Supporting Information File

Anion directed structural tuning of azomethine derived two Zn^{2+}-complexes with optoelectronic recognition of Cu^{2+} from aqueous medium with Anti-cancer activities: Expedition from micromolar to femtomolar sensitivity with DFT revelation

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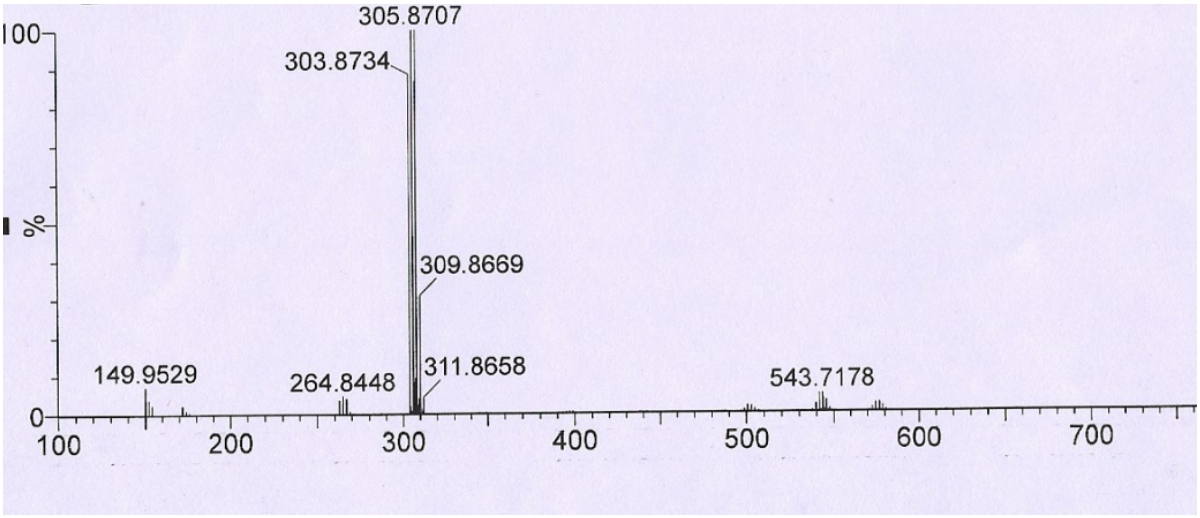
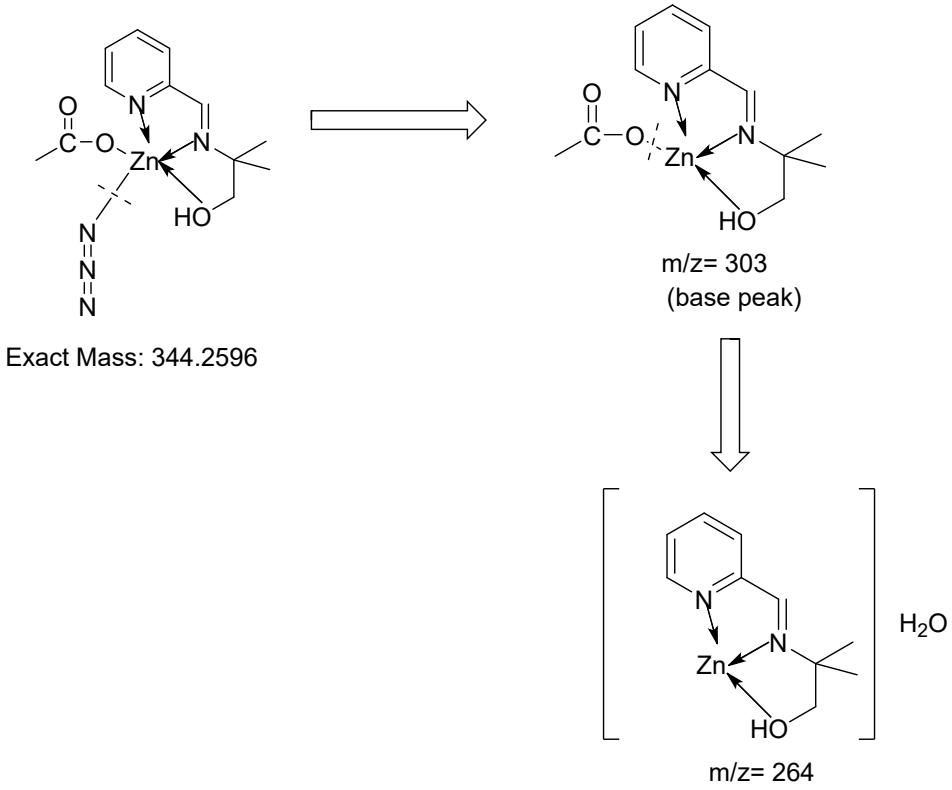


