Supplementary Information

Self-Assembled Tetracyanoquinodimethane Derivatives: Differential Fluorescent Responses on Sensing Copper and Mercury Ions in Aqueous Medium

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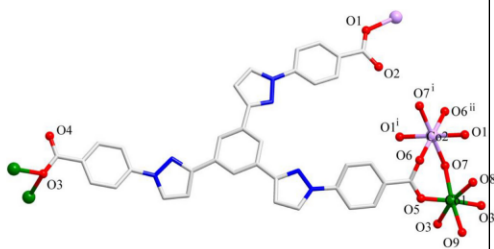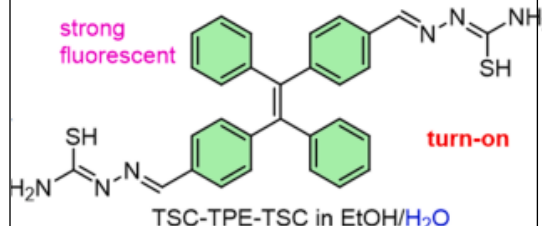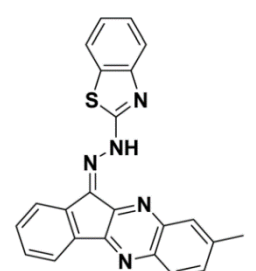
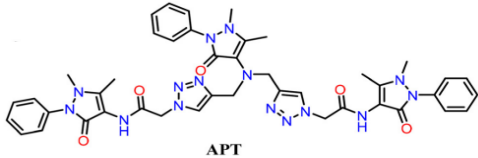Correspondence e-mail: jslakshmi@hyderabad.bits-pilani.ac.in

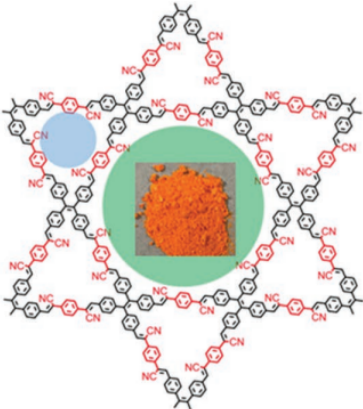**S:** *Supplementary information*

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Table S1 Comparative table for fluorescent probes with respect to synthesis condition, sensing ions, detection method, LOD, solvent medium.

Fluorescent Probe	Synthesis Condition	Sensing Ions & Detection Method	LOD (M)	Solvent Medium	References
[Co3(L)2(H2O)6]n (1) L= 1,3,5-(tris(1-(4- carboxyphenyl) −1h-pyrazol-3-yl) benzene (H3L) 	In autoclave Temperature :140 °C, Time : 72 h, Multistep synthesis	Cu^{2+} Fluorescence (Quenching) Hg^{2+} Fluorescence (Quenching)	Cu^{2+} 9.91×10^{-7} Hg^{2+} 1.26×10^{-5}	N,N-dimethylac etamide (DMA)	[1]
2-(4-Bromophenyl)ethene-1,1,2-triyl)tribenzene (2) and 4-(1,2,2-triphenylvinyl)benzaldehyde 	Temperature : -78 °C, Time : 48 h, Multistep synthesis	Cu^{2+} Fluorescence (Quenching) Hg^{2+} Fluorescence (Quenching)	Cu^{2+} 2.42×10^{-6} Hg^{2+} 0.39×10^{-6}	EtOH/H2O (v/v:1/1)	[2]
Quinoxaline–hydrazinobenzothiazole 	Temperature : 70 °C, Time : 12 h, Multistep synthesis	Cu^{2+} Fluorescence (Enhancement) Co^{2+} Fluorescence (Enhancement) Ni^{2+} Fluorescence (Enhancement) Hg^{2+} Fluorescence (Enhancement)	Cu^{2+} 1.16×10^{-7} Hg^{2+} 1.14×10^{-7}	THF : H2O (1 : 9, v/v) (pH 7.4, 20 mM HEPES buffer)	[3]

4-amino antipyrine linked bis-1,2,3-triazole 	Temperature : RT, Time : 18 h, Multistep synthesis	Cu^{2+} Absorbance (Enhancement) Hg^{2+} Absorbance (Enhancement)	Cu^{2+} 63×10^{-6} Hg^{2+} 56×10^{-6}	DMSO	[4]
Tetraphenylethylene (TPE) based COF nanosheets 	Temperature : 120 °C, Time : 5 days, Multistep synthesis	Cu^{2+} Fluorescence (Quenching)	0.28×10^{-9}	Neutral F127 surfactant in aqueous media	[5]
This Work	**Temperature : 75 °C, Time: 3 h, Simple single step synthesis**	**Cu^{2+} Fluorescence (Quenching) Hg^{2+} Fluorescence (Quenching in case of [2,3] and enhancement in [1])**	**Cu^{2+} 0.751×10^{-6} Hg^{2+} 3.1937×10^{-6}**	**MeCN: H_2O (1:9)**	

References

1. Y. Xi, M. Hua , L. Gao, Q. Sun , E. Ma , W. Hu , M. Li , W. Liu , J. Sun and C. Zhang, *J. Mol. Struct.*, 2023, **1284**, 135456.
2. S. Bayindir , A. S. Hussein, F. Lafzi and M. Toprak, *J. Mol. Liq.*, 2023, **382**, 121939.
3. D. B. C. Leslee, U. Venkatachalam, J. Gunasekaran, S. Karuppannan and S. Bharathi Kuppannan, *Org. Biomol. Chem.*, 2023, **21**, 4130–4143.
4. S. Kumar, B. Lal, R. K. Tittal, G. Singh, J. Singh, G. Vikas D, R. Sharma and J. K. Sabane *Sens. Diagn.*, 2023, **2**, 1267–1276.
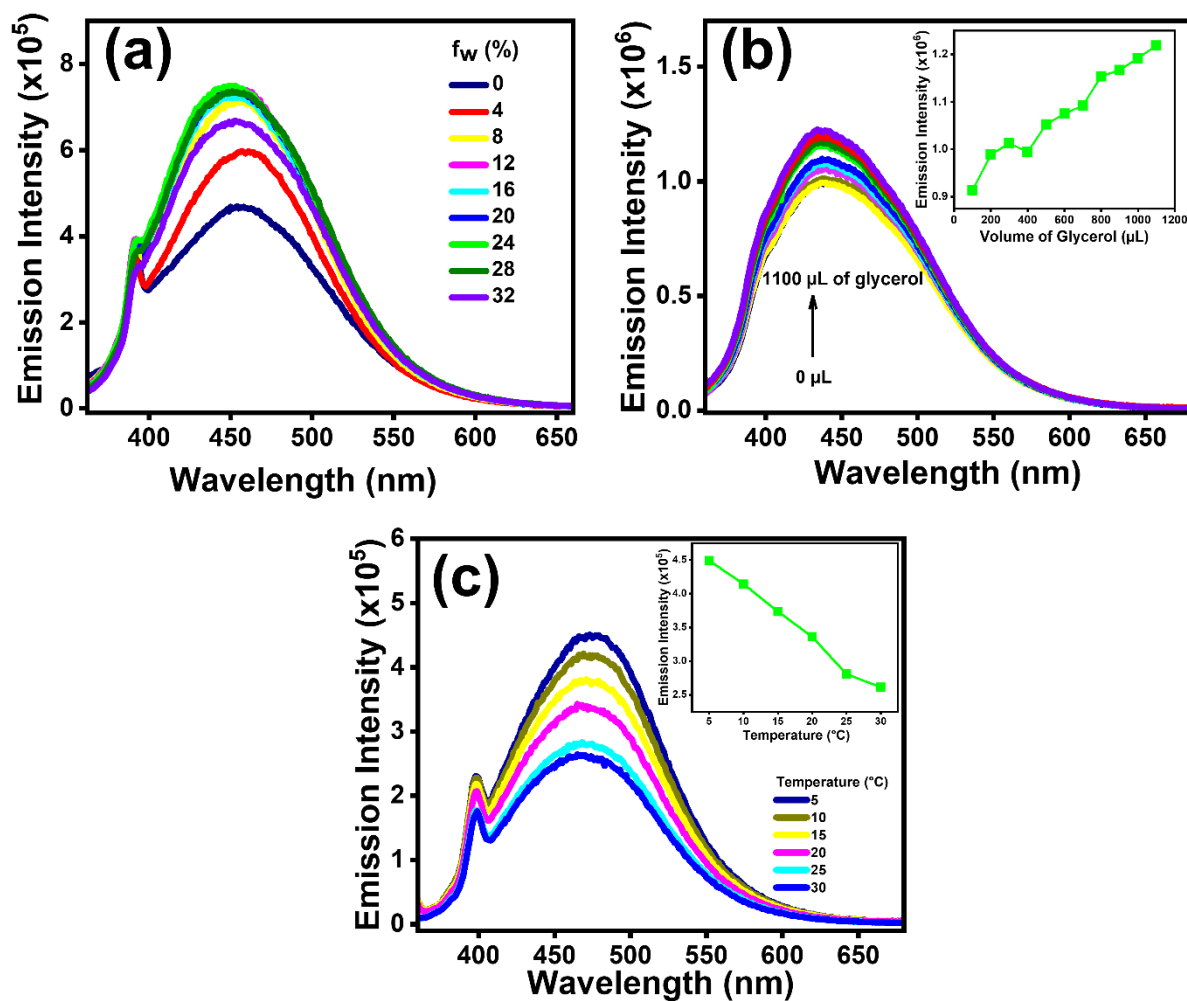5. Zi. Yan, L. Fang, Z. He, H. Xie, B. Liu , B. Guo and Y. Yao, *Small*, 2022, **18**, 2200388.

