Electronic Supporting Information

Highly effective chemosensor for mercury ions based on bispyrenyl derivative

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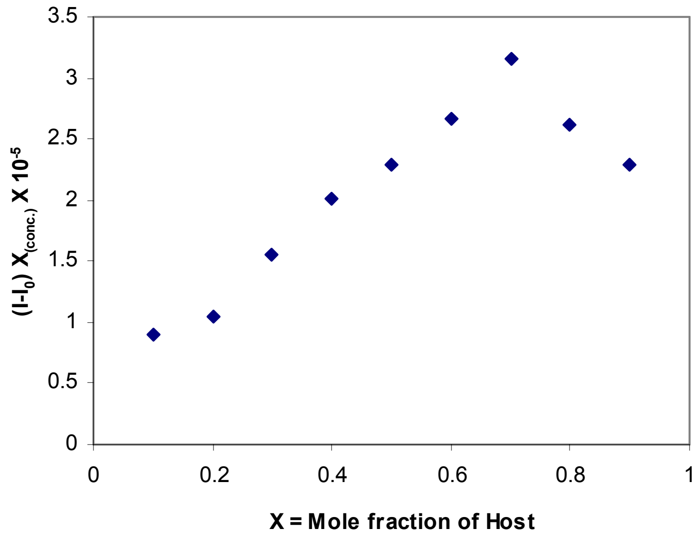


Figure S1. Job's Plot of Hg^{2+} with receptor **3.**

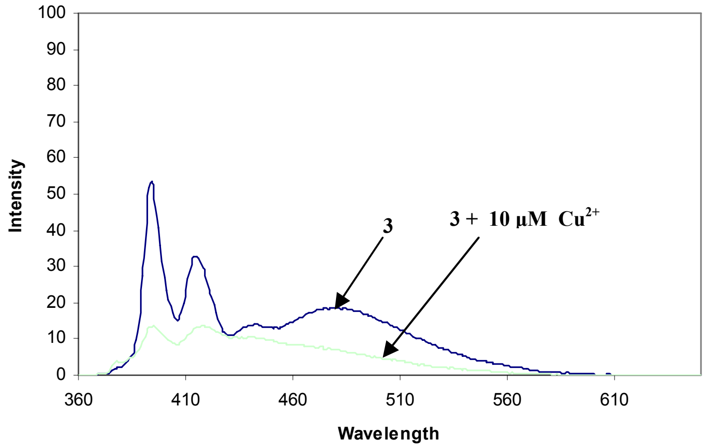


Figure S2. Fluorescence emission spectra of **3** (5 µM) in the presence of 10 µM **of Cu^{2+}** ions in THF. Excitation wavelength was 343 nm.

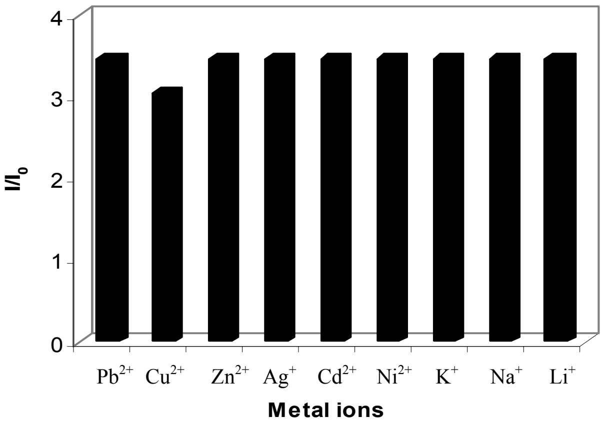


Figure S3. Fluorescence response of **3** (5 μM) on addition of 10 μM of Hg^{2+} ions in the presence of 50 μM of other selected metal ions .