Figure S1: Mass spectrometric data of **NS-1**



Scheme S1: Probable Mass spectrometric analysis of NS-1

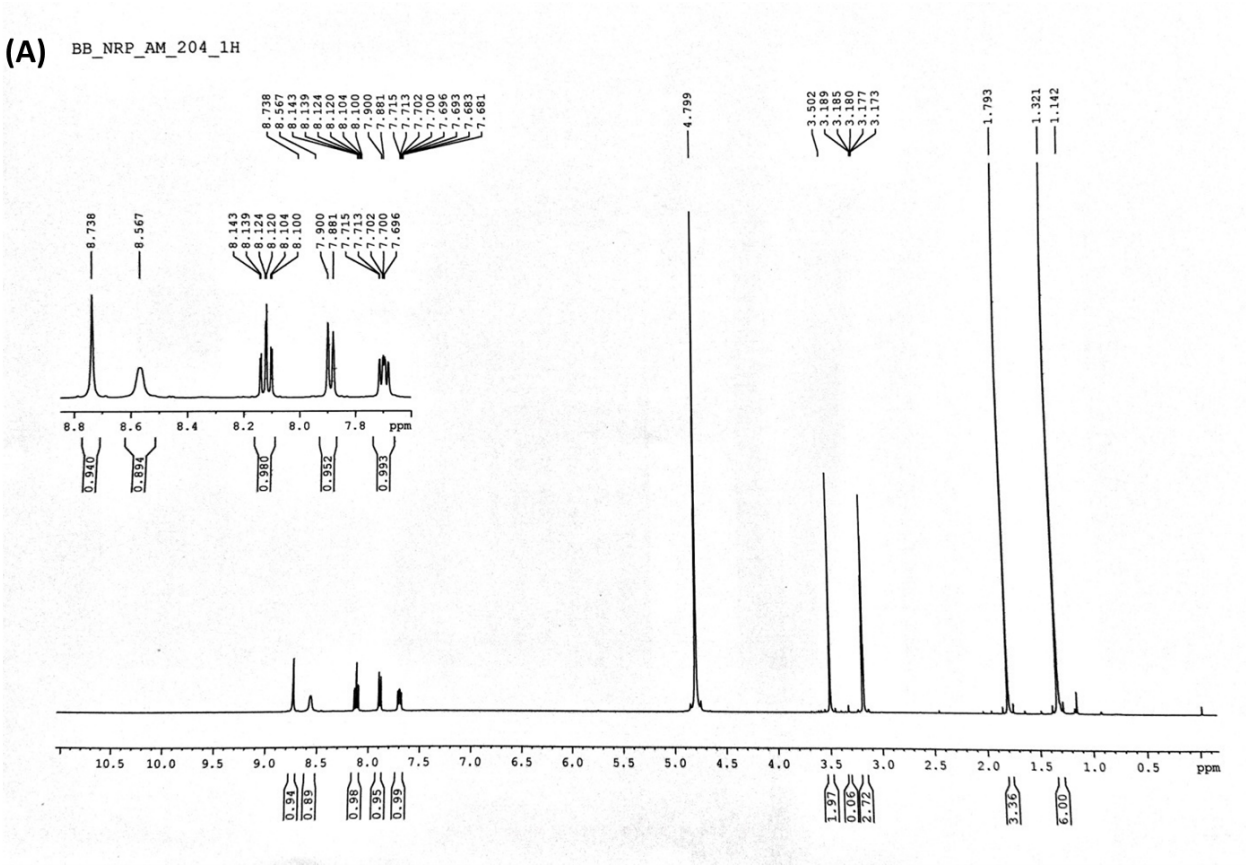


Figure S2: (A) ^{1}H-NMR spectra of **NS-1**

^{1}H-NMR(400 MHz, D_2O): 1H, s, 8.74 ppm (H_d), 1H, d, 8.57 ppm(H_h), 1H, dd, 8.10-8.14 ppm (H_g), J= 16Hz, 1H, d, 7.88-7.90 ppm, J= 8 Hz, (H_e), 1H, dd, 7.70-7.72 ppm, J= 8 Hz (H_f), 2H, s, 3.50 ppm(H_b), 3H, s, 1.79 ppm (H_i), 6H, s, 1.32 ppm (H_c).