Fig. S1 (a) Increase of emission intensity with the increase in water fraction, (b) enhanced emission intensity with higher viscosity, (c) decrease in emission intensity with higher temperature for **[1]**.
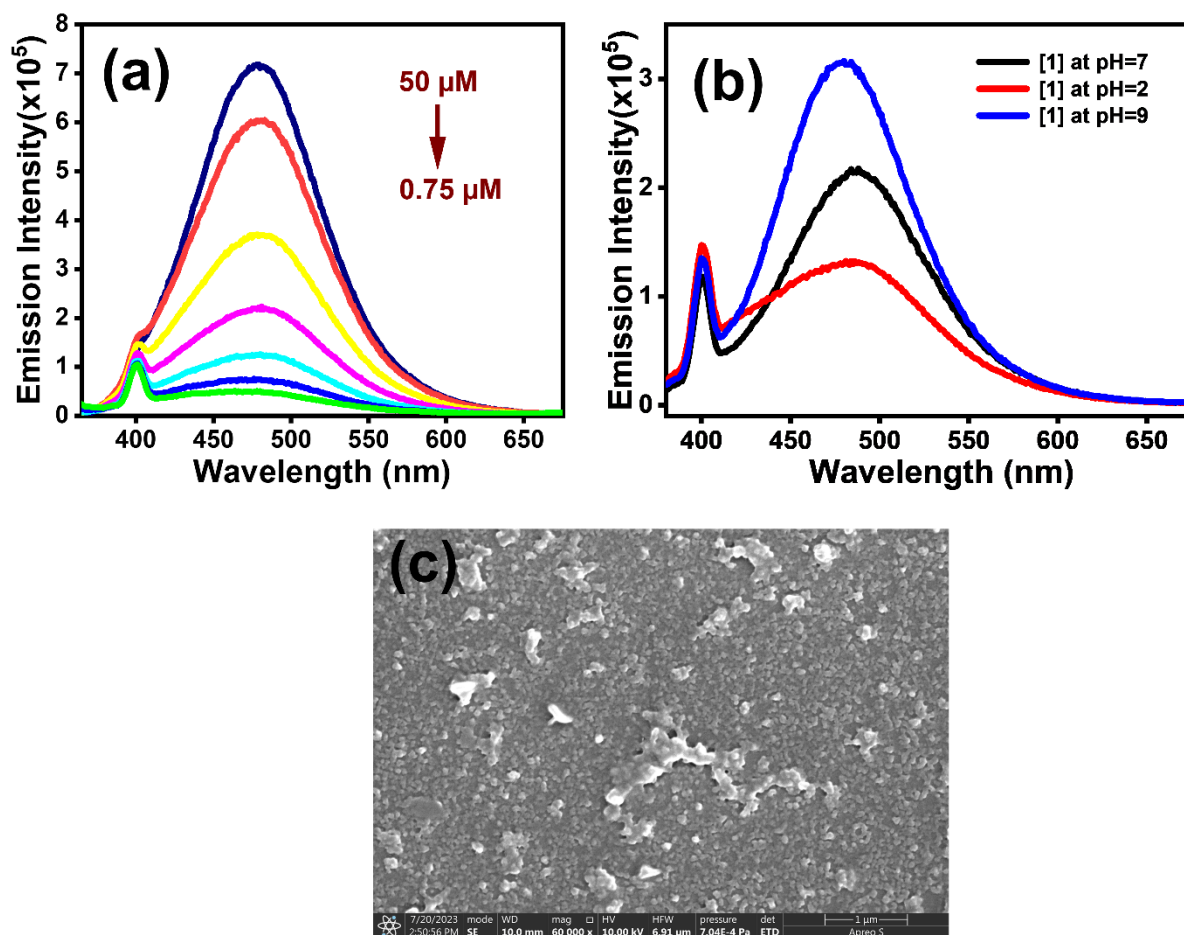
Fig. S2 (a) Lowering of emission intensity with the decrease in concentration, (b) enhanced emission intensity with higher pH, (c) formation of aggregates observed in SEM image for **[1]**.
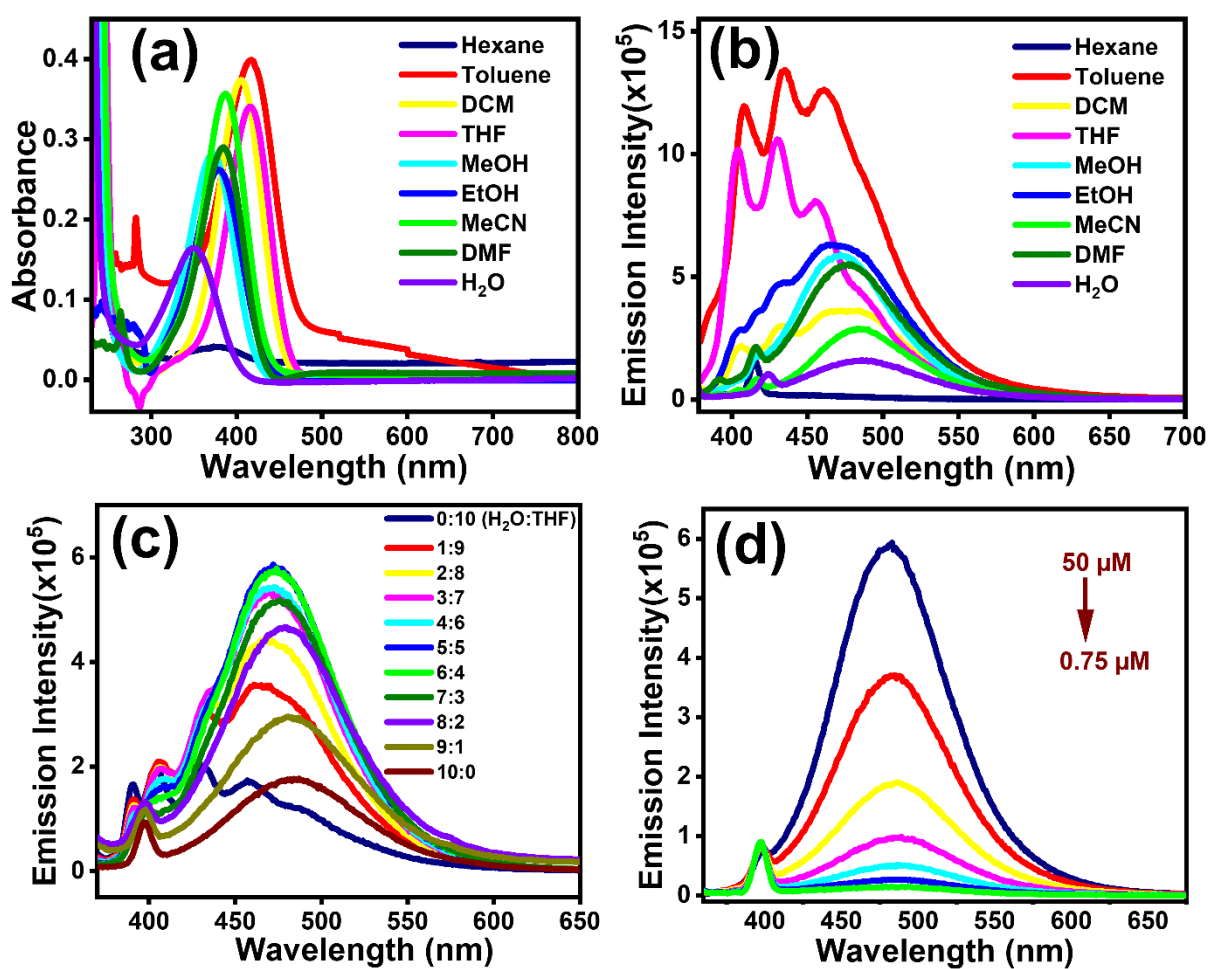
Fig. S3 [2] (a) Shift in absorption spectra and (b) emission spectra ($\lambda_{exc} \sim 370$ nm) with increase in polarity depicting solvatochromism, (c) quenching of emission intensity due to aggregation in varying proportions of H_2O:THF solvent mixture, (d) lowering of emission intensity with the decrease in concentration.
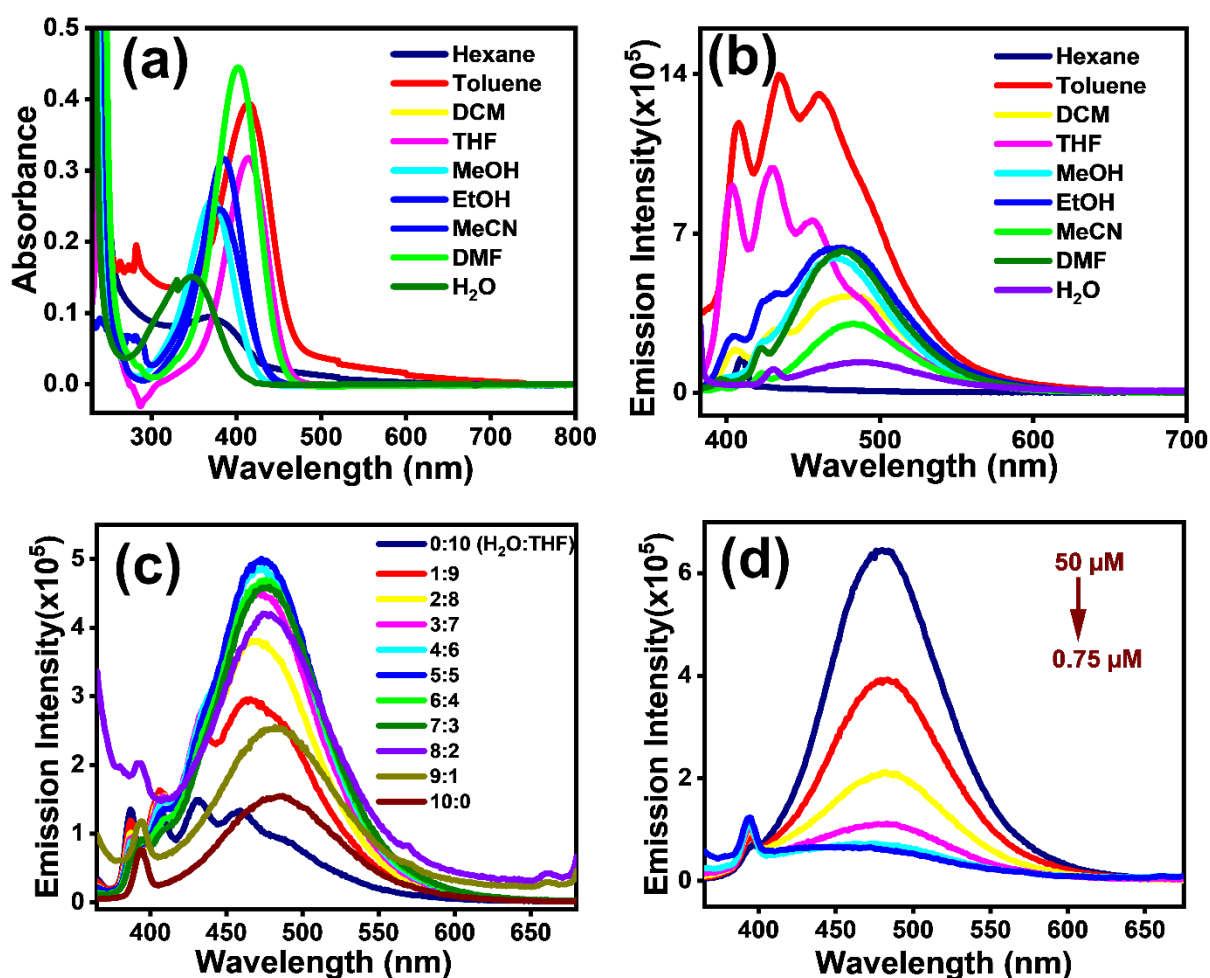

