Electronic Supporting Information

A Simple Chemosensor for Hg^{2+} and Cu^{2+} that Works as a Molecular Keypad Lock.

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Contents

1. Experimental Section:

Chemicals.

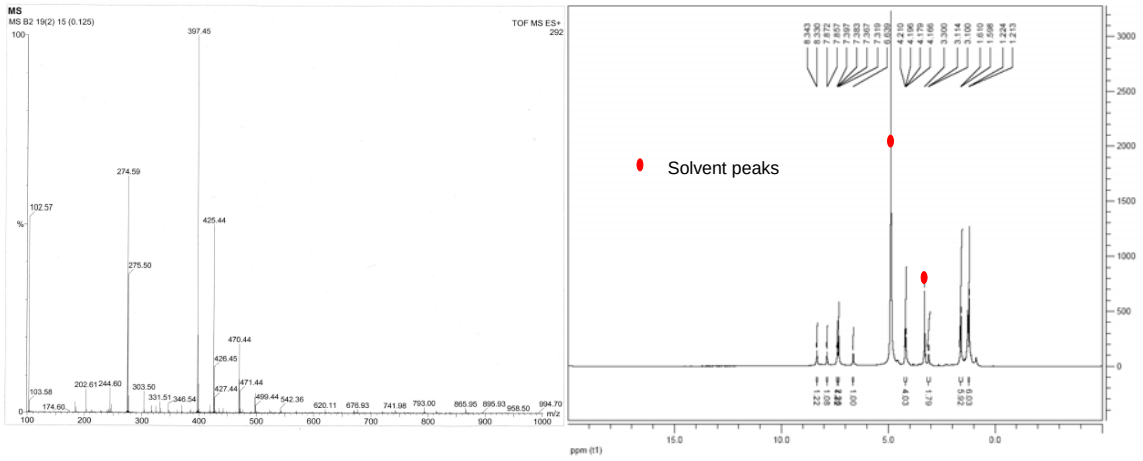
1-amino-8-naphthalene sulphonic acid, ethyl-2-bromopropionate, diisopropyl amine, was purchased from Sigma-Aldrich (USA). Acetonitrile (AR Grade) and HPLC water were obtained from S.D. Fine Company (India).

Absorption and Emission spectra.

Absorption Spectra were recorded with Varian Cary 500 Scan UV-VIS-NIR Spectrophotometer. While room temperature luminescence spectra and Fluorescence decay spectra were recorded with HORIBA JOBIN YVON Fluorog-3 FluorEssence spectrophotometer. 340 nm LED source was used as the laser excitation source for the time resolved studies.

Synthesis of ANSE

A solution of 1-amino-8-naphthalene sulfonicacid (500 mg, 2.24 mmol), ethyl-2-bromo propionate (810 mg, 4.5 mmol), potassium iodide (2 mmol) and diisopropyl amine (1.1 ml, 10 mmol) in 100 ml dry acetonitrile and the reaction mixture was refluxed under nitrogen atmosphere for 7 hours, then cooled and poured into 100 ml of water. The resulting mixture was extracted with dichloromethane (3 x 150 ml). The extract was dried over sodium sulfate and was concentrated. Finally it was purified by column chromatography using methanol/Chloroform (2% methanol and 98% chloroform) as an eluent. Finally yellowish color **ANSE** was obtained (48 %). ^{1}H NMR (500MHz, MeOD), δ (ppm): δ 8.34 – 8.33 (Ar–H, 1H , d, J = 6.5 Hz,), 7.872 – 7.857(Ar–H, 1H , d, J = 7.5 Hz), 7.397 – 7.367(Ar–H, 1H, t, J = 7 Hz,), 7.319 (Ar–H, 2H, s), 6.639 (Ar–H, 1H, s), 4.210 – 4.166 (–CH_2, 4H, q, J = 7Hz,), 3.114 – 3.100 (–CH, 2H, q, J = 7 Hz), 1.610 – 1.598 (–CH_3, 6H, d, J = 6.0 Hz), 1.224 – 1.213 (–CH_3, 6H, t, J = 7Hz). ESI mass: *m/z* 425.44 for [**ANSE** + 2]$^{+}$, calc. For $C_{20}H_{25}NO_7S$, **ANSE**, 423.48. mp: 178 °C.