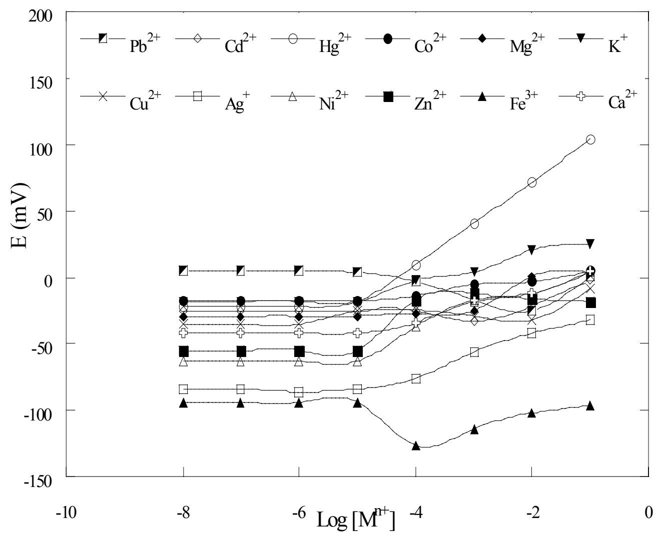


Figure. S4. Potentiometric response curves of ISEs based on **3** towards different metal ions.

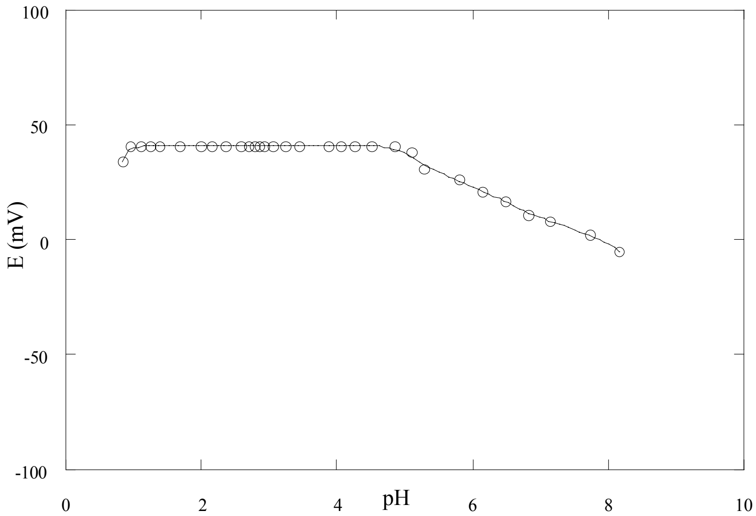


Figure S5. Effect of pH on potential response of **Hg^{2+}** ion selective electrode based on **3**.