Fig. S4 [3] (a) Shift in absorption spectra and (b) emission spectra ($\lambda_{exc} \sim 375$ nm) with increase in polarity depicting solvatochromism, (c) quenching of emission intensity due to aggregation in varying proportions of H_2O:THF solvent mixture, (d) lowering of emission intensity with the decrease in concentration.
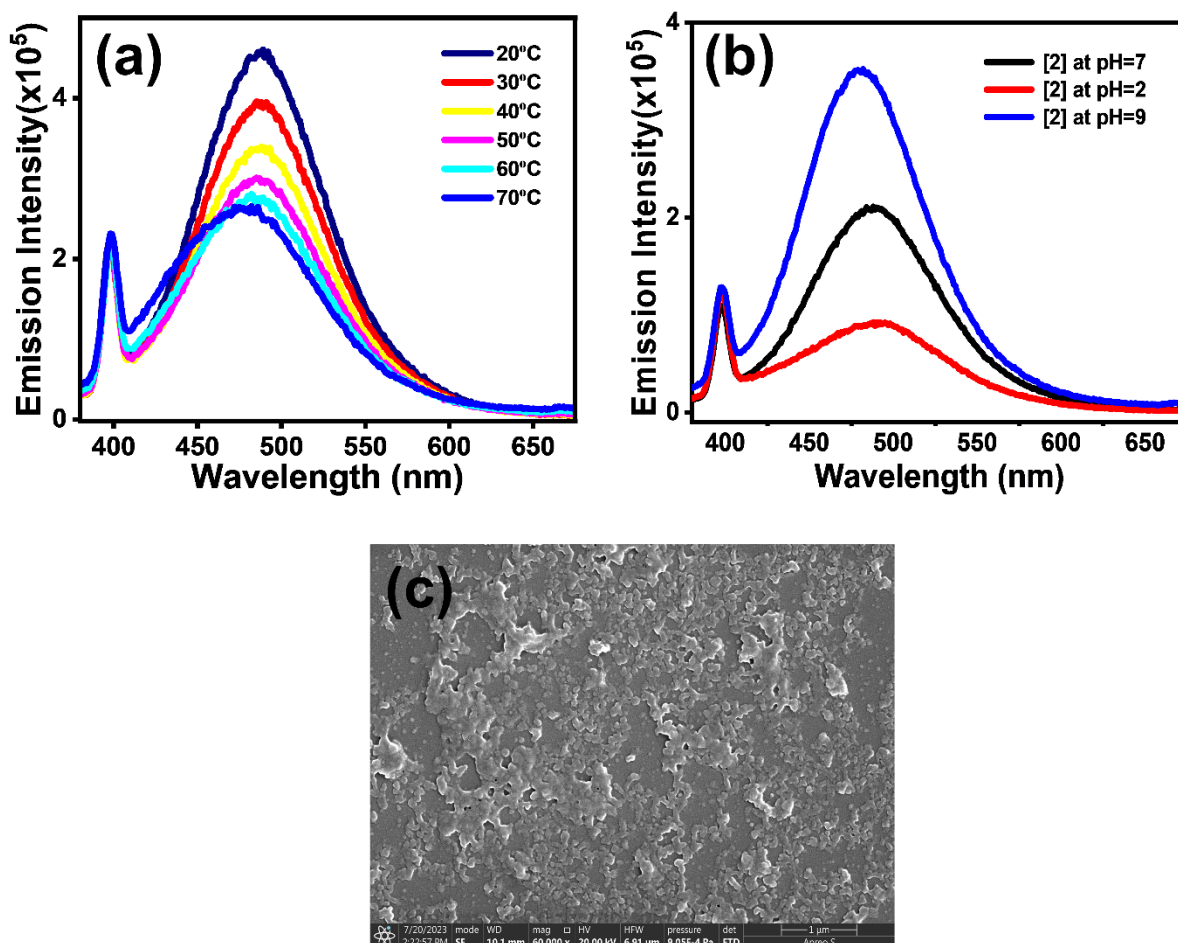
Fig. S5 (a) Lowering of emission intensity with the increase in temperature, (b) enhanced emission intensity with higher pH, (c) formation of aggregates observed in SEM image for **[2]**.
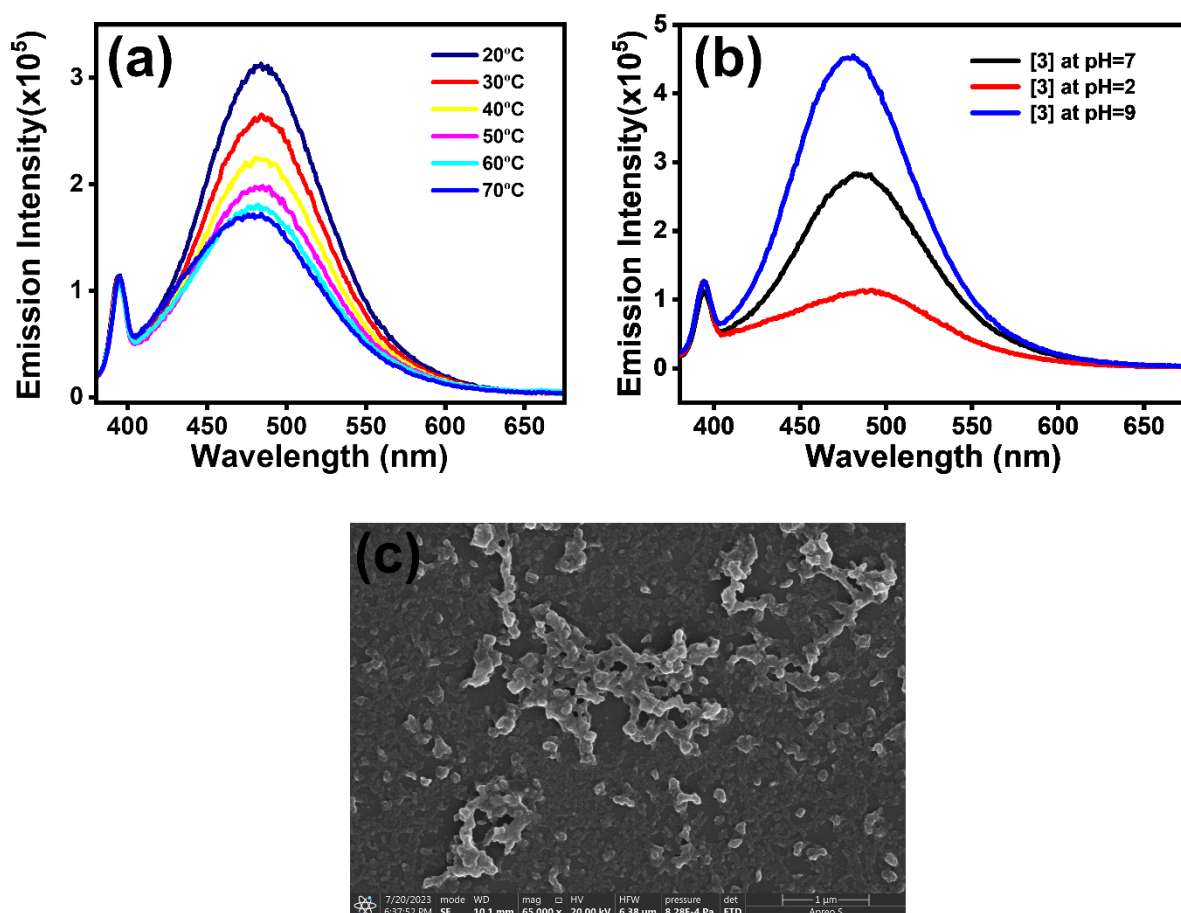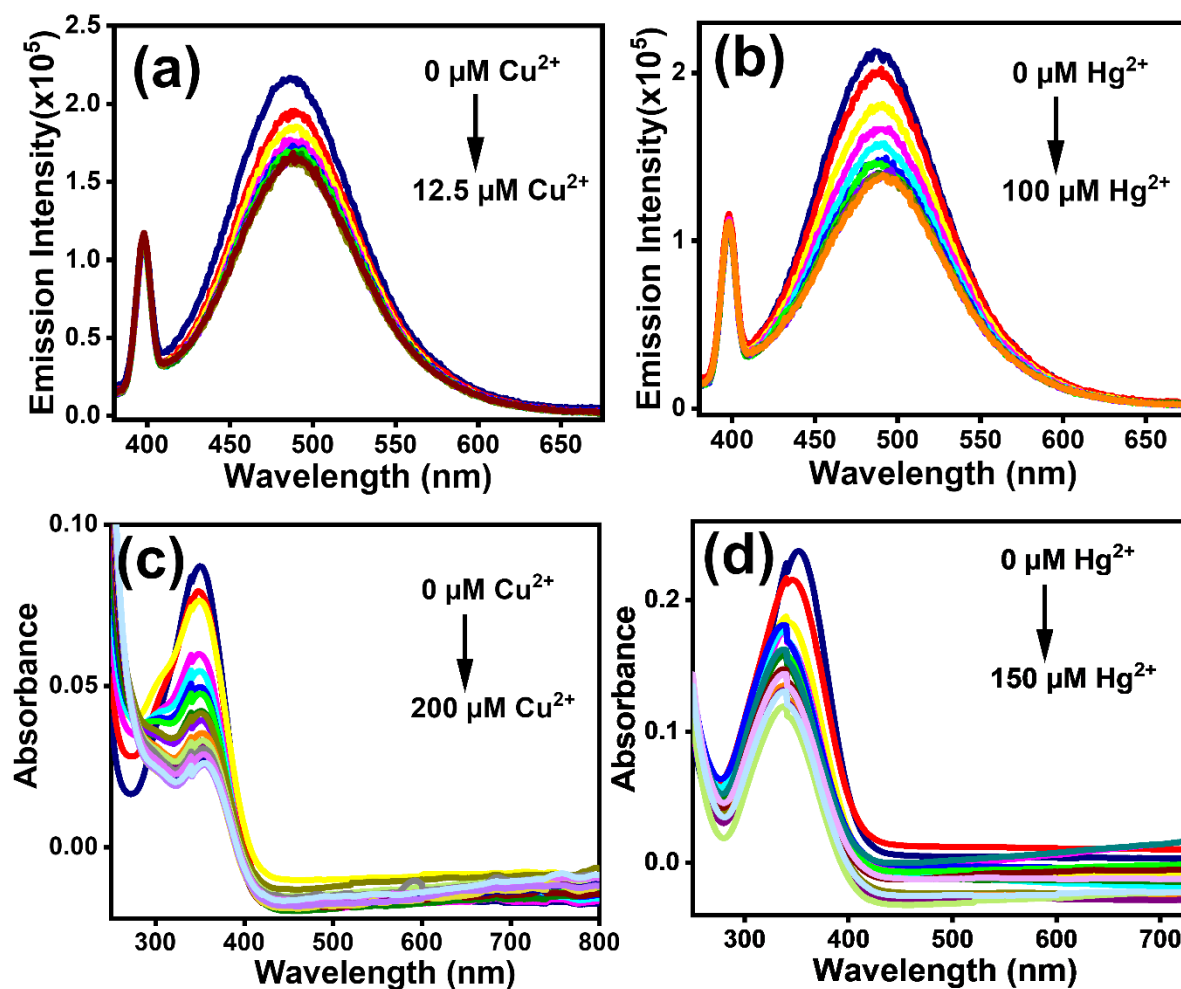