2. Absorption spectra of ANSE in water with various metal ions.

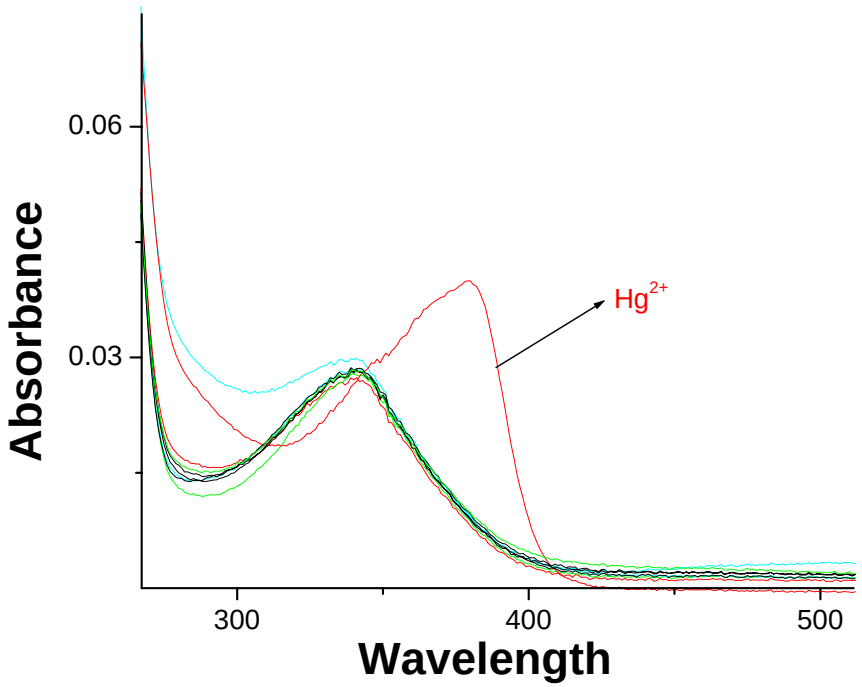


Figure S1 : Changes in the absorption spectra of **ANSE** (1.5×10^{-5}M) in the presence of various other metal ions (Co^{2+}, Ni^{2+}, Cu^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Mg^{2+}, Zn^{2+}, Hg^{2+}, Na^{+}, K^{+}, Fe^{2+}) in neutral water (4.0×10^{-4}M).