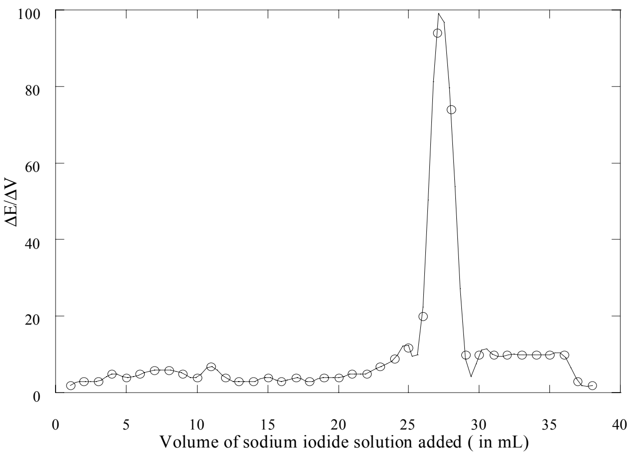
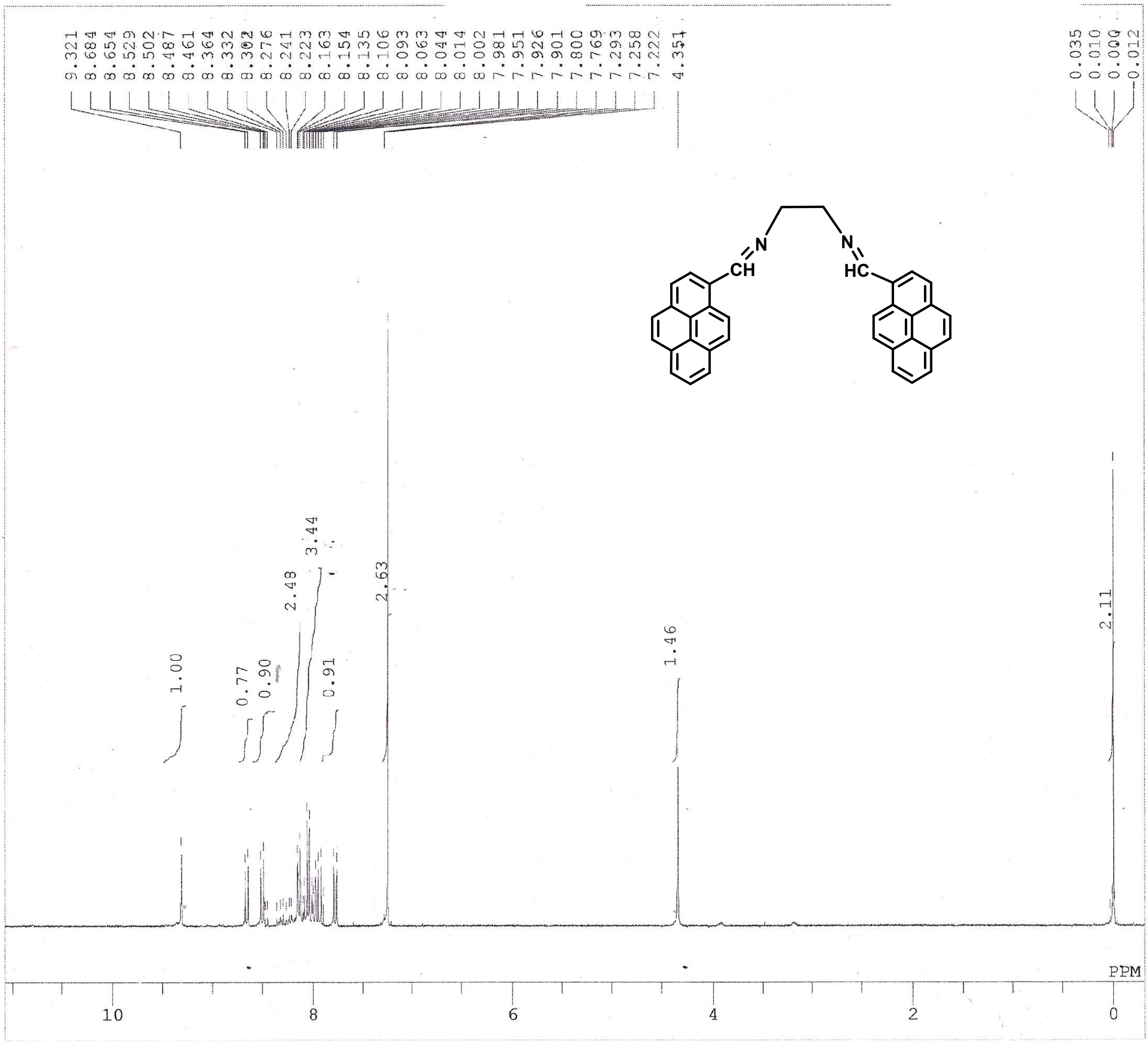