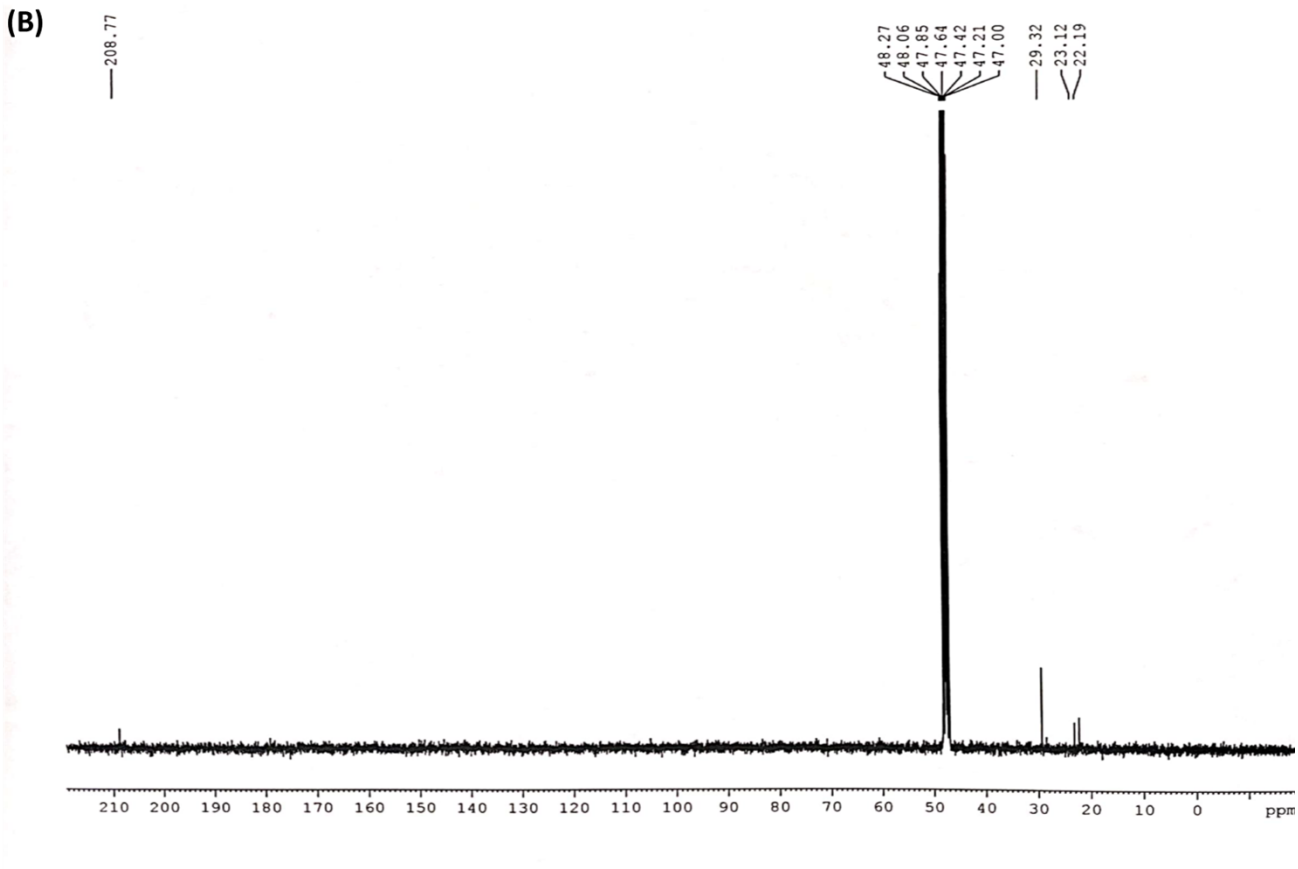


Figure S2: (B) ^{13}C-NMR spectra of **NS-1**

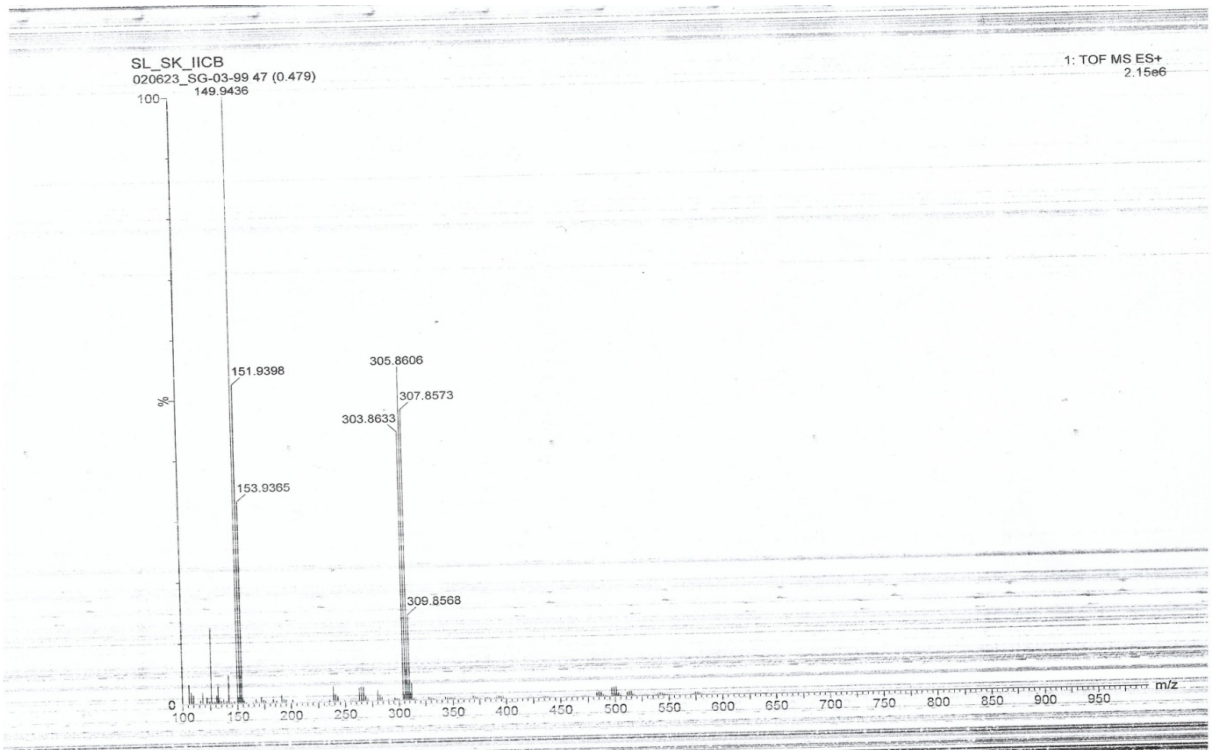
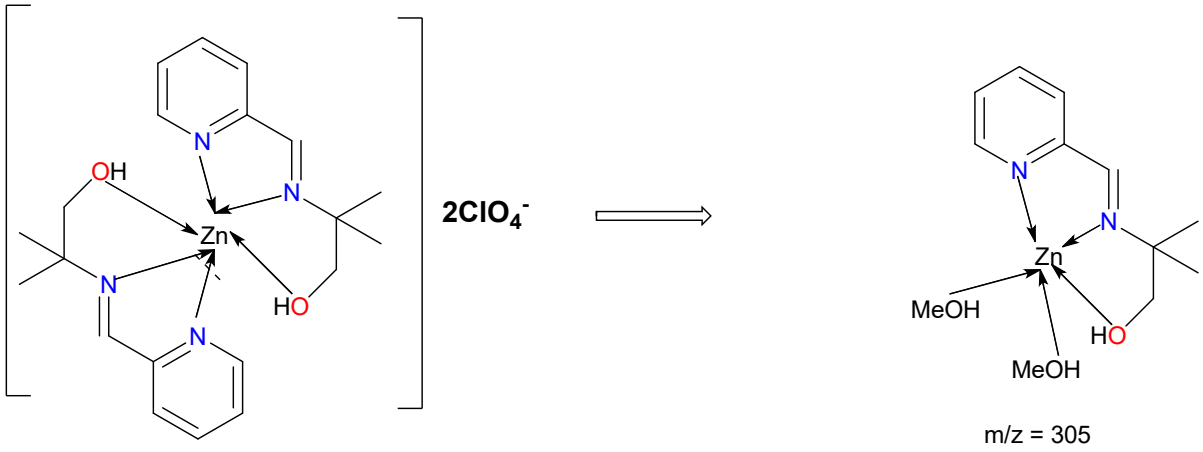


