i) $-x, y, z+1/2$.

13. Characteristics of tap water:

S.NO.	Parameter	Requirement desirable Limit	Remarks
1.	Colour	5	May be extended up to 50 if toxic substances are suspected
2.	Turbidity	10	May be relaxed up to 25 in the absence of alternate
3.	pH	6.5 to 8.5	May be relaxed up to 9.2 in the absence
4.	Total Hardness	300	May be extended up to 600
5.	Calcium as Ca	75	May be extended up to 200
6.	Magnesium as Mg	30	May be extended up to 100
7.	Copper as Cu	0.05	May be relaxed up to 1.5
8.	Iron	0.3	May be extended up to 1
9.	Manganese	0.1	May be extended up to 0.5
10.	Chlorides	250	May be extended up to 1000
11.	Sulphates	150	May be extended up to 400
12.	Nitrates	45	No relaxation
13.	Fluoride	0.6 to 1.2	If the limit is below 0.6 water should be rejected, Max. Limit is extended to 1.5
14.	Phenols	0.001	May be relaxed up to 0.002
15.	Mercury	0.001	No relaxation
16.	Cadmium	0.01	No relaxation
17.	Selenium	0.01	No relaxation
18.	Arsenic	0.05	No relaxation
19.	Cyanide	0.05	No relaxation
20.	Lead	0.1	No relaxation
21.	Zinc	5.0	May be extended up to 10.0
22.	Anionic detergents (MBAS)	0.2	May be relaxed up to 1
23.	Chromium as Cr^{+6}	0.05	No relaxation
24.	Poly nuclear aromatic Hydrocarbons	--	--
25.	Mineral Oil	0.01	May be relaxed up to 0.03
26.	Residual free Chlorine	0.2	Applicable only when water is chlorinated
27.	Pesticides	Absent	--
28.	Radio active	--	--

14. Fluorescence spectra of DPNO with different types of water samples:

Fluorescence emission spectra of DPNO ($c=2 \times 10^{-5}$ M) with different water samples (total volume 500 μ M for each) in $\text{CH}_3\text{CN} : \text{H}_2\text{O}$ (1:9, v/v).



15. pH effect on the sensing phenomena:

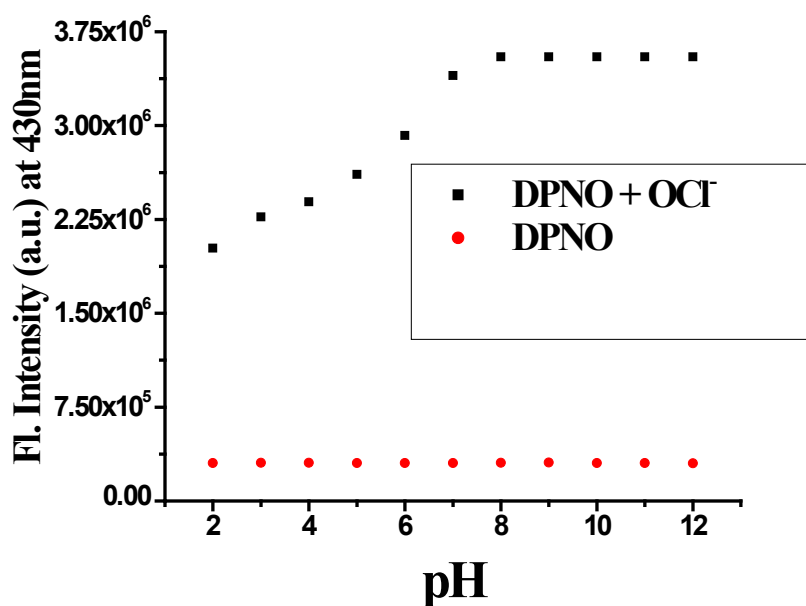


Figure S8: Change of fluorescence intensity of DPNO ($c=2 \times 10^{-5}$ M) and DPNO in presence of 1 equivalent OCl⁻ at different pH at a fixed wave length (430 nm).

16. References:

- [S1] M. Zhu, M. Yuan, X. Liu, J. Xu, J. Lv, C. Huang, H. Liu, Y. Li, S. Wang, D. Zhu, *Org. Lett.* 2008, **10**, 1481-1484
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- [S5]. M. J. Frisch, et al. Gaussian 09, Revision B.01, Gaussian, Inc., Wallingford CT, 2010.