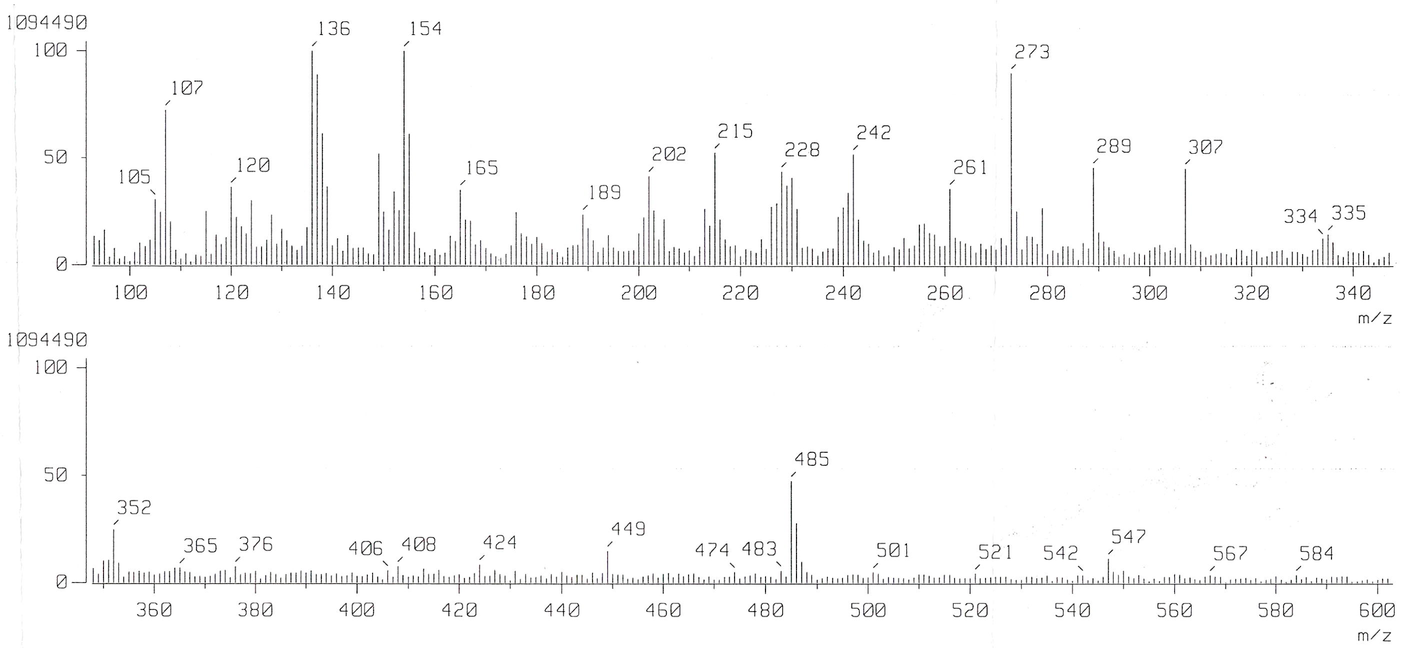


