Supporting Information

Detection and discrimination of Zn^{2+} and Hg^{2+} using a single molecular fluorescent probe

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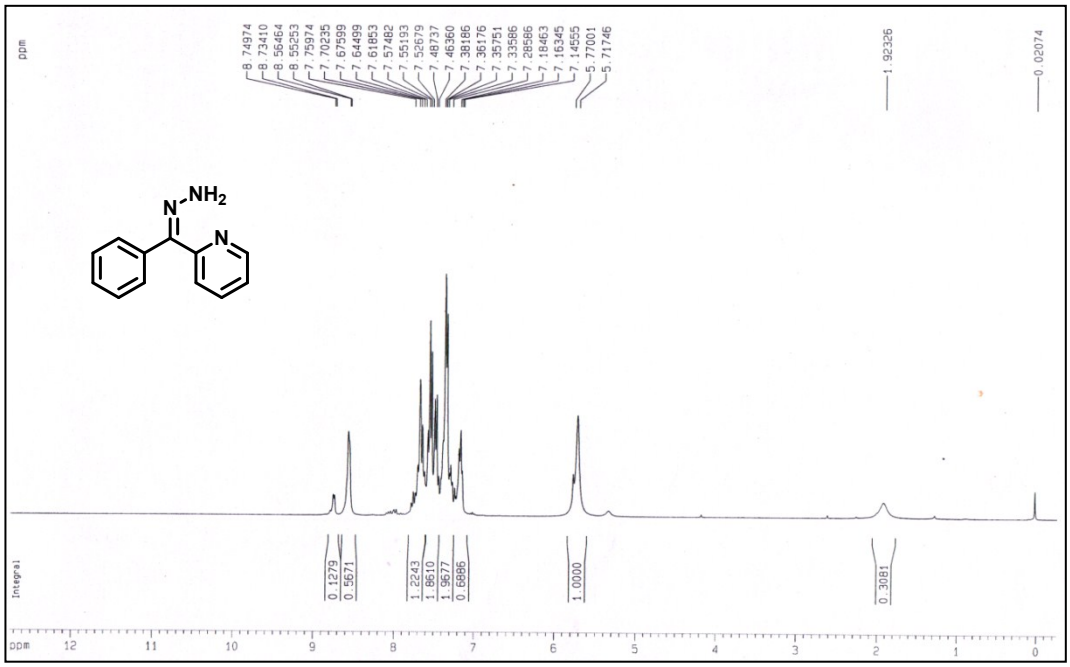