Fig. S6 (a) Lowering of emission intensity with the increase in temperature, (b) enhanced emission intensity with higher pH, (c) formation of aggregates observed in SEM image for **[3]**.
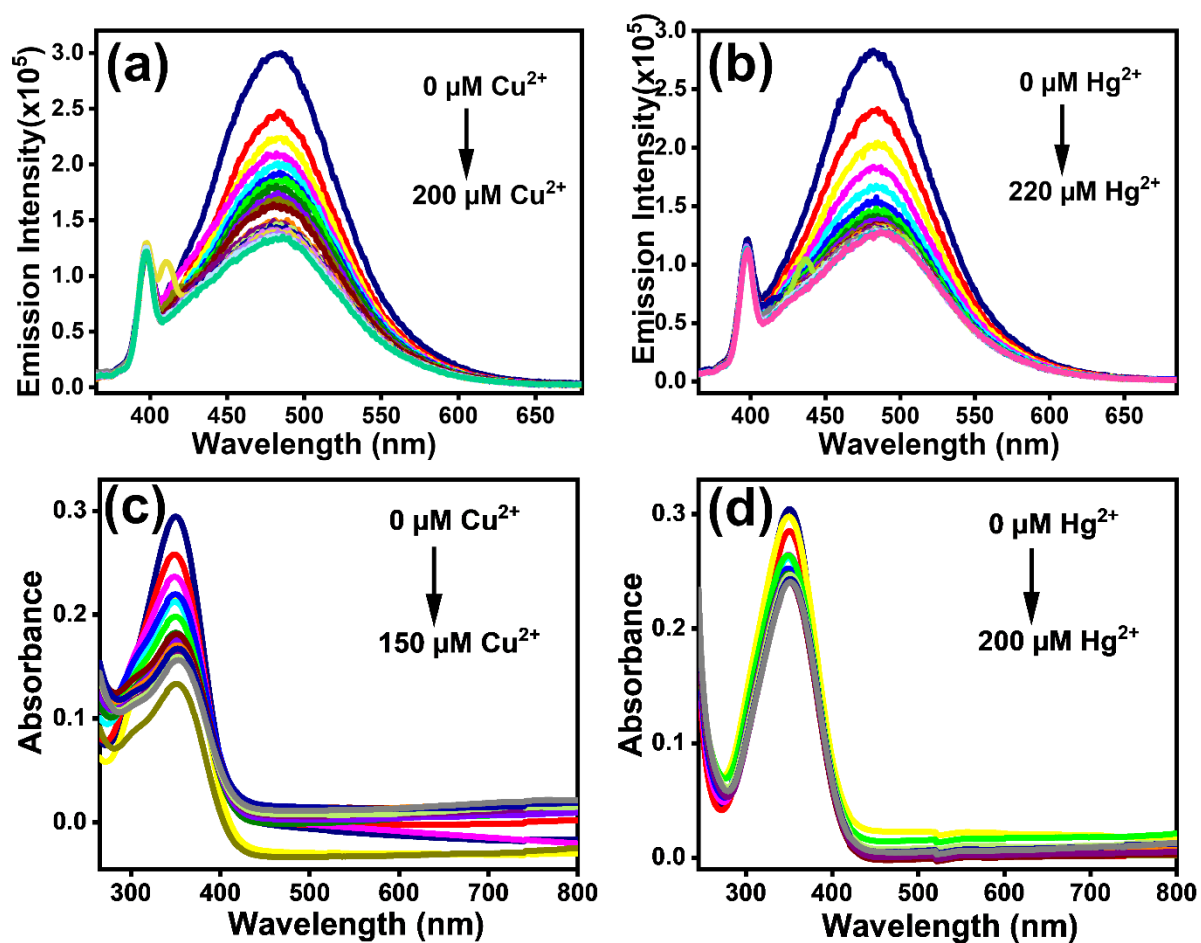
Fig. S7 Variation in emission intensity of **[2]** with increase in metal ion concentration: quenching effect for (a) Cu^{2+} and (b) Hg^{2+}. Lowering of absorbance with an increase in concentration of (c) Cu^{2+} and (d) Hg^{2+} for **[2]**.
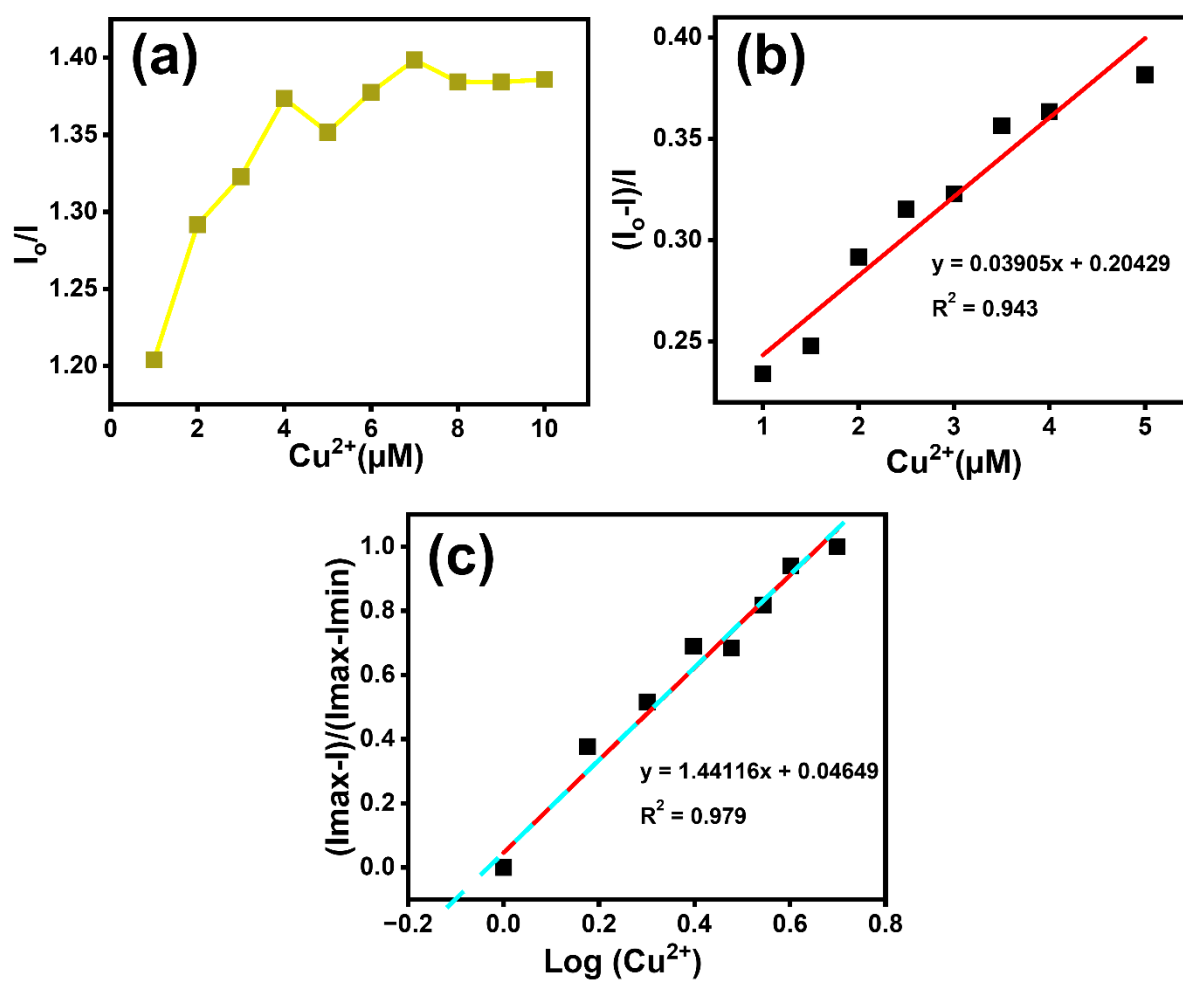
Fig. S8 Variation in emission intensity of **[3]** with increase in metal ion concentration: quenching effect for (a) Cu^{2+} and (b) Hg^{2+}. Lowering of absorbance with an increase in concentration of (c) Cu^{2+} and (d) Hg^{2+} for **[3]**.