Figure S6. Derivative plot for titration of $\mathbf{Hg^{2+}}$ ions *vs* iodide ions using $\mathbf{Hg^{2+}}$ ion selective electrode E-1 as indicator electrode.

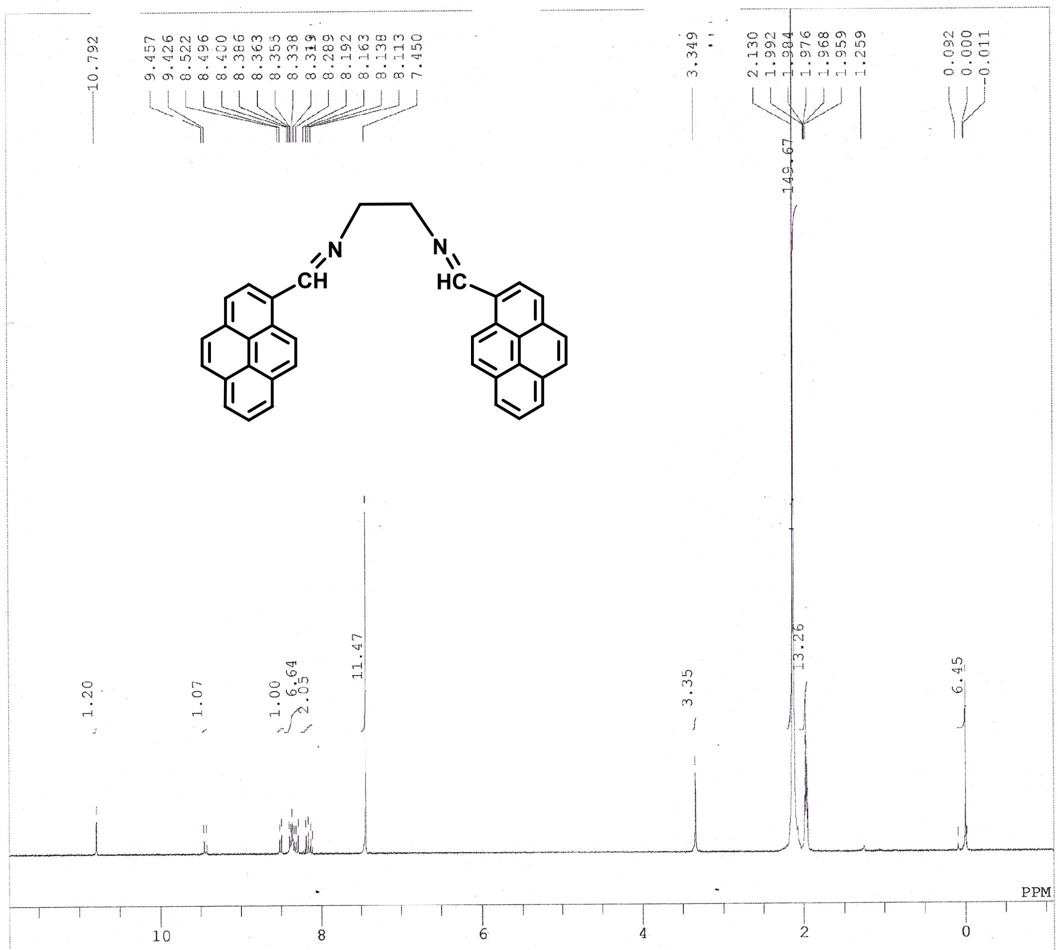
^{1}H NMR of compound **3**



Mass Spectrum of compound **3**



^{1}H NMR of compound **3 + 2 equiv. of Hg^{2+}** in $CDCl_3$:CD_3CN (8:2).



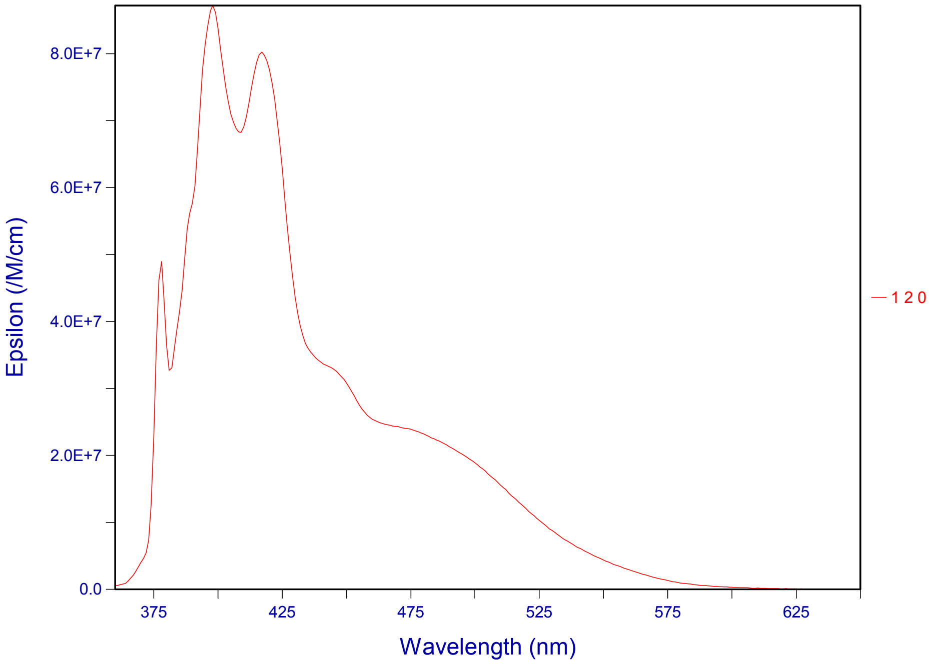


Figure. S7 Absorptivity graph for 1:2 (Hg^{2+} : ligand) obtained from SPECFIT data.