3. Emission Spectra of ANSE in water with various metal ions.

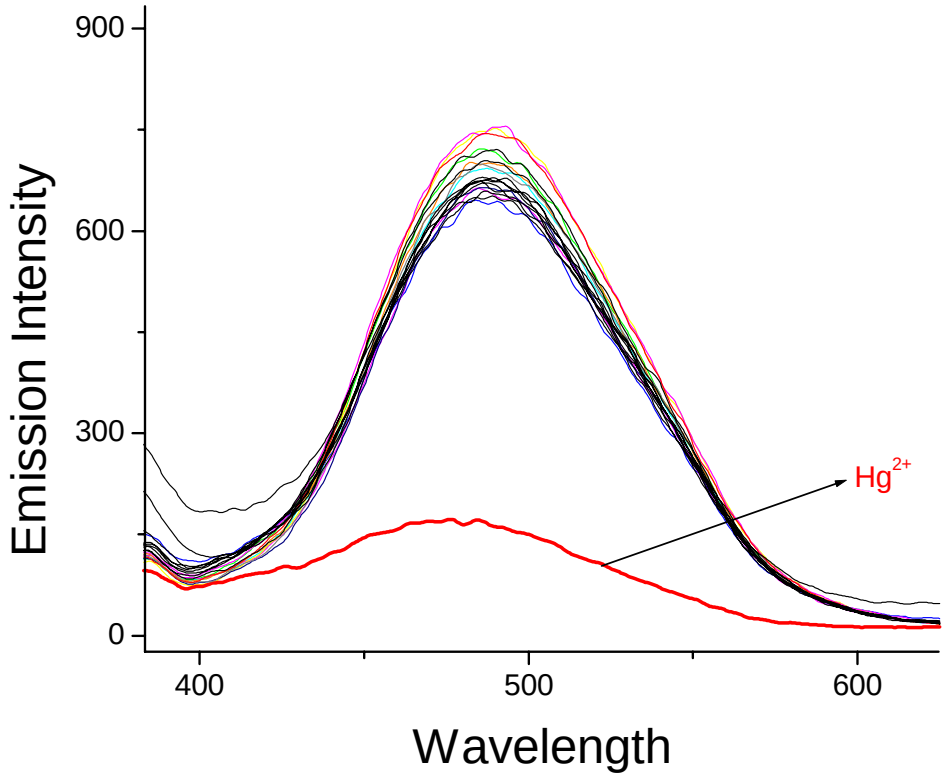


Figure S2 : Changes in the emission spectra of **ANSE** (3.0×10^{-6}M) in the presence of various other metal ions (Co^{2+}, Ni^{2+}, Cu^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Mg^{2+}, Zn^{2+}, Hg^{2+}, Na^{+}, K^{+}, Fe^{2+} Ce^{3+}, Er^{3+}, La^{3+}, Nd^{3+}, Pr^{3+}, Sm^{3+}, Yb^{3+}, Eu^{3+}) in neutral water (1.6×10^{-3}M). Excitation wavelength is 340 nm.

4. Absorption spectra of ANSE in acetonitrile with various metal ions.

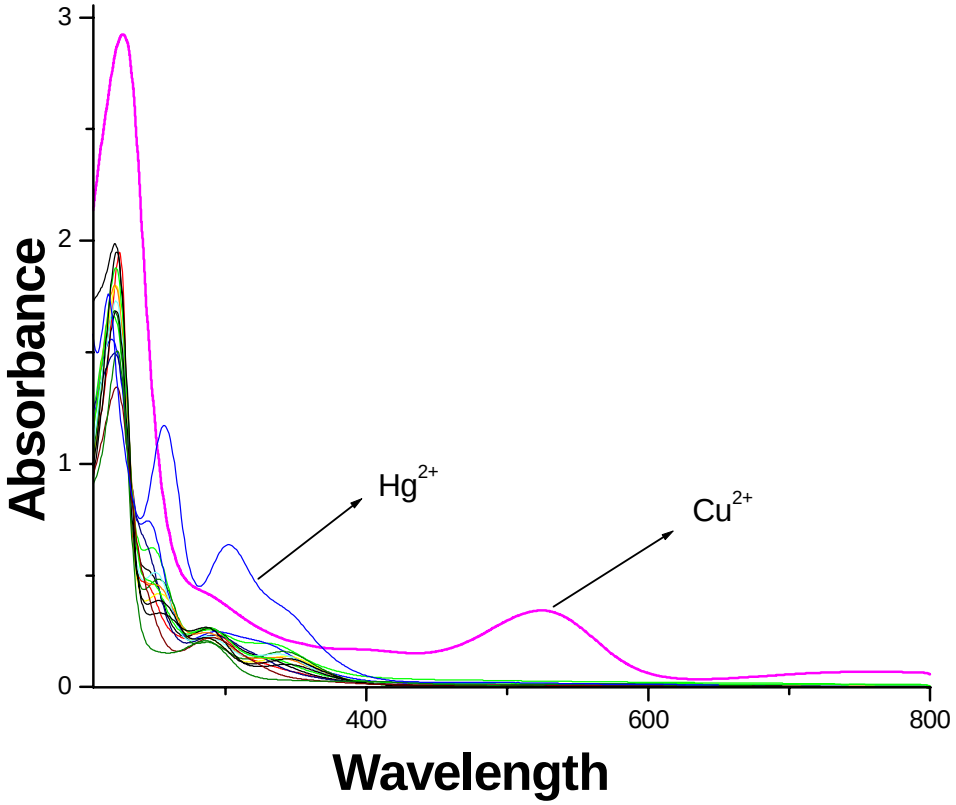


Figure S3: Changes in the absorption spectra of **ANSE** (4.0×10^{-5}M) in the presence of various other metal ions (Co^{2+}, Ni^{2+}, Cu^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Mg^{2+}, Zn^{2+}, Hg^{2+}, Na^{+}, K^{+}, Fe^{2+}) (2.0×10^{-4} M) in acetonitrile.