Figure S1: ^{1}H NMR (300 MHz) spectra of compound **1** in $CDCl_3$

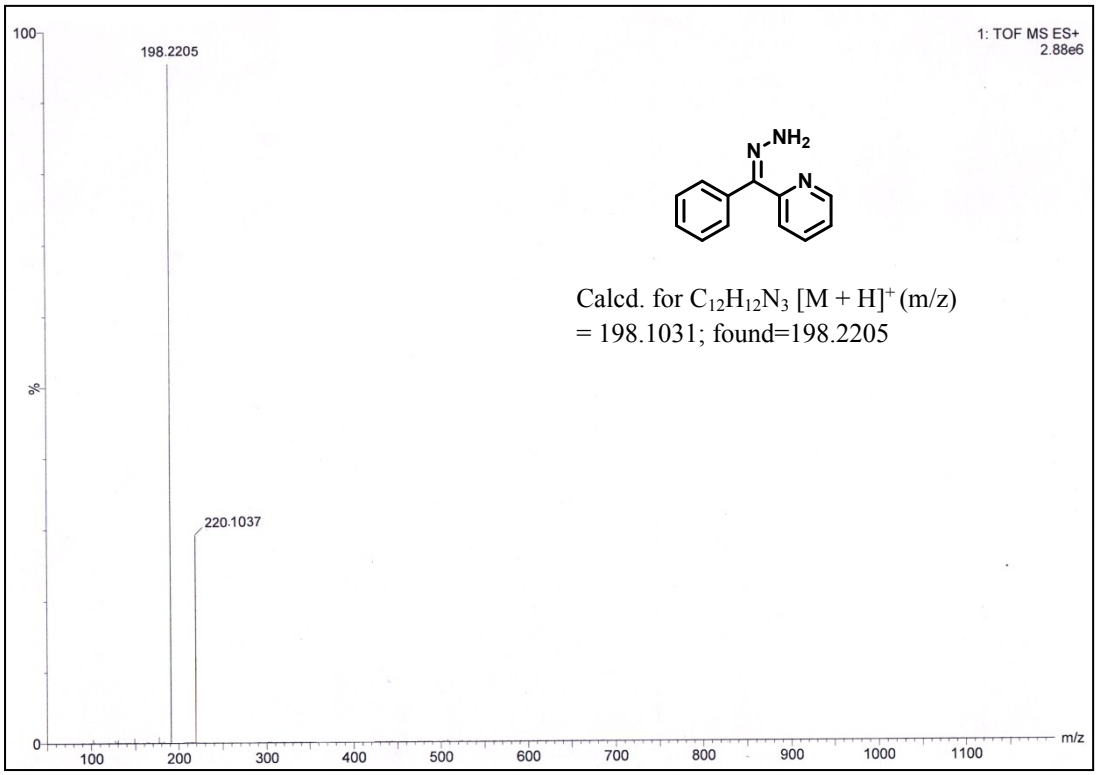


Figure S2: HRMS of Compound 1

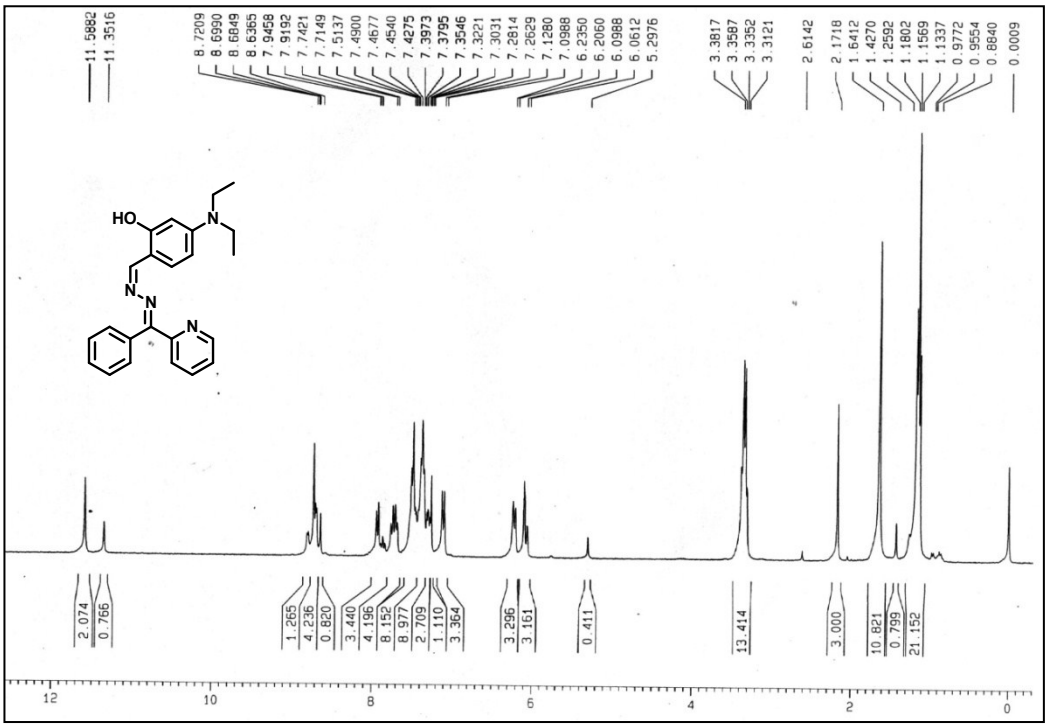


Figure S3: ^{1}H NMR (300 MHz) spectra of the probe (SAPH) in $CDCl_3$

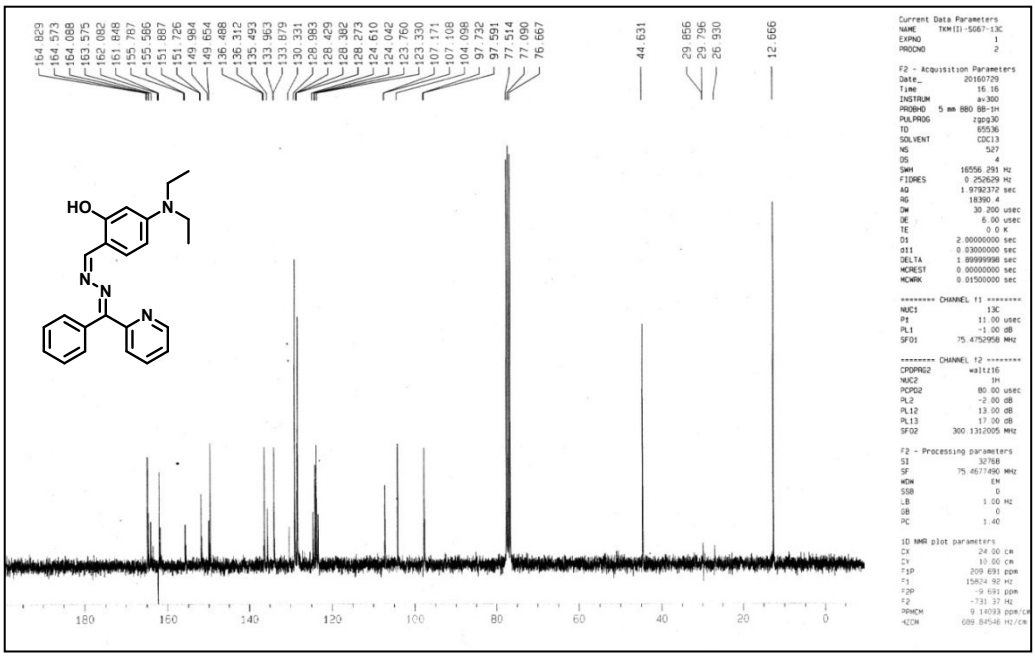


Figure S4: ^{13}C NMR (75 MHz) spectra of the probe (SAPH) in $CDCl_3$

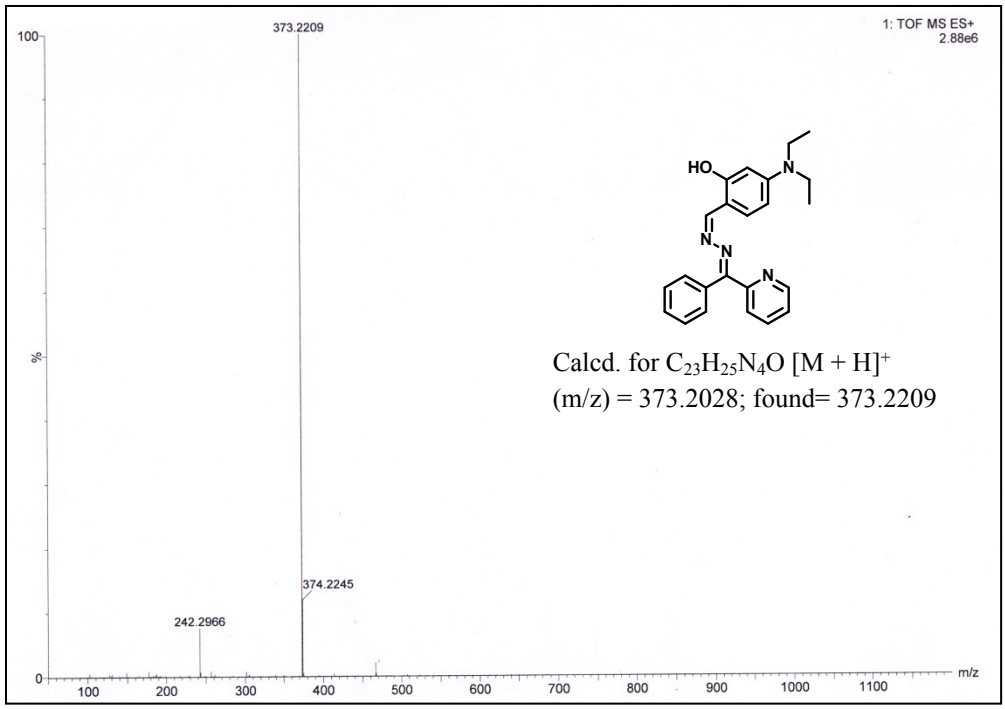
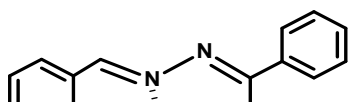