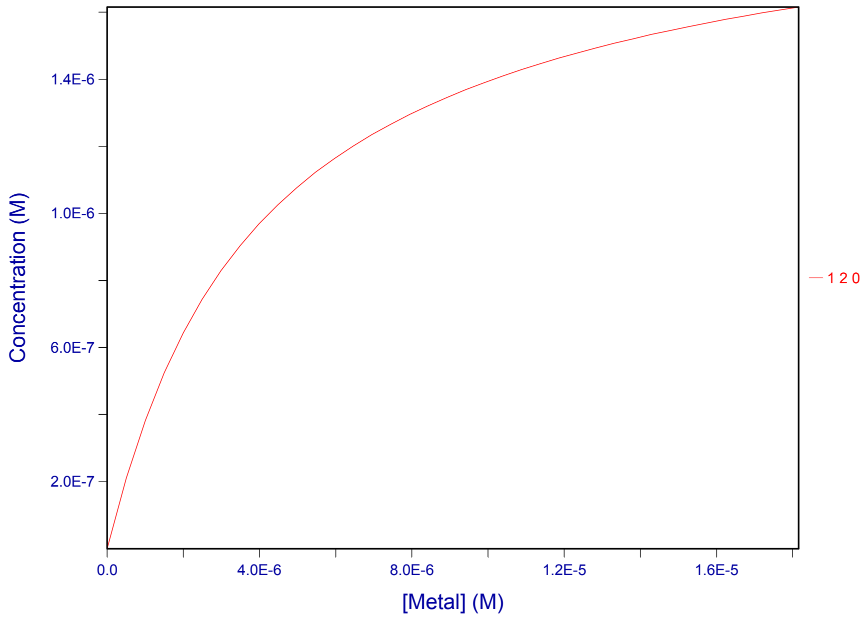


Figure. S8 Concentration plot for 1:2 (Hg^{2+} : ligand) obtained from SPECFIT data.

Optimization of Mercury (II) ion selective electrode

Table S1. Optimization of receptor **3** based mercury(II) ion-selective membrane electrode (PME)

S.No	PVC (mg)	Plasticiser (mg)	NaTPB (mg)	Ionophore (mg)	Linear Range (M)	Detection Limit (M)	Slope (mV/decade)
E-1	100.6	201.6 DOS	1.4	5.7	$1.0 X 10^{-1}$ - $1.0 X 10^{-5}$	$7.08 X 10^{-6}$	30.67
E-2	100.6	201.6 DOS	1.4	4.1	$1.0 X 10^{-1}$ - $5.0 X 10^{-5}$	$3.16 X 10^{-5}$	24.87
E-3	100.6	201.6 DOS	1.4	8.3	$1.0 X 10^{-1}$ - $5.0 X 10^{-5}$	$1.77 X 10^{-5}$	39.78
E-4	100.6	201.6 DOS	-	5.7	$1.0 X 10^{-1}$ - $1.0 X 10^{-4}$	$7.94 X 10^{-5}$	52.02
E-5	100.6	201.6 DOS	3.2	5.7	$1.0 X 10^{-2}$ - $5.0 X 10^{-5}$	$1.36 X 10^{-5}$	62.49
E-6	100.3	199.7 DOA	1.4	5.8	$1.0 X 10^{-2}$ - $1.0 X 10^{-5}$	$9.18 X 10^{-6}$	42.10
E-7	100.4	201.7 DOP	1.4	5.7	$1.0 X 10^{-1}$ - $5.0 X 10^{-5}$	$2.29 X 10^{-5}$	21.86
E-8	100.4	198.6 DBP	1.4	5.7	$1.0 X 10^{-1}$ - $1.0 X 10^{-5}$	$8.46 X 10^{-6}$	46.73
E-9	100.7	199.5 TBP	1.4	5.7	$1.0 X 10^{-1}$ - $5.0 X 10^{-5}$	$6.84 X 10^{-5}$	38.65

Optimization of receptor 3 based mercury (II) ion selective electrode was carried out by studying the effect of different membrane components (Ionophore, lipophilic negatively charged additives and plasticizer) on membrane response.

Effect of ionophore content on response characteristics of mercury(II) ion selective electrode incorporating **3** as ion carrier was studied incorporating varying amounts of ion carrier **3** in membrane preparation (Table S1). From the different membranes sensors so prepared (E1-E3), the membrane sensor E1 containing 5.7 mg of ionophore exhibited lower detection limit of 7.08 X 10^{-6} M within a wide concentration range of 1.0 X 10^{-1} M to 1.0 X10^{-5} M of mercury(II) ions with Nernstian slope of 30.67mV per decade.