Figure S3: HR-MS data of **NS-2**



Scheme S2: Probable Mass spectrometric analysis of **NS-2**

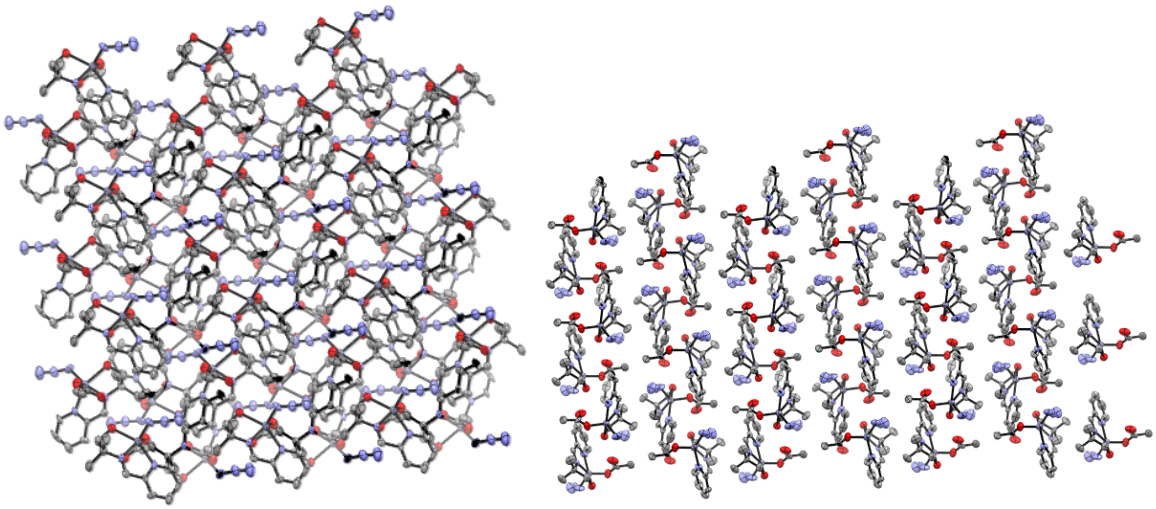


Figure S4: packing of the complex **NS-1** in different directions.