Figure S5: HRMS of the probe (SAPH)



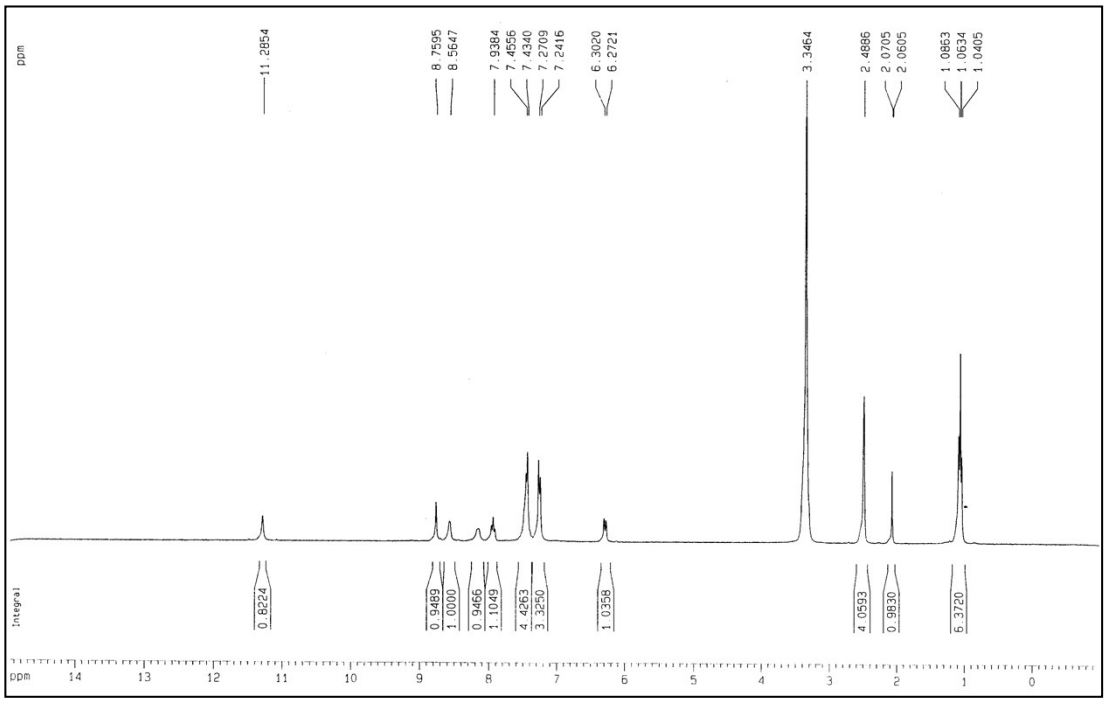


Figure S6: ^{1}H-NMR spectrum of SAPH-Zn^{2+} complex in DMSO-d_6

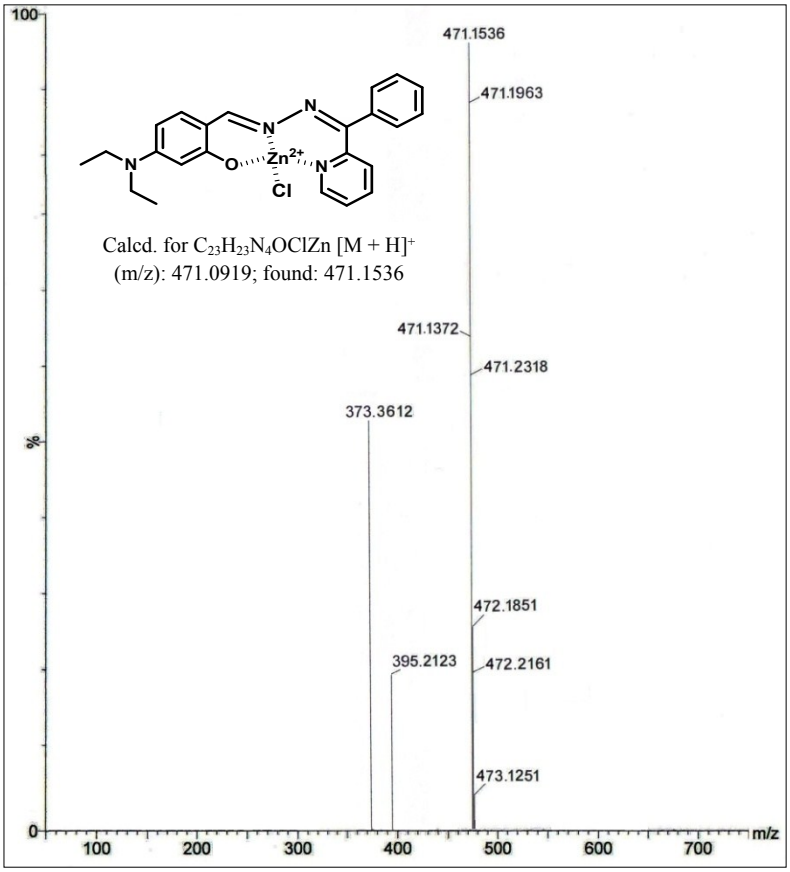


Figure S7: HRMS of SAPH-Zn^{2+} complex

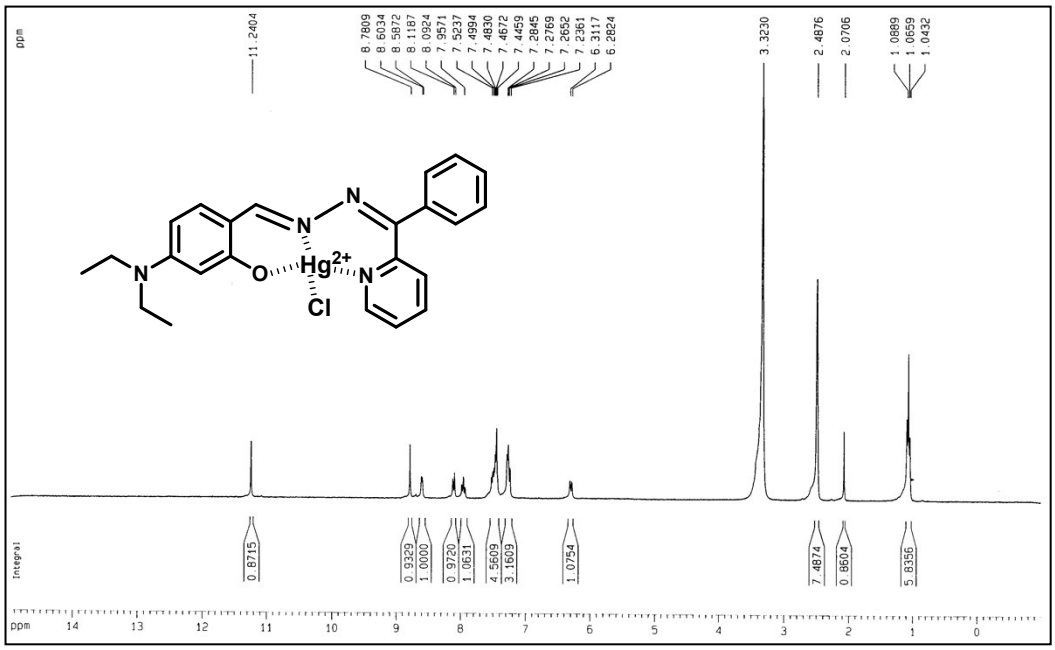