Fig. S9 (a) Stern-Volmer plot, (b) K_{sv} calculation, (c) LOD calculation, depicting quenching of **[1]** on addition of Cu^{2+} ion.
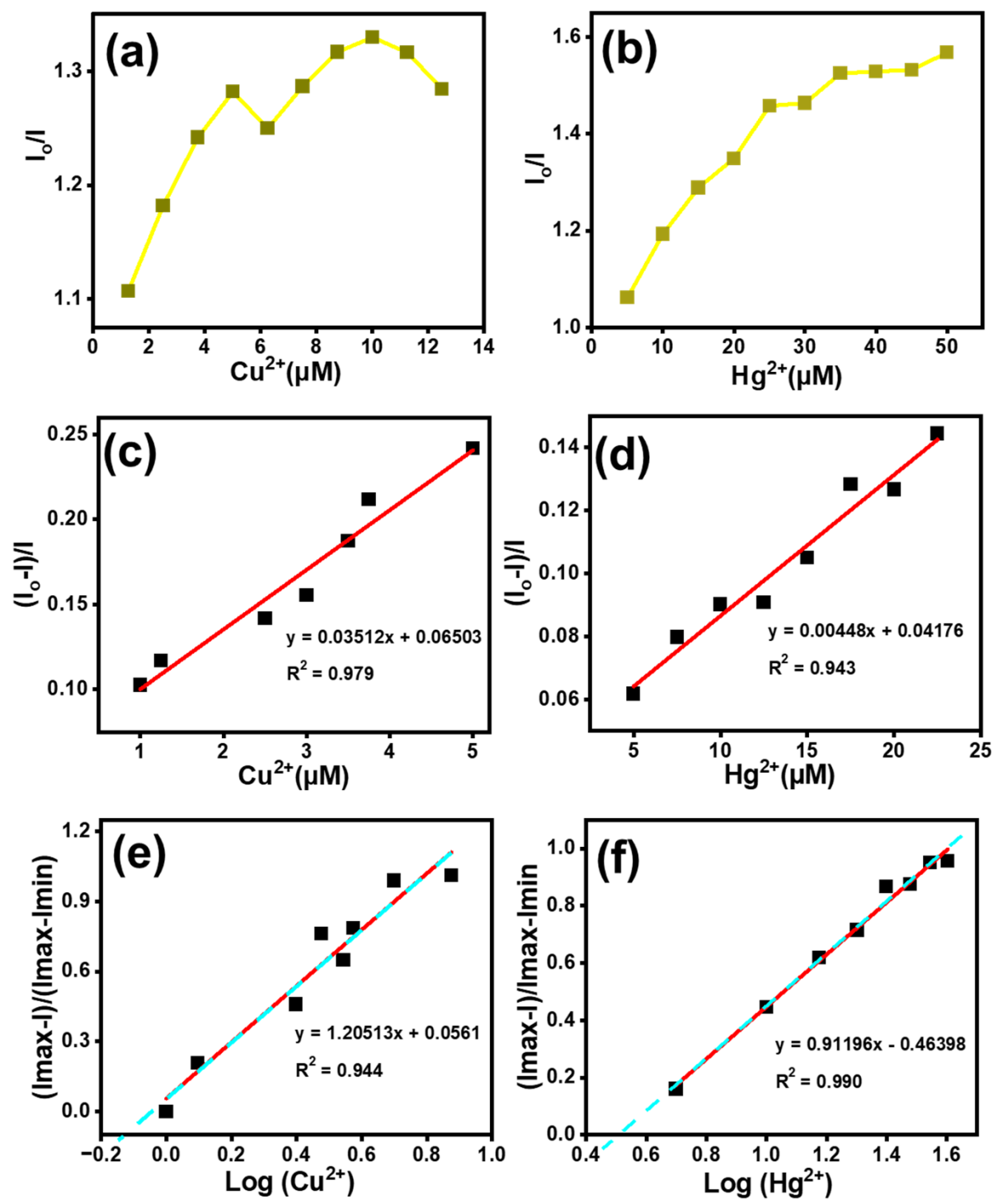
Fig. S10 Stern-Volmer plots for (a) Cu^{2+} and (b) Hg^{2+}, K_{sv} calculation (c) Cu^{2+} and (d) Hg^{2+}, LOD calculation (e) Cu^{2+} and (f) Hg^{2+}, depicting quenching of **[2]** on addition of metal ion.
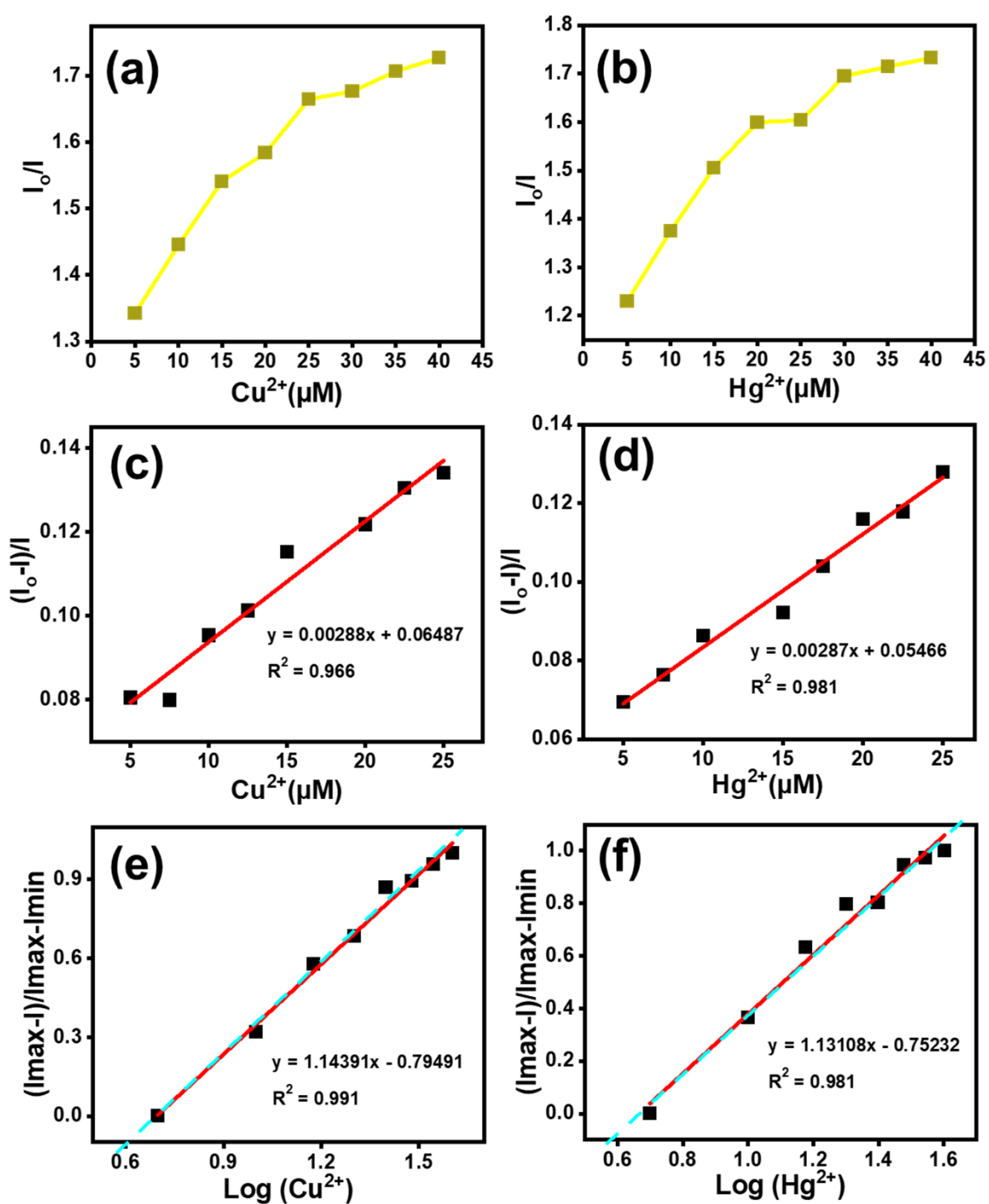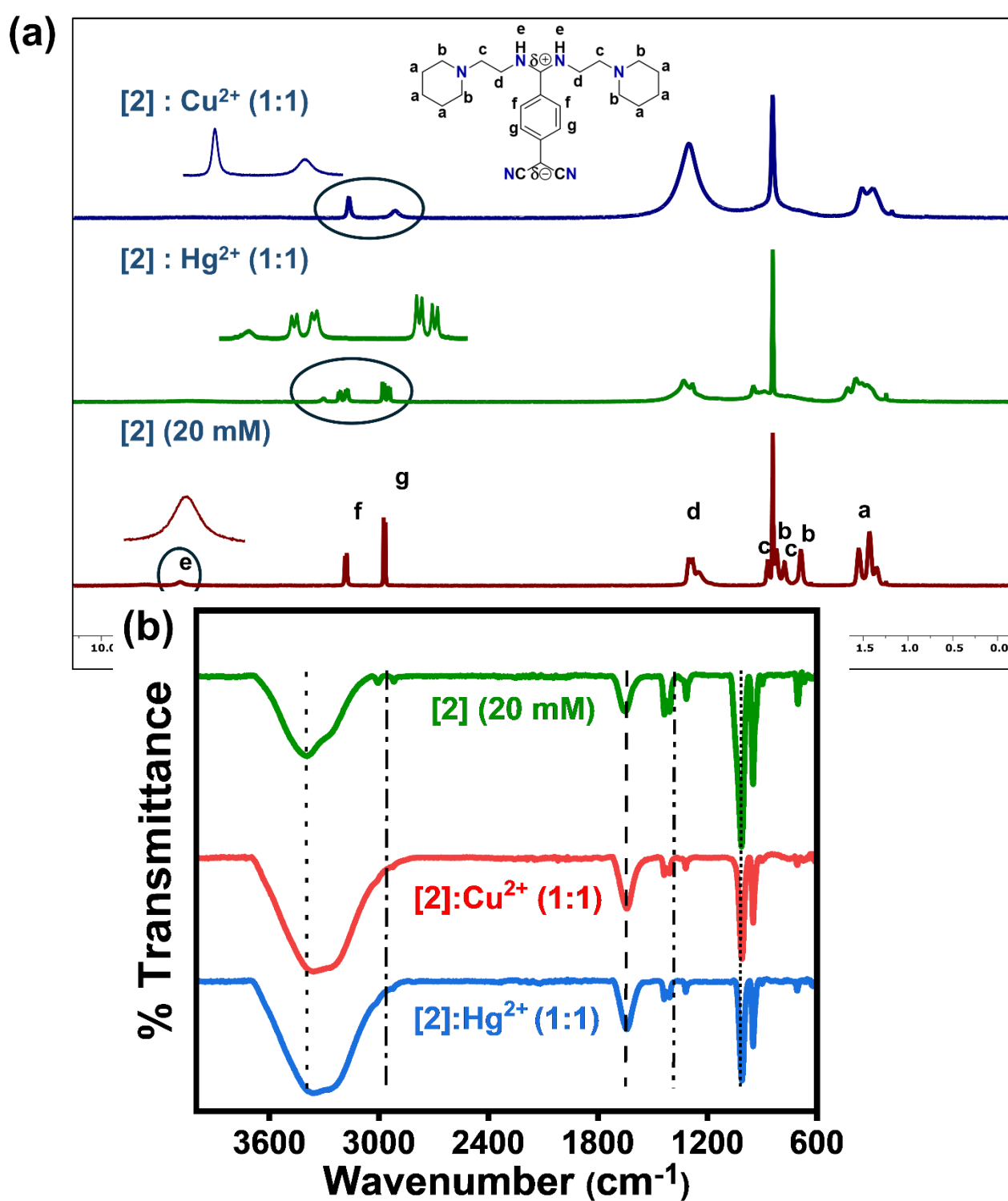
Fig. S11 Stern-Volmer plots for (a) Cu^{2+} and (b) Hg^{2+}, K_{sv} calculation (c) Cu^{2+} and (d) Hg^{2+}, LOD calculation (e) Cu^{2+} and (f) Hg^{2+} depicting quenching of **[3]** on addition of metal ion.