Table S1: Bond length associated with the hydrogen bonding of the complex **NS-1**

Bond	**Distance**
O(1)----O(3)	2.571(2)

Table S2: Selected bond lengths around the coordination environment of the complex **NS-1**

Bonds	**Distance (in A°)**
Zn(1)-N(1)	2.20(1)
Zn(1)-N(2)	2.07(1)
Zn(1)-N(3)	1.95(2)
Zn(1)-O(1)	2.22(1)
Zn(1)-O(2)	1.95(1)

Table S3: Bond length associated with the Schiff base of the complex **NS-1**

Bond	Distance
C(6)-N(2)	1.26(2)

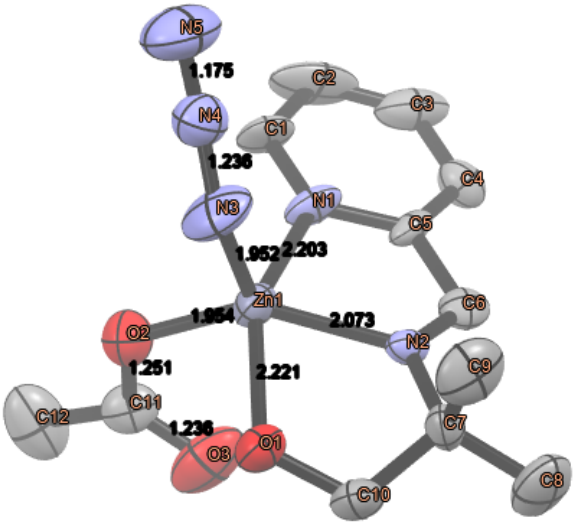


Figure S5: Selected bond lengths around the coordination environment of the complex **NS-1**

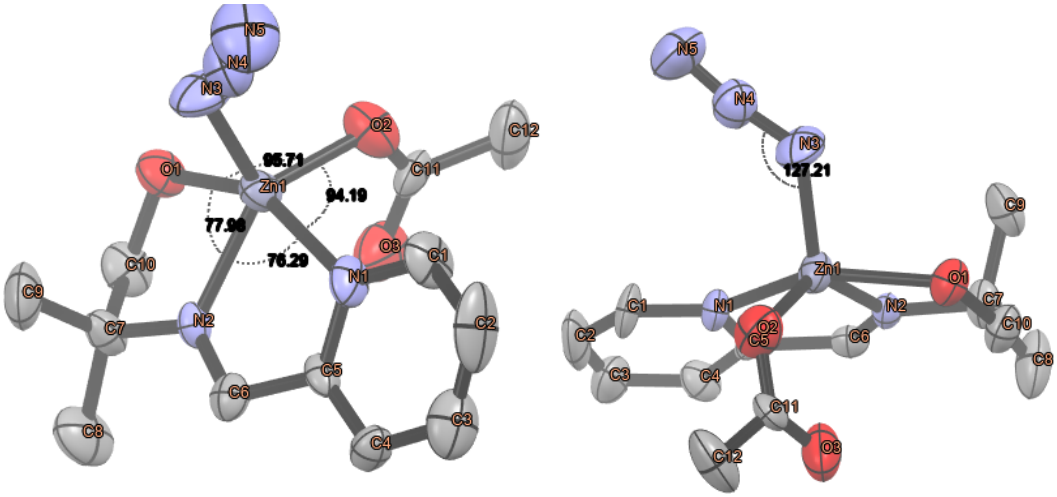


Figure S6: Selected bond angles around the coordination environment of the complex **NS-1**

Table S4: Selected bond angles around the coordination environment of complex **NS-1**

Bond	Angles in degree
N(2)- Zn (1)-N(1)	76.29
N(1)- Zn (1)-O(2)	94.13
O(1)-Zn(1)-N(2)	77.96
N(3)- Zn (1)-O(2)	91.86
O(2)-Zn(1)-O(1)	96.71