Figure S8: ^{1}H-NMR spectrum of SAPH-Hg^{2+} complex in DMSO-d_6

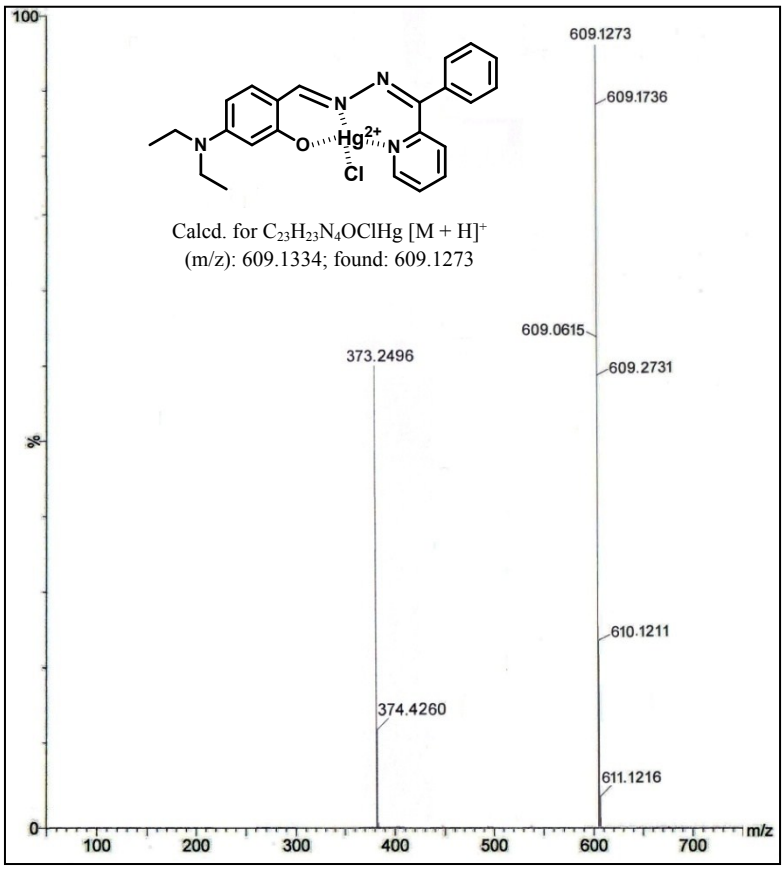


Figure S9: HRMS of SAPH-Hg^{2+} complex

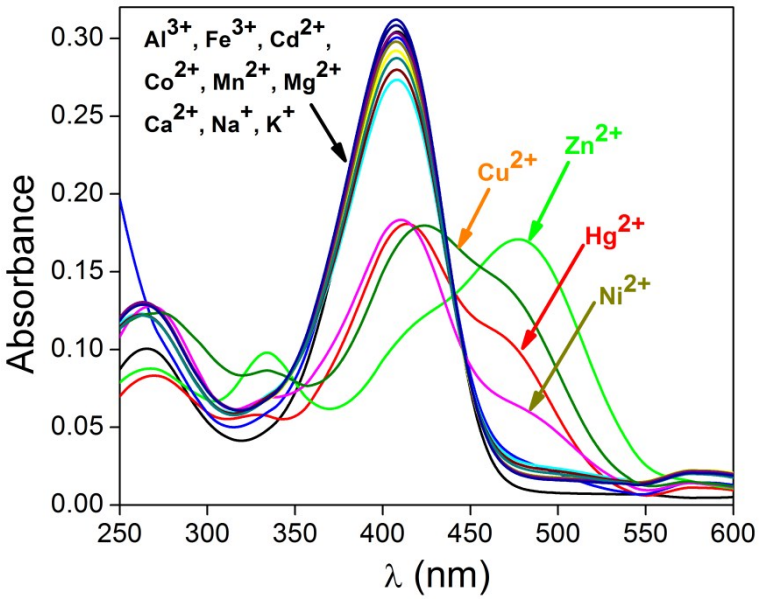


Figure S10: UV-vis change of SAPH (10 μM) upon addition of different metal ions (2 equiv.)