Fig. S12 (a) ^{1}H NMR to understand the mechanistic insights on addition of metal ions on **[2]**. (b) FT-IR spectra to understand the mechanistic insights on the addition of metal ions with **[2]**.
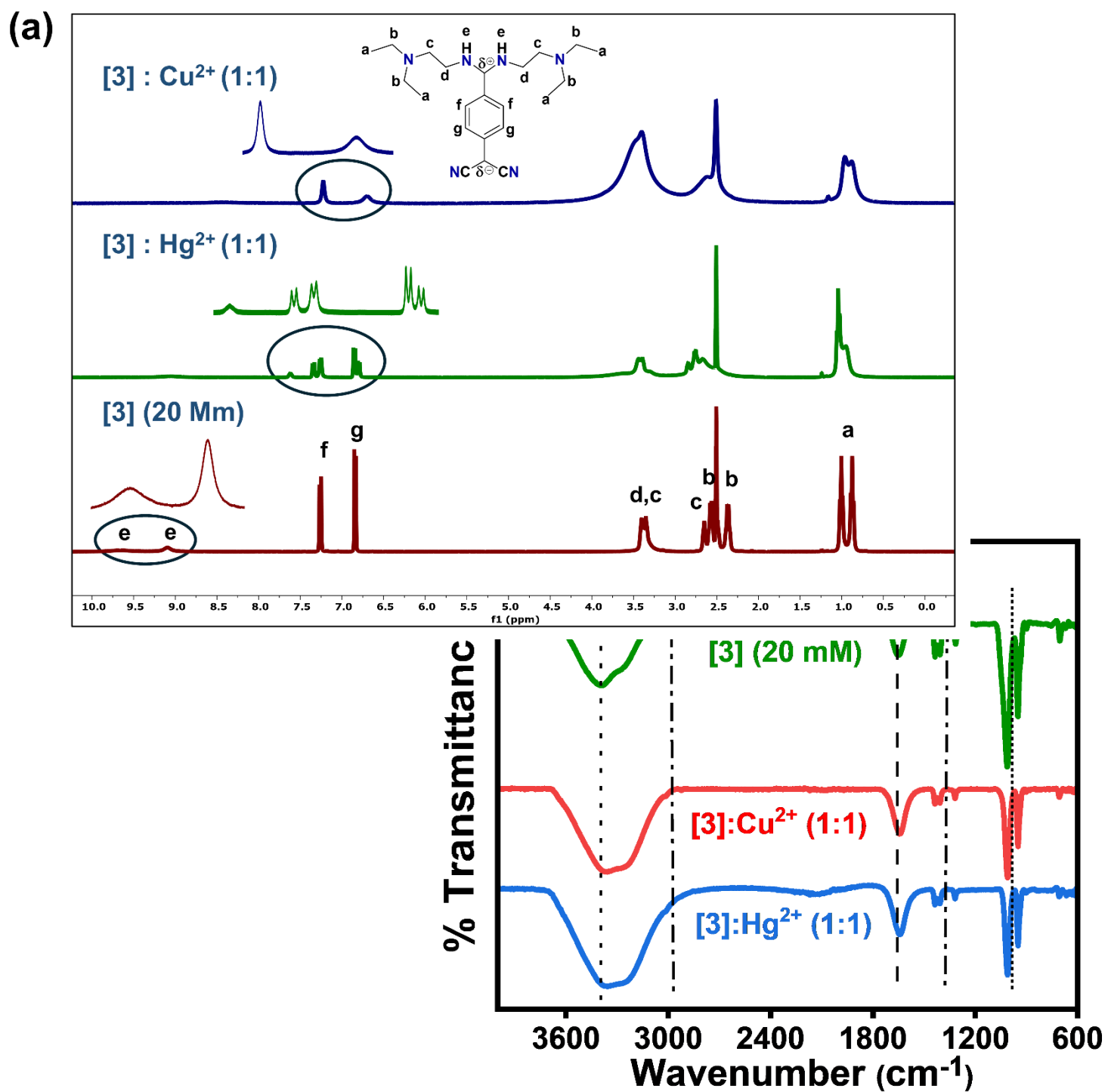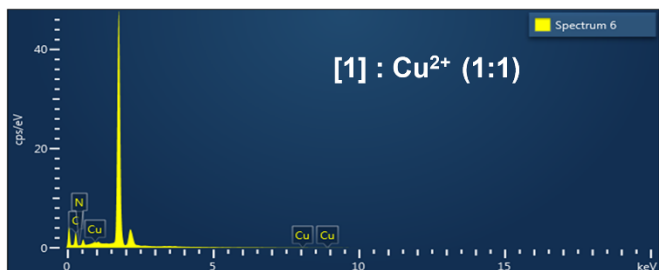
Fig. S13 ^{1}H NMR to understand the mechanistic insights on addition of metal ions on **[3]**. **(b)** FT-IR spectra showcasing binding of metal ion with **[3]**.
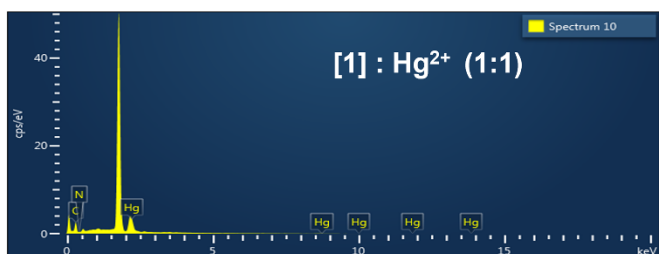
(a)