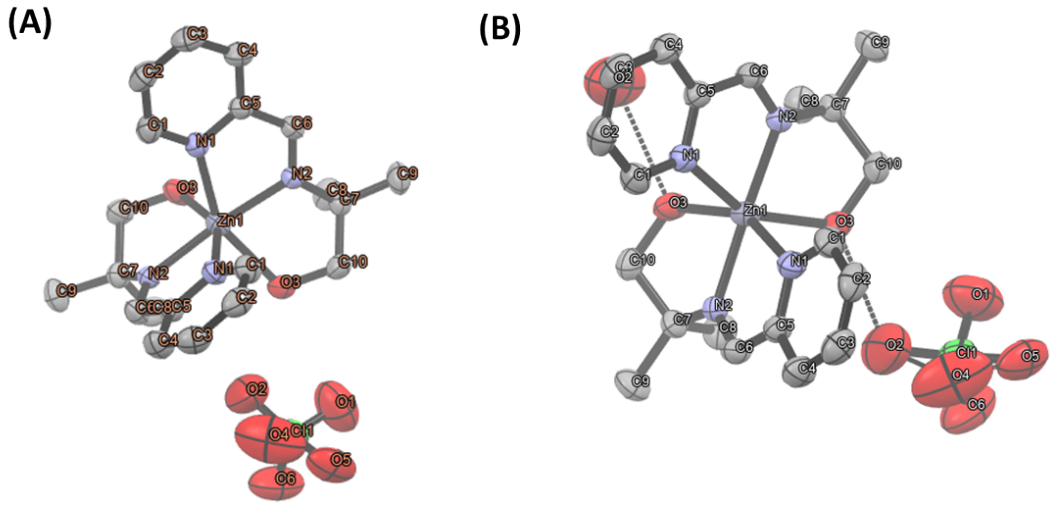


Figure S7: (A) X-ray structure of the complex **NS-2** (B) Hydrogen bonding network of **NS-2**

Table S7: Bond lengths associated with the hydrogen bonding of the complex **NS-2**

Bond	Distance
O(2)----O(3)	2.824(9)

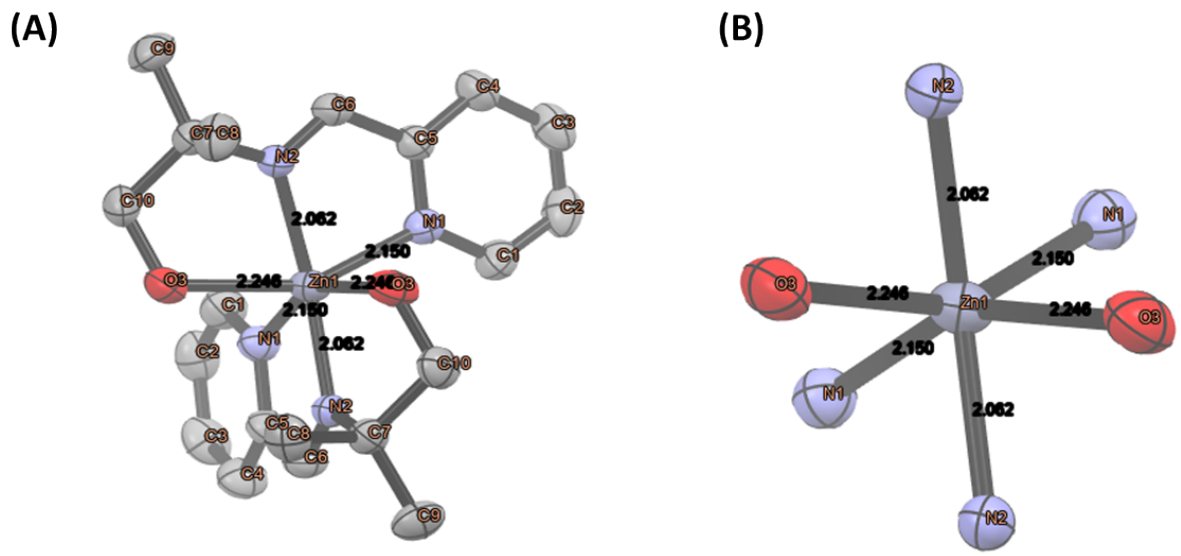


Figure S8: **(A)** Selected bond lengths around the coordination environment of the complex **NS-2 (B)** Enlarged coordination view of **NS-2**.

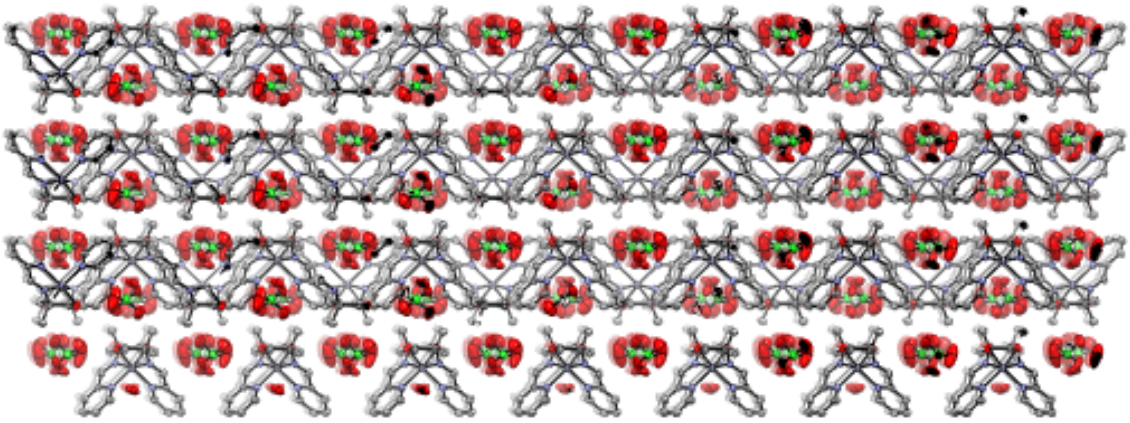


Figure S9: packing of the complex **NS-2**.