5. Emission spectra of ANSE in acetonitrile with various metal ions.

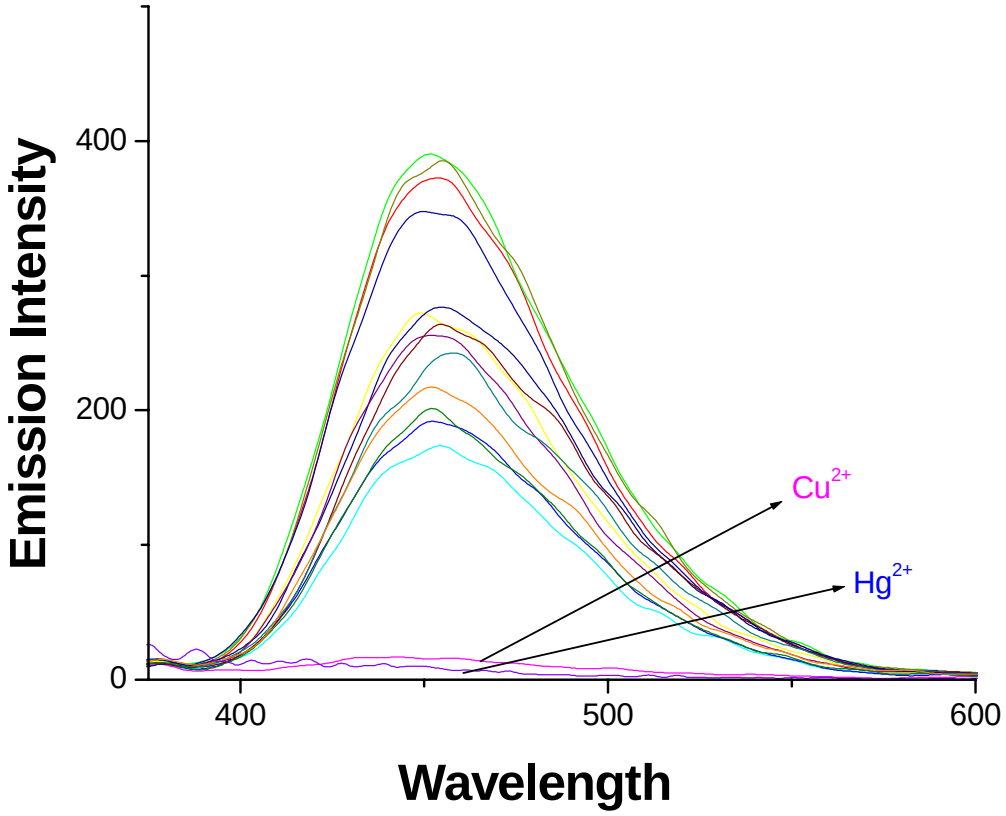


Figure S4: Changes in the emission spectra of **ANSE** (2.0×10^{-6}M) in the presence of various other metal ions (Co^{2+}, Ni^{2+}, Cu^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Mg^{2+}, Zn^{2+}, Hg^{2+}, Na^{+}, K^{+}, Fe^{2+}) in acetonitrile (6.0×10^{-6}M). Excitation wavelength is 352 nm.

7. Visible color change of ANSE.

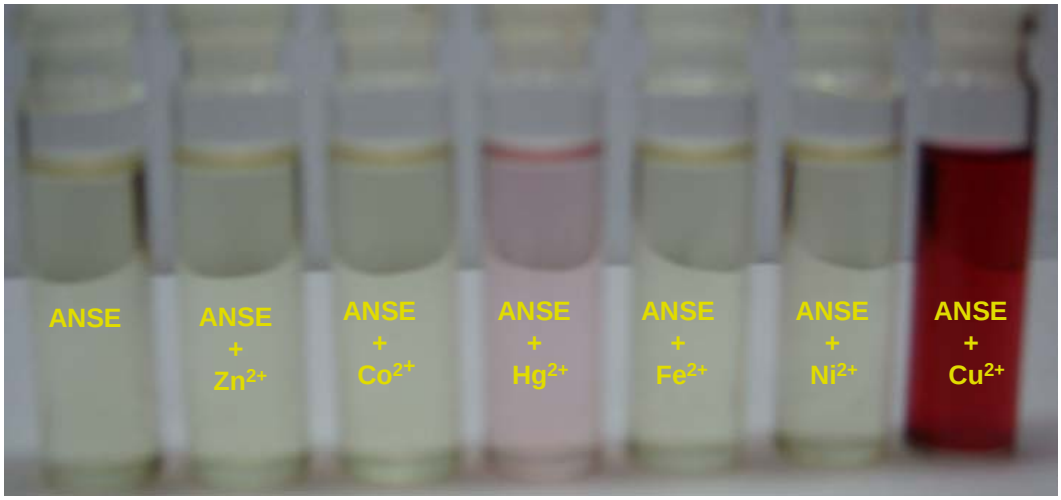


Figure S5: Visible color changes of **ANSE** with different metal ions in acetonitrile.