[1] (10 μM) — Spectrum 4

Element	Wt%	Atomic%
C	71.62	74.63
N	28.38	25.37
Total	100	100

[1] : Cu^{2+} (1:1) — Spectrum 6

Element	Wt%	Atomic%
C	74.96	79.50
N	21.84	19.86
Cu	3.20	0.64
Total	100	100

[1] : Hg^{2+} (1:1) — Spectrum 10

Element	Wt%	Atomic%
C	64.43	88.28
N	8.06	9.47
Hg	27.51	2.26
Total	100	100

(b)

[1] : Cu²⁺ (1:1)

C Kα1_2

N Kα1_2

Cu Kα1

[1] : Hg^{2+} (1:1)

C Kα1_2

EDS Layered Image 15

Map Data 15

2.5 µm

Hg N C Electron

2.5µm

Map Data 15

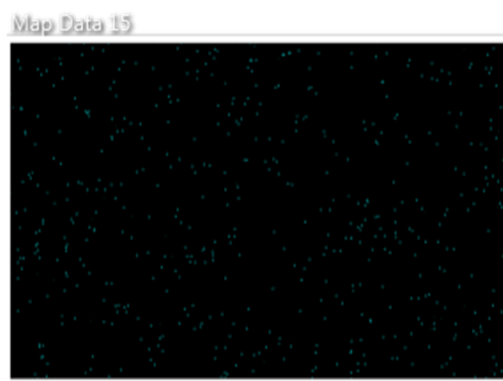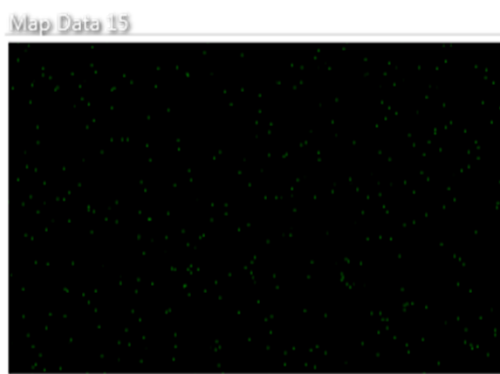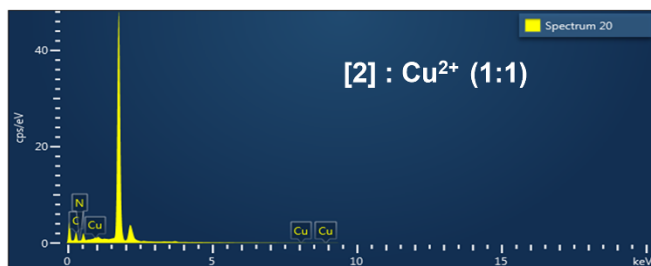**N Kα1_2**

Map Data 15

Hg Mα1

Map Data 15
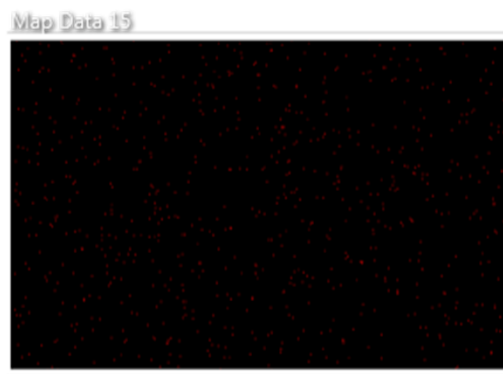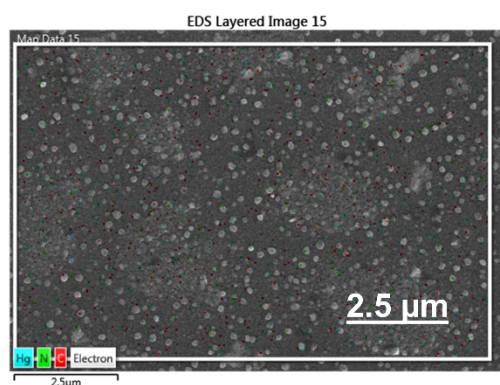
Fig. S14 (a) EDAX spectra showing change in elemental composition for **[1]** with addition of metal ion. (b) EDAX mapping depicting elemental presence for **[1]** on metal ion addition.
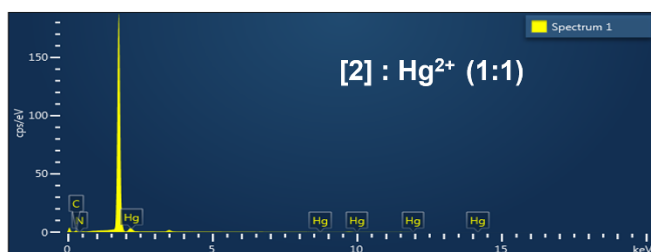
(a)

[2] (10 µM) — Spectrum 14

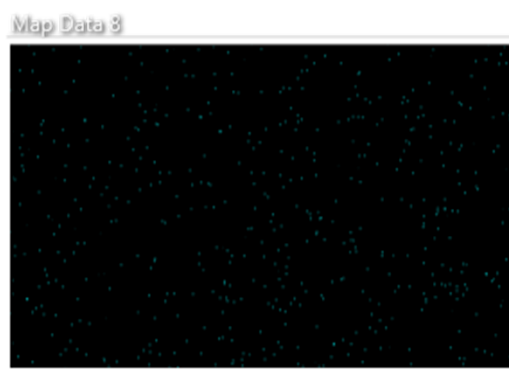| Element	Wt%	Atomic%
C	68.43	71.66
N	31.57	28.34
Total	100	100

[2] : Cu^{2+} (1:1) — Spectrum 20

Element	Wt%	Atomic%
C	63.69	68.13
N	34.31	31.47
Cu	2.00	0.41
Total	100	100

[2] : Hg^{2+} (1:1) — Spectrum 1

Element	Wt%	Atomic%
C	78.85	95.02
N	3.60	3.72
Hg	17.56	1.27
Total	100	100

(b)

[2] : Cu²⁺ (1:1)

C Kα1_2

EDS Layered Image 6

Map Data 6

2.5 μm

Cu N C Electron

[2] : Hg²⁺ (1:1)

C Kα1_2

EDS Layered Image 8

Map Data 8

5 μm

Hg N C Electron

5μm

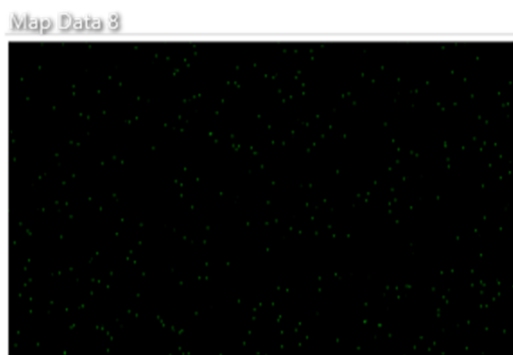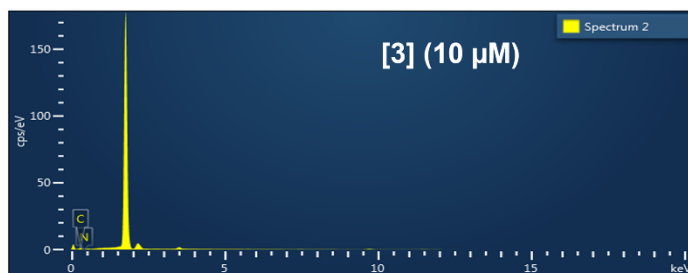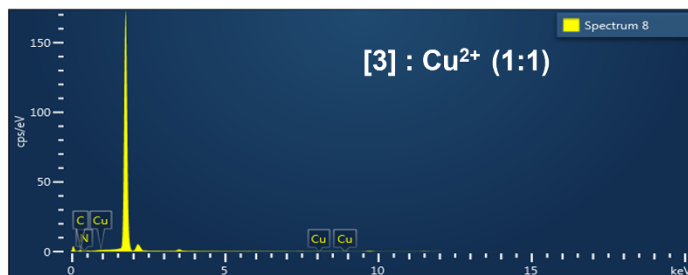N Kα1_2

Map Data 8

Hg Mα1

Map Data 8
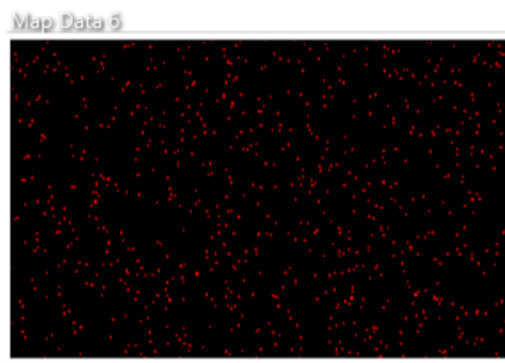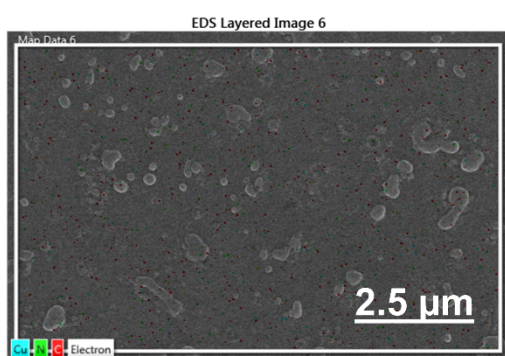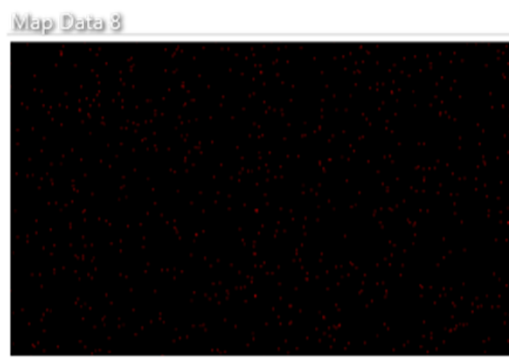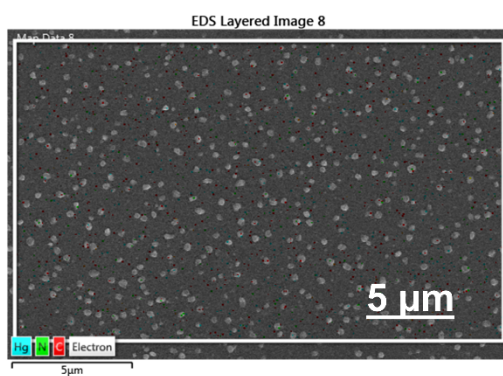
Fig. S15 (a) EDAX spectra showing change in elemental composition for **[2]** with addition of metal ion. (b) EDAX mapping depicting elemental presence for **[2]** on metal ion addition.
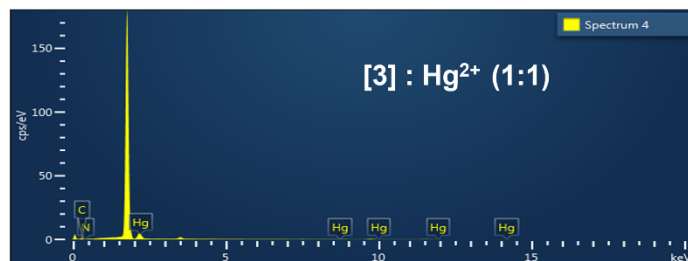
(a)