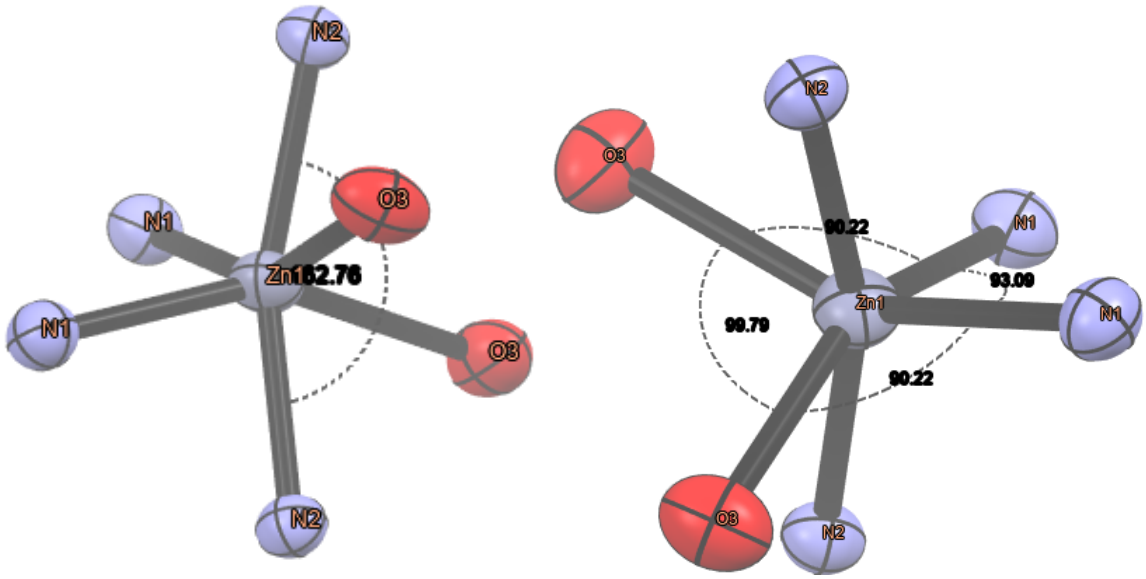


Figure S10: Selected bond angles around the coordination environment of the complex **NS-2**.

Table S8: Selected bond lengths around the coordination environment of the complex **NS-2**

Bonds	**Distance (in A°)**
Zn(1)-N(2)	2.062
Zn(1)-N(1)	2.150
Zn(1)-O(3)	2.246

Table S9: Bond angle associated with the Schiff base of the complex **NS-2**

Bond	**Distance**
C(6)-N(2)	1.259(5)

Table S10: Selected bond angles around the coordination environment of complex **NS-2**

Bond	Angles in degree
N(1)-Zn(1)-N(1)	93.06
O(3)-Zn(1)-O(1)	90.79
N(1)-Zn(1)-O(3)	90.22

Table S11: crystallographic parameters of **NS-1 and NS-2**

Complex	**NS-1**	**NS-2**
Formula	$C_{12}H_{17}N_5ZnO_3$	$C_{20}H_{28}N_4O_2Zn$, $2(ClO_4)$
Formula Weight	343.67	620.75
Temperature (K)	293	273
Crystal System	Orthorhombic	Monoclinic
Space group	P 2_1 2_1 2_1	P 2/n
a (Å)	9.508(7)	10.7236(8)
b (Å)	9.719(7)	7.8448(6)
c (Å)	16.852(13)	15.7025(12)
α (˚)	90	90
β (˚)	90	96.744(3)˚
γ (˚)	90	90
Z	4	2
d_{cal} (g cm^{-3})	1.466	1.571
μ(mm^{-1})	1.593	1.199
F(000)	708.0	640.0
Total reflection	10775	19282

Unique Reflections	2736	2910
Observe data[I>2σ(I)]	2736	2549
R(int)	0.1766	0.0336
R1, *w*R2 (all data)	0.1382, 0.1948	0.0695, 0.1883
R1, *w*R2 [I>2σ(I)]	0.0867, 0.1738	0.0621, 0.1796