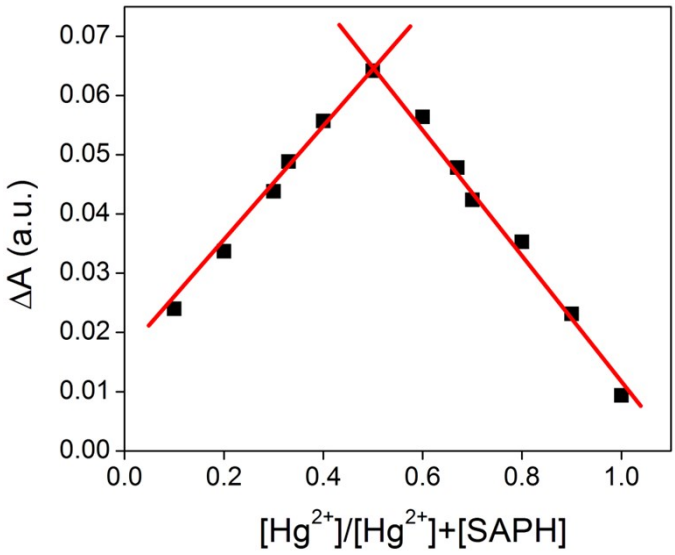


Figure S11a: Job's plot of SAPH for Hg^{2+}

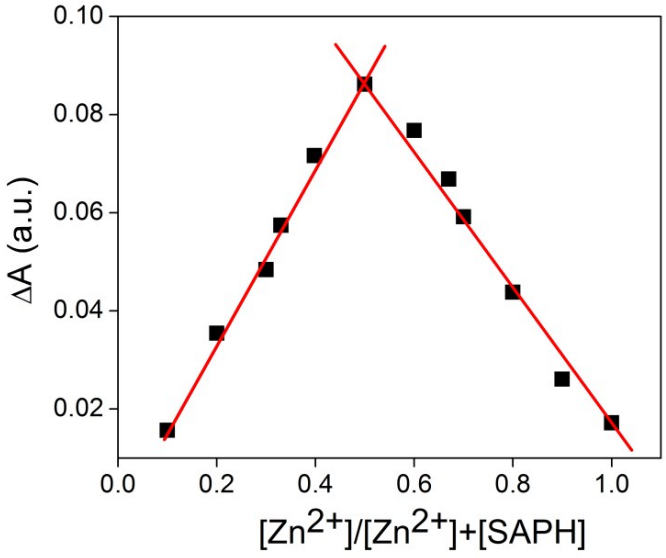


Figure S11b: Job's plot of SAPH for Zn^{2+}

Determination of binding constant from Fluorescence titration data:

Binding constant was calculated according to the Benesi-Hildebrand equation. K_a was calculated following the equation stated below.

$$1/(F-F_o) = 1/\{K_a(F_{max}–F_o)\ [M^{n+}]^x\} + 1/[F_{max}-F_o]$$

Here F_0, F and F_{max} indicate the emission in absence of, at intermediate and at infinite concentration of metal ion respectively.

Plot of $1/\ [F-F_0]$ vs $1/[Hg^{2+}]$ gives a straight line indicating 1:1 complexation between SAPH and Hg^{2+} where K_a is found to be $6.05\times 10^4\ M^{-1}$ for SAPH.

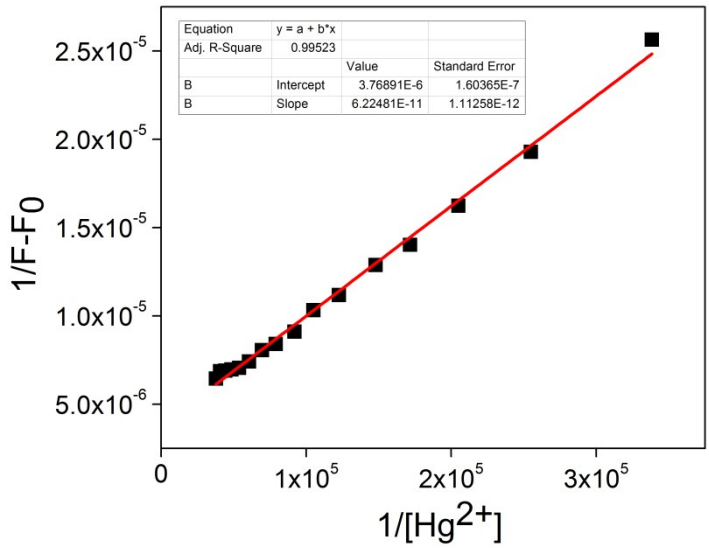


Figure S12a: Determination of association constant of SAPH at 647 nm depending on the Hg^{2+} concentration using Benesi-Hildebrand equation

Plot of 1/ [F-F_0] vs 1/[Zn^{2+}] gives a straight line indicating 1:1 complexation between SAPH and Zn^{2+} where K_a is found to be 3.03×10^5 M^{-1}.

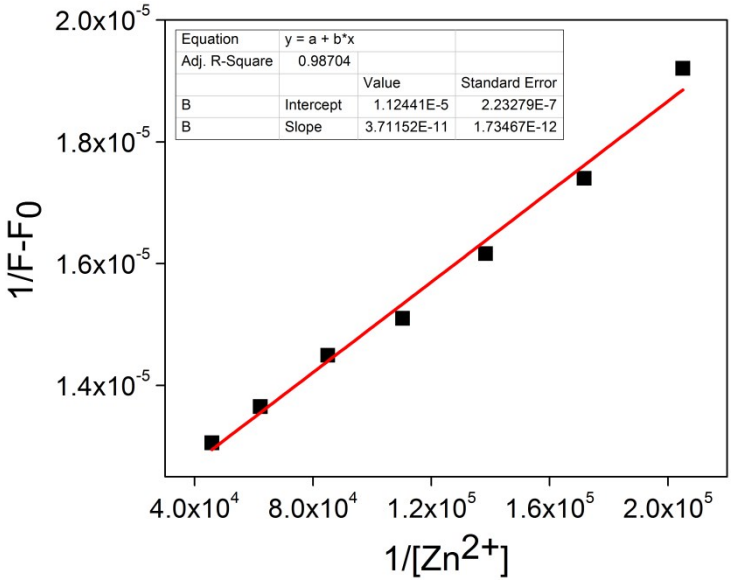


Figure S12b: Determination of association constant of SAPH at 678 nm depending on the Zn^{2+} concentration using Benesi-Hildebrand equation