[3] (10 µM)

Element	Wt%	Atomic%
C	69.29	72.46
N	30.71	27.54
Total	100	100

[3] : Cu^{2+} (1:1)

Element	Wt%	Atomic%
C	73.94	79.07
N	21.92	20.09
Cu	4.14	0.84
Total	100	100

[3] : Hg^{2+} (1:1)

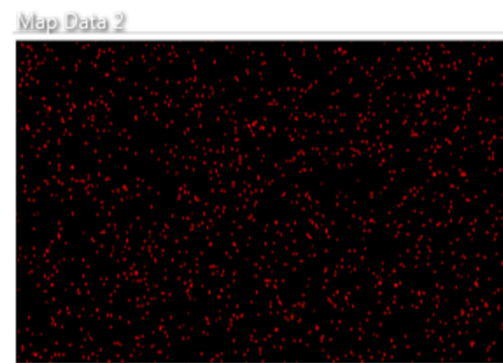| Element	Wt%	Atomic%
C	68.74	88.92
N	8.40	9.31
Hg	22.87	1.77
Total	100	100

(b)

[3] : Cu²⁺ (1:1)
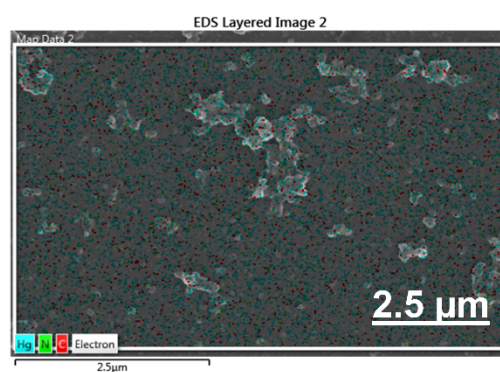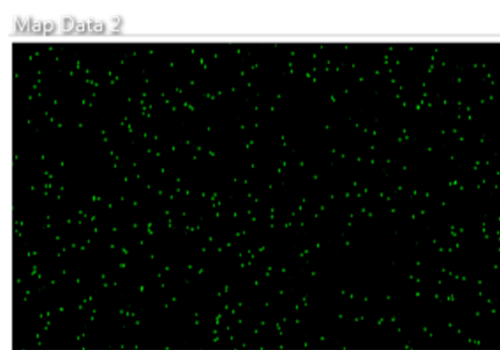
C Kα1_2

N Kα1_2

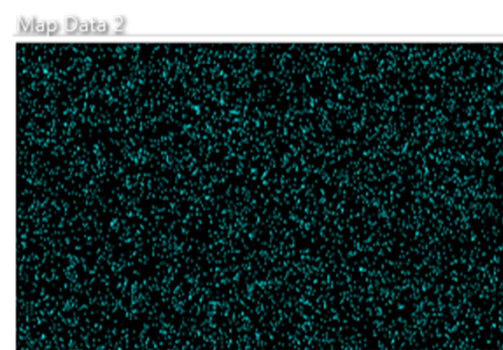Cu Kα1

[3] : Hg²⁺ (1:1)

C Kα1_2

N Kα1_2
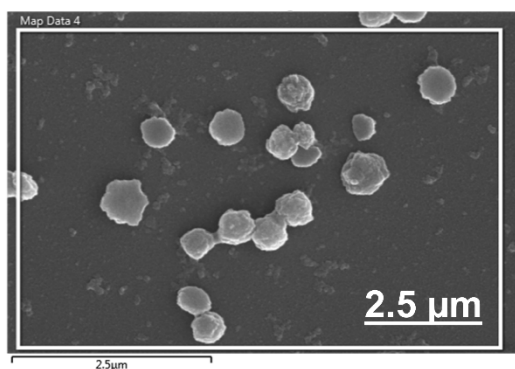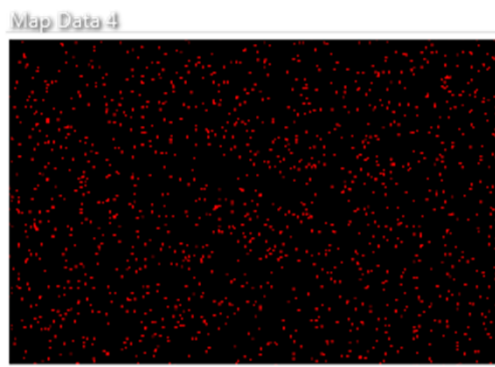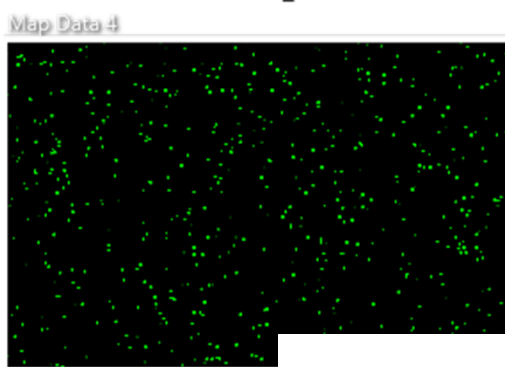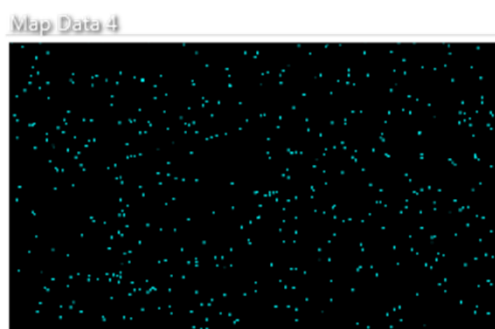
Hg Mα1

Fig. S16 (a) EDAX spectra showing change in elemental composition for **[3]** with addition of metal ion. (b) EDAX mapping depicting elemental presence for **[3]** on metal ion addition.
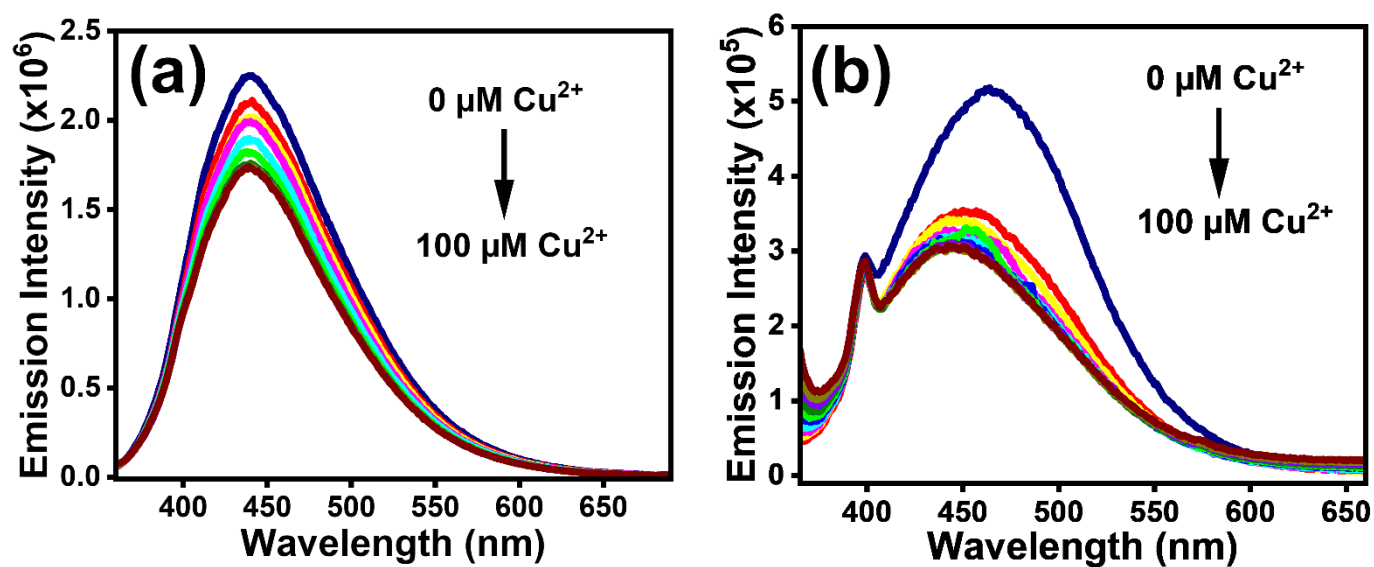

Fig. S17 Variation in emission intensity of **[1]** against Cu^{2+} ions with (a) pond water sample and (b) tap water sample.