Hyperbranched polyethylenimine based multiple metal ions (Cu²⁺, Co²⁺ and Fe²⁺) sensor: Colorimetric sensing via coordination complex and silver nanoparticles formation

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Fig. S1. Selectivity studies of HPEI for Cu^{2+} (μM) in presence of different metal ions (mM) in aqueous solution. Black bar (different metal ions) and red bar (different metal ions along with Cu^{2+}).



Fig. S2. Digital and absorption spectra of HPEI with different metal ions at pH 8.0.



Fig. S3. Absorption spectra of HPEI-Ag⁺ with different metal ions at pH 10.0.



Fig. S4. Absorption spectra of HPEI-Ag $^+$ with different metal ions at pH 6.0.



Fig. S5. HR-TEM images of HPEI-Ag⁺ after the addition of Co²⁺ at pH 10.0



Fig. S6. HR-TEM images of HPEI-Ag⁺ after the addition of Fe^{2+} at pH 10.0.



Fig. S7. Absorption of HPEI-Ag⁺ Vs concentration of (a) Co^{2+} and (b) Fe^{2+} .



Fig. S8. Selectivity studies of HPEI-Ag⁺ for Co^{2+} (μM) in presence of different metal ions (mM) in aqueous solution. Black bar (different metal ions) and red bar (different metal ions along with Co^{2+}).



Fig. S9. Selectivity studies of HPEI-Ag⁺ for Fe²⁺ (μ M) in presence of different metal ions (mM) in aqueous solution. Black bar (different metal ions) and red bar (different metal ions along with Fe²⁺).



Fig. S10. Digital images of HPEI-Ag+ with Co^{2+} and Fe^{2+} at inert and ambient condition (air equilibrated condition). There is no color or AgNPs formation in obscene of oxygen, however, exposing to air produced yellow or brownish-yellow color immediately.



Fig. S11. Digital images of Ag^+ with Co^{2+} and Fe^{2+} in PVA and PVP polymer instead of HPEI. Co^{2+}/Fe^{2+} was added into PVA- Ag^+/PVP - Ag^+ . There is no color formation was observed with both PVA or PVP polymer and suggest that HPEI polymer promotes the oxidation of Co^{2+}/Fe^{2+} in presence of oxygen and silver ions.

Limit of detection calculation (LOD)

$$LOD = \frac{F \times SD}{b}$$

Where,

F: Factor of 3.3 for LOD

SD: Standard deviation of the blank, standard deviation of the ordinate intercept, or residual

standard deviation of the linear regression

b: Slope of the regression line

Validation of Analytical Method

Construction of calibration curve & analysing its data

X axis—Concentration (µg/ml)

Y axis—Analytical signal (Absorbance, Fluorescence, Peak Area)

Obtaining a 1st Order regression equation—Y=aX+b, (a= Slope, b=intercept) & R²

Calc. the found Conc. (x) From the eqn,

found Conc. (X)=(Y-b)/a =(Analytical signal-Intercept)/Slope

Calc. Recovery%----recovery%=Found Conc./labelled (or claimed) Conc. *100

Calc. Mean of recoveries-----By excel function (<u>mean= Σ recoveries/n</u>) i.e (n=no. of conc. i.e no.

of calibration points)

Calc. SD of recoveries----By excel function

Assay Validation Sheet

Accuracy=mean±SD

Slope=a

Intercept=b

Linearity range (lowest conc: highest conc) within which the curve is linear

Correlation coefficient (r)= $\sqrt{R^2}$

SE of intercept—By Excel function (Data analysis>Regression>Third table)

SD of intercept—SE of intercept $*\sqrt{n}$

LOD=3.3(SD of intercept/Slope)

For Cu²⁺

Parameter	Value
Accuracy	115.558 ± 33.170
Slope	1.4812
Intercept	0.2373
Linearity range	0.2-1 μg/ml
Correlation coefficient (r)	0.9937
SE of intercept	0.036
SD of intercept	0.115
LOD	0.257 μg/ml

For Co²⁺

Parameter	Value
Accuracy	107.722 ± 24.70871
Slope	0.0015
Intercept	0.2207
Linearity range	100-900µg/ml
Correlation coefficient (r)	0.9822
SE of intercept	0.06388
SD of intercept	0.201862
LOD	40.0972 μg/ml

For Fe²⁺

Parameter	Value
Accuracy	72.519942 ± 14.471
Slope	0.0013
Intercept	0.0787
Linearity range	200-900 µg/ml
Correlation coefficient (r)	0.9905
SE of intercept	0.0392
SD of intercept	0.1240
LOD	30.167µg/ml