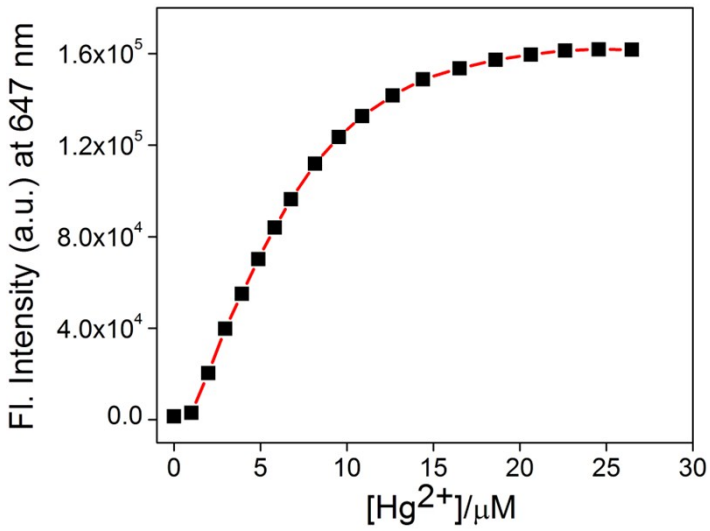


Figure S13a: Mole ratio plot of SAPH for Hg^{2+}

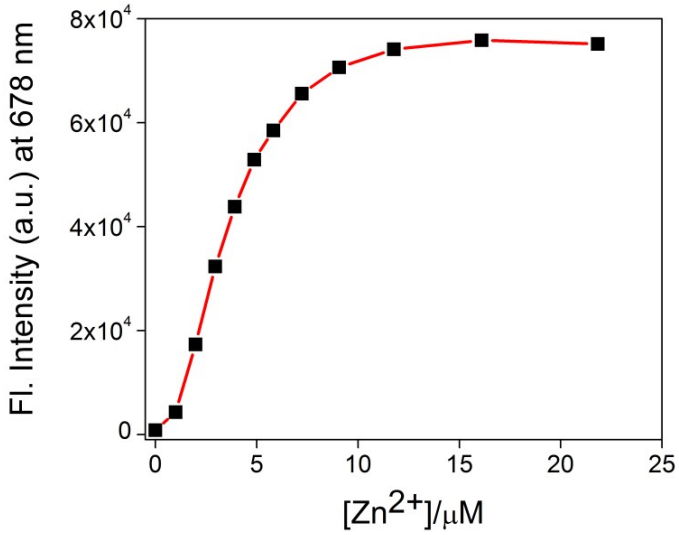


Figure S13b: Mole ratio plot of SAPH for Zn^{2+}

Determination of detection limit:

The detection limit was calculated based on the fluorescence titration. To determine the S/N ratio, the emission intensity of SAPH without the ions (Hg^{2+} and Zn^{2+}) was measured by 10 times and the standard deviation of blank measurements was determined. The detection limit of **SAPH** for Hg^{2+} and Zn^{2+} were determined from the following equation[1]:

$DL = K \times Sb_1/S$

Where K = 2 or 3 (we take 3 in this case); Sb_1 is the standard deviation of the blank solution; S is the slope of the calibration curve.

For Hg^{2+}:

From the graph we get slope = 1.28×10^{10} and Sb_1 value is 2.12844

Thus using the formula we get the Detection Limit = 4.98×10^{-10} M i.e., SAPH can detect Hg^{2+} in this minimum concentration by fluorescence techniques.

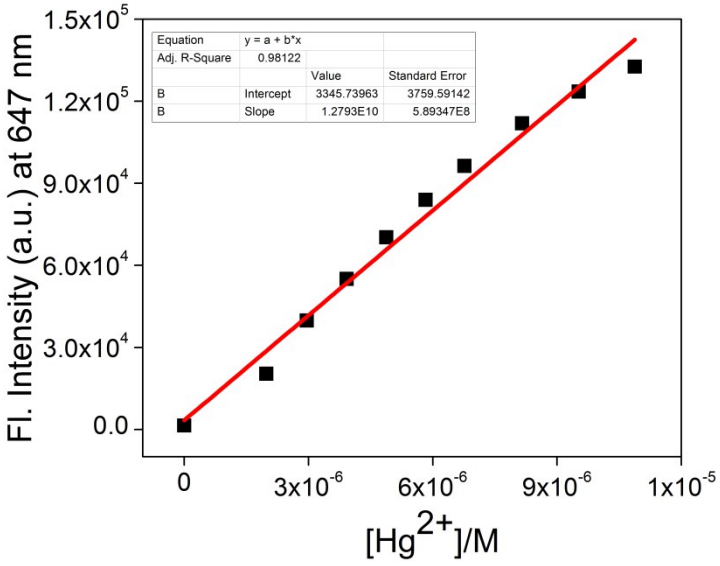


Figure S14a: Linear response curve of SAPH at 647 nm depending on the Hg^{2+} concentration

For Zn^{2+}:

From the graph we get slope = 1.09×10^{10} and Sb_1 value is 4.49294

Thus using the formula we get the Detection Limit = 1.23×10^{-9} M i.e., SAPH can detect Zn^{2+} in this minimum concentration by fluorescence techniques.

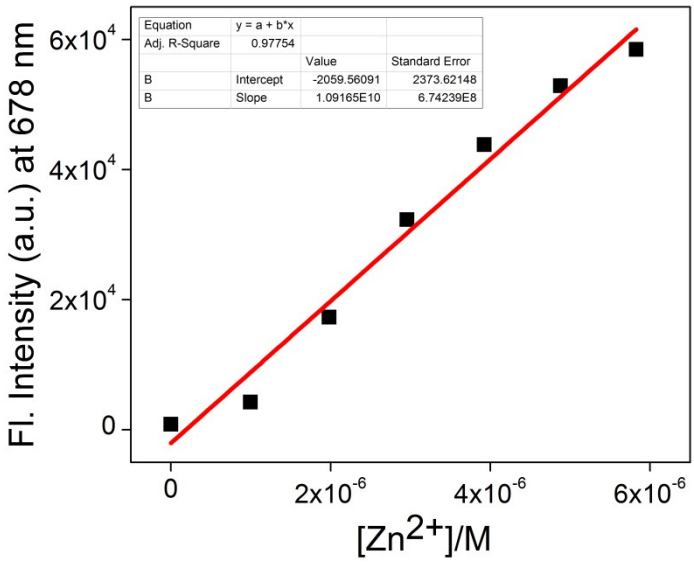


Figure S14b: Linear response curve of SAPH at 678 nm depending on the Zn^{2+} concentration

pH study:

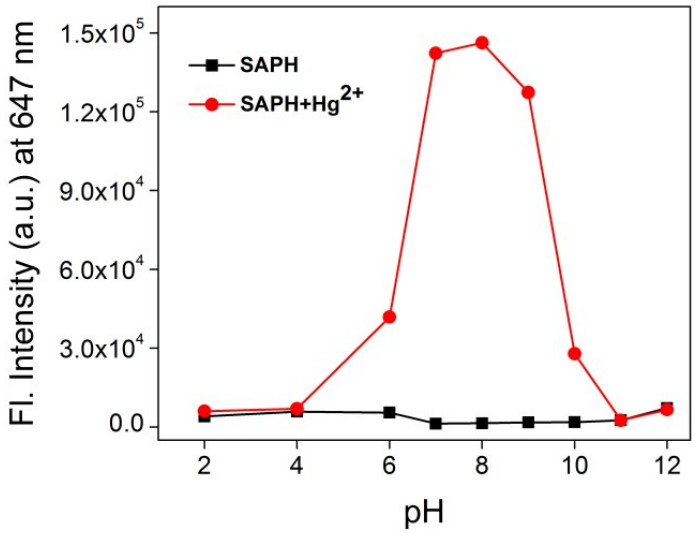


Figure S15a: pH study of SAPH for Hg^{2+}

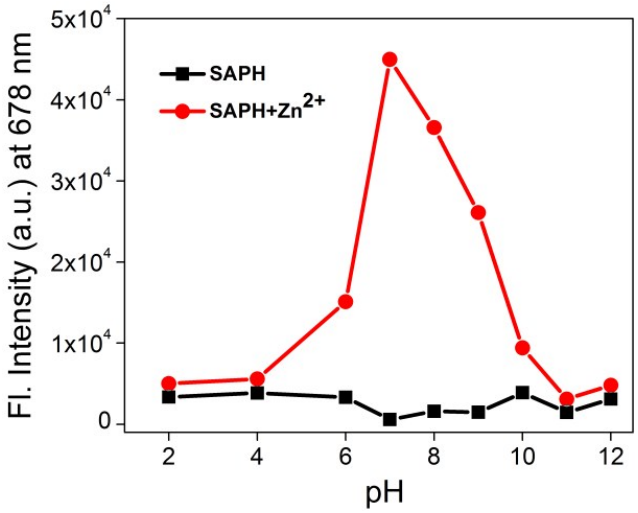


Figure S15b: pH study of SAPH for Zn^{2+}

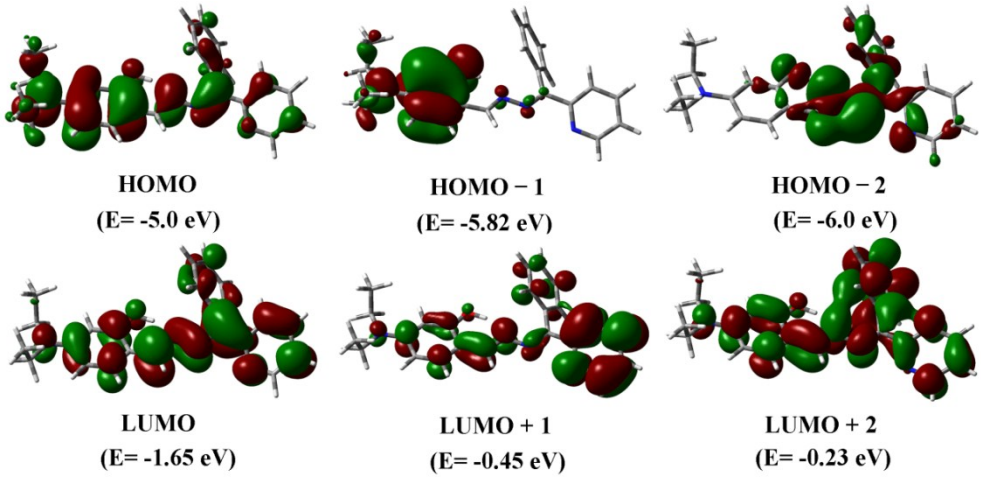


Figure S16. Contour plots of some selected molecular orbitals of SAPH

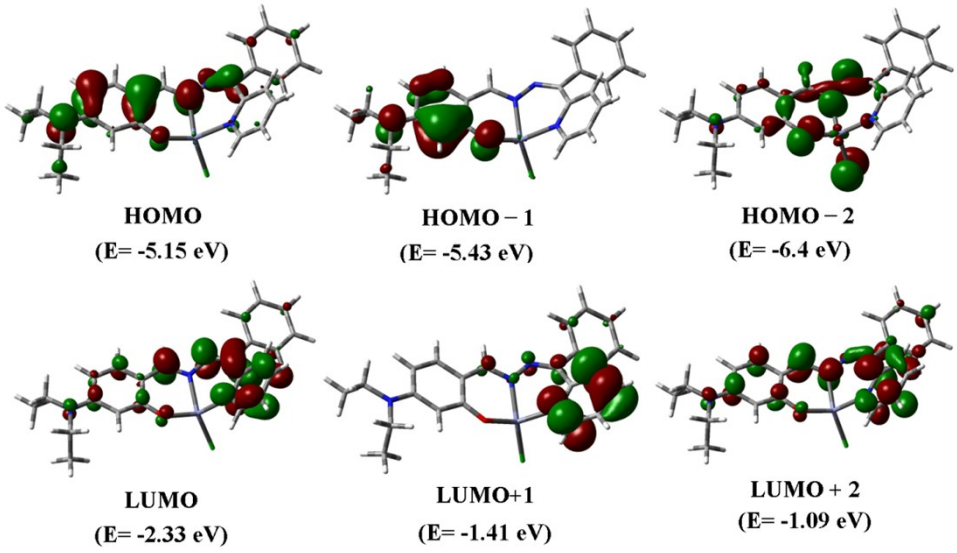


Figure S17. Contour plots of some selected molecular orbitals of SAPH-Zn^{2+}

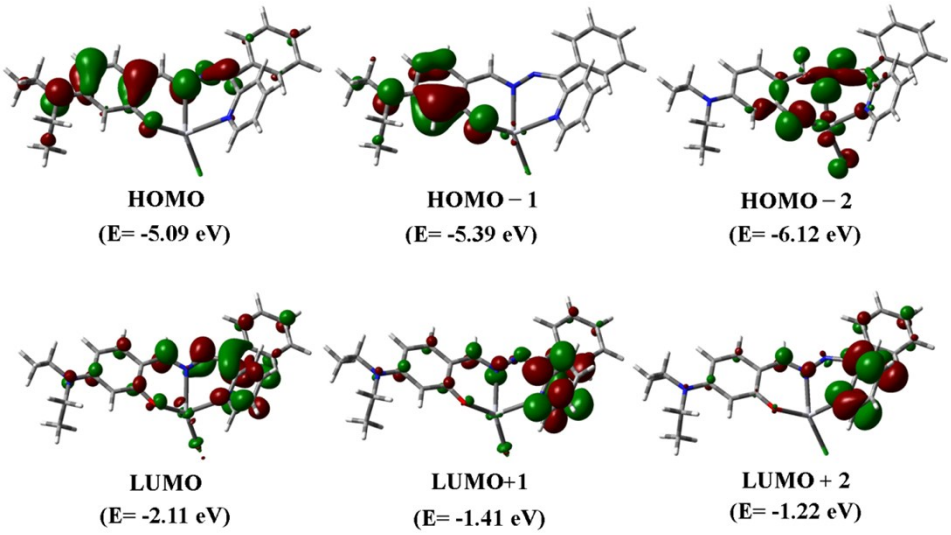


Figure S18. Contour plots of some selected molecular orbitals of SAPH-Hg^{2+}

MO	Energy (eV)	% of composition		
		SAPH	Zn	Cl
LUMO+5	0.6	96	4	0
LUMO+4	-0.15	100	0	0
LUMO+3	-0.5	99	1	0
LUMO+2	-1.09	99	0	0
LUMO+1	-1.41	99	1	0
LUMO	-2.33	99	0	0
HOMO	-5.15	99	1	0
HOMO-1	-5.43	98	1	1
HOMO-2	-6.4	80	2	19
HOMO-3	-6.54	6	3	90

HOMO-4	-6.58	78	1	22
HOMO-5	-6.67	39	3	58
HOMO-6	-6.98	99	0	0
HOMO-7	-7.25	95	3	2
HOMO-8	-7.44	48	7	45
HOMO-9	-7.65	65	7	29
HOMO-10	-7.92	98	1	2

Table S1. Energy and compositions of some selected molecular orbitals of SAPH-Zn^{2+}

Table S2. Energy and compositions of some selected molecular orbitals of SAPH-Hg^{2+}

MO	**Energy**	**% of composition**		
	(eV)	**Hg**	**Cl**	**SAPH**
LUMO+5	-0.12	1	0	99

LUMO+4	-0.51	5	0	95
LUMO+3	-0.96	7	1	92
LUMO+2	-1.22	1	0	99
LUMO+1	-1.41	3	4	93
LUMO	-2.11	6	2	92
HOMO	-5.09	1	0	98
HOMO-1	-5.39	2	1	97
HOMO-2	-6.12	7	5	88
HOMO-3	-6.53	0	0	100
HOMO-4	-6.92	7	22	71
HOMO-5	-6.98	1	4	95