7. Excited state properties:

No	Life time		Compound
	Acetonitrile	Water	
1	$\chi 2 = 1.0129$ B1: 100% τ_1: 1.12 x 10^{-8} sec λ_{ext}: 340 nm λ_{emi}: 450 nm	$\chi 2 = 1.130$ B1: 100% τ_1: 5.28 x 10^{-9} sec λ_{ext}: 340 nm λ_{emi}: 490 nm	**ANSE**
2	$\chi 2 = 1.217$ B1: 100% τ_1: 3.32 x 10^{-9} sec. λ_{ext}: 340 nm λ_{emi}: 450 nm	---	**ANSE** + Cu^{2+}
3	$\chi 2 = 1.126$ B1: 25.99% B2: 74.01% τ_1: 1.26 x 10^{-9} sec. τ_2: 5.42 x 10^{-9} sec. λ_{ext}: 340 nm λ_{emi}: 450 nm	$\chi 2 = 1.190$ B1: 100% τ_1: 2.639 x 10^{-9} sec λ_{ext}: 340 nm λ_{emi}: 490 nm	**ANSE** + Hg^{2+}
4	$\chi 2 = 0.9896$ B1: 100% τ_1: 4.8 x 10^{-9} sec λ_{ext}: 340 nm, λ_{emi}: 500 nm	---	**ANSE** + 1st Input Cu^{2+} + 2nd Input F^-
5	$\chi 2 = 1.014$ B1: 100% τ_1: 1.102 x 10^{-8} sec λ_{ext}: 340 nm, λ_{emi}: 450 nm	---	**ANSE** + 1st Input F^- + 2nd Input Cu^{2+}

8. Fluorescence decay curves:

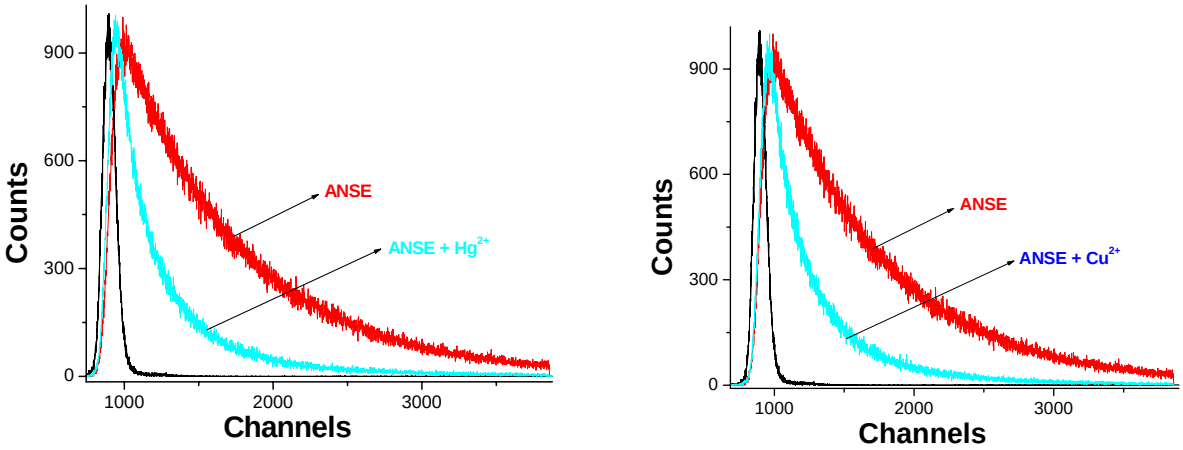


Figure S6: Fluorescence decay curve for **ANSE** in the presence of Hg^{2+} and Cu^{2+} in acetonitrile. λ_{ext} = 340 nm and the emission decay was monitored at 450 nm