Presence of lipophilic negatively charged additives is known to improve the response characteristics of ion selective electrodes by reducing its ohmic resistance and increasing the extraction capability of ionophore. Effect of amount of additive on the response characteristics of mercury(II) ion selective electrodes incorporating **3** as ion carrier was studied using varying amounts of NaTPB as an additive for membrane preparation (Table S1). Out of different membranes electrodes so prepared (E1, E4, E5), membrane electrode E1 containing 1.4 mg, NaTPB exhibited the lower detection limit of 7.08×10^{-6} M within a wide concentration range of 1.0×10^{-1} M to 1.0×10^{-5} M of mercury(II) ions. The better slope of Nernstian nature i.e. 30.67mV per decade was also obtained with electrode E1.

Plasticizers are known to influence the membrane response by changing its dielectric constant, affecting the ligand state and ionic mobility. The effect of plasticizer on potential response of mercury(II) ion selective electrode incorporating **3** as ion carrier was studied by preparing different membrane sensors (E1, E6-E9) containing plasticizers such as DOS, DOA, DOP, DBP, TBP and the results obtained are summarized in Table S1. The electrodes prepared by incorporating DOA, DBP and TBP (E6, E8 and E9) exhibited super-Nernstian slope while one with DOP (E7) exhibited sub-Nernstian response. The potential response of membrane sensor (E1) incorporating DOS as a plasticizer was found to be better in terms of slope (30.67±1mV per decade) and the linear concentration range (1.0×10^{-1} M to 1.0×10^{-5} M).

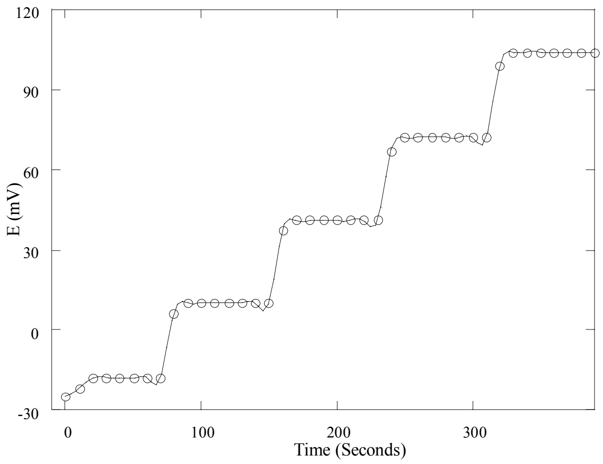


Figure. S9 Time response curve of **Hg^{2+}** ion selective electrode E-1 based on **3**.

Table S2: Comparison of proposed **3** mercury (II) ion-selective electrodes to the reported $\mathbf{Hg^{2+}}$ sensors

Ionophore	Linear Range (M)	Detection Limit (M)	Slope (mV per decade)	Log $K^{Pot.}_{Hg^{2+},Ag^{+}}$	Log $K^{Pot.}_{Hg^{2+},Fe^{3+}}$
Receptor 3 (Present work)	1.0×10^{-1} - 1.0×10^{-5}	7.08×10^{-6}	30.67	-0.20	-4.09
[53] PME (1-furan-2-yl-4-(4-nitrophenyl)-2-phenyl-5H-imidazole-3-oxide**)**	1.0×10^{-1} - 1.0×10^{-5}	6.3×10^{-6}	29.40	3.40	-2.75
[54] Antimony III arsenate	1.0×10^{-2} - 5.0×10^{-5}	5.0×10^{-5}	28.00	1.25	-0.3
[55]N-(o, o-diisopropylthiophosphoryl) Thiobenzamide	1.0×10^{-2} - 5.0×10^{-5}	$> 10^{-5}$	29.00	-0.02	-3.41
[56]Diaza-18-crown-6	1.0×10^{-3} - 1.0×10^{-5}		28.40	2.60	4.00
[57][5,11,17,23,29,35-Hexa(1-thiazole)azo] 37,38,39,40,41,42-hexahydroxycalix[6] arene	1.0×10^{-2} - 5.0×10^{-6}	4.0×10^{-6}	28.70	0.70	-1.54
[58] MB1M	1.0×10^{-1} - 1.0×10^{-5}	7.0×10^{-6}	28.50	0.56	