HOMO-6	-7.23	5	68	27
HOMO-7	-7.26	5	70	25
HOMO-8	-7.54	4	13	84
HOMO-9	-7.74	1	2	98
HOMO-10	-7.86	14	36	50

Table S3. Vertical electronic transitions calculated by TDDFT/B3LYP/CPCM method for SAPH, SAPH-Zn^{2+} and SAPH-Hg^{2+} in acetonitrile

Compds.	**Energy (eV)**	**Wavelength (nm)**	**Osc. strength (f)**	**Transition**	**Character**
SAPH	2.9161	425.2	1.1171	(98%) HOMO→LUMO	$\pi(L)\rightarrow \pi^*(L)$
	3.4033	364.3	0.0368	(96%) HOMO-2→LUMO	$\pi(L)\rightarrow \pi^*(L)$
	4.0733	304.4	0.1959	(63%) HOMO→LUMO+1	$\pi(L)\rightarrow \pi^*(L)$
				(32%) HOMO-3→LUMO	
	4.6013	269.5	0.1398	(59%) HOMO-6→LUMO	$\pi(L)\rightarrow \pi^*(L)$
SAPH-Zn^{2+}	2.5364	488.8	0.7440	(95%) HOMO→LUMO	$\pi(L)\rightarrow \pi^*(L)$
	2.8585	433.7	0.0279	(97%) HOMO-1→LUMO	$\pi(L)\rightarrow \pi^*(L)$
	3.3770	367.1	0.0364	(61%) HOMO-2→LUMO	$\pi(L)\rightarrow \pi^*(L)$
				(31%) HOMO-3→LUMO	
	3.5301	351.2	0.2192	(89%) HOMO→LUMO+1	$\pi(L)\rightarrow \pi^*(L)$
	3.7052	334.6	0.3119	(74%) HOMO→LUMO+2	$\pi(L)\rightarrow \pi^*(L)$
SAPH-Hg^{2+}	2.5745	481.6	0.4651	(85%) HOMO→LUMO	$\pi(L)\rightarrow \pi^*(L)$
	2.9435	421.2	0.1531	(85%) HOMO-1→LUMO	$\pi(L)\rightarrow \pi^*(L)$
	3.2613	380.1	0.3207	(74%) HOMO→LUMO+1	$\pi(L)\rightarrow \pi^*(L)$
	3.5629	347.9	0.1596	(80%) HOMO→LUMO+3	$\pi(L)\rightarrow \pi^*(L)$
	3.9524	313.6	0.2178	(38%) HOMO-2→LUMO+1	$\pi(L)\rightarrow \pi^*(L)$
				(30%) HOMO-3→LUMO	$\pi(L)\rightarrow \pi^*(L)$