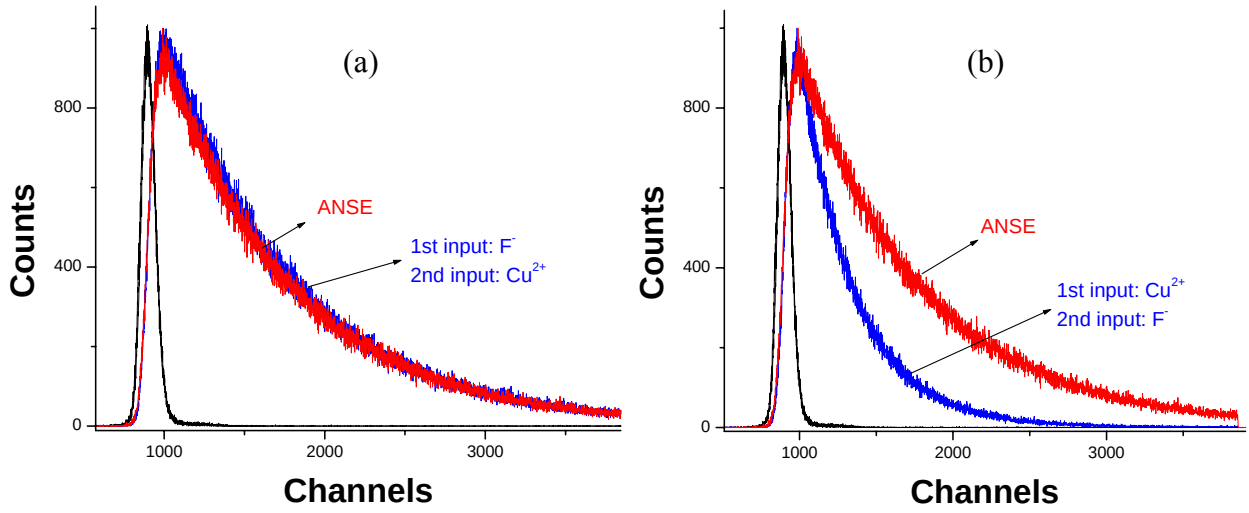


Figure S7: Fluorescence decay curve for **ANSE** in the presence of two different sequence of inputs in acetonitrile. λ_{ext} = 340 nm and emisson decay was monitored at 450 nm and 500 nm for (a) and (b) respectively. Trace shown in black is the lamp response time.

9. Fluorescence spectra with different sequence of ionic inputs at different time interval:

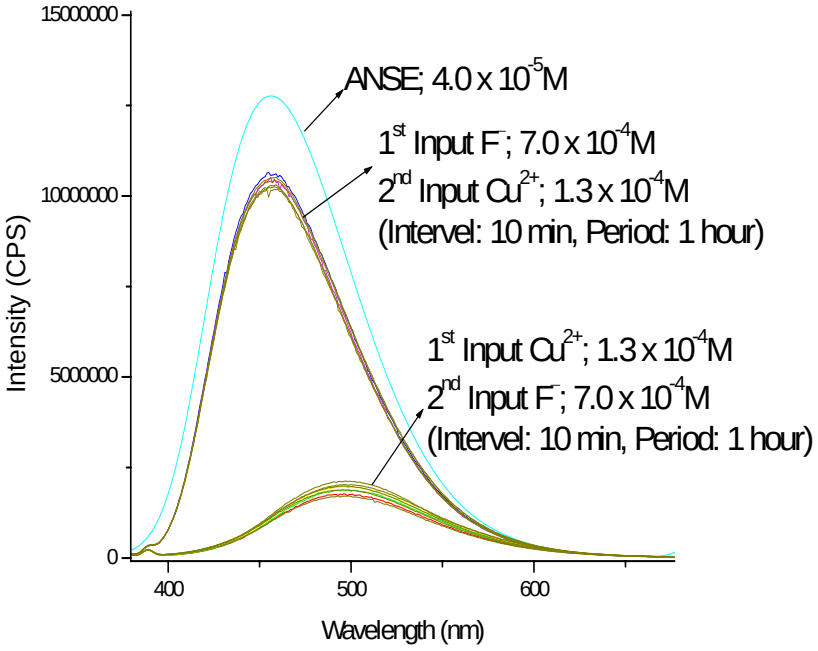


Figure S8: Emission output of **ANSE,** following excitation at 352 nm with different input sequences recorded at 10 min intervel over a period of one hour.