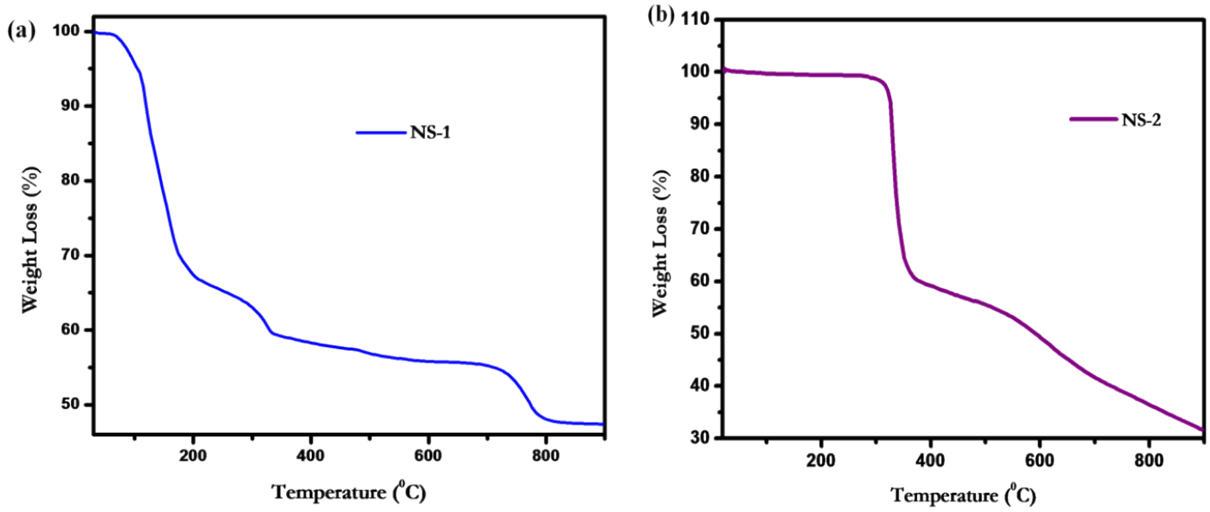


Figure S11: TGA data of **(a) NS-1** and **(b) NS-2**

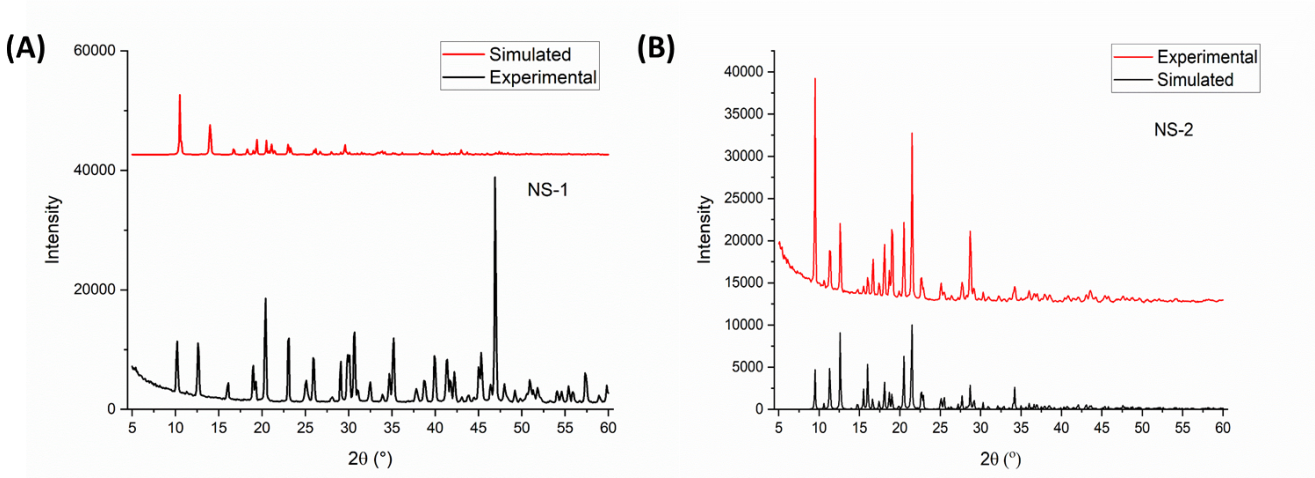


Figure S12: Comparison between P-XRD pattern of experimental data and simulated data of **(A) NS-1 (B) NS-2.**

The sharp band at 2066 cm^{-1} corresponds to the azide ion. The C-H bands are at 3088 cm^{-1} and 2973 cm^{-1}, broad band at 2816 cm^{-1} corresponds to -OH of the protonated Schiff base ligand. Band at 1752 cm^{-1} corresponds to the C-N bond of the Schiff base, another band at 1603 cm^{-1} corresponds to the C-O of acetate ion which is directly attached with Zn in **NS-1**.

On the other hand, the broad band at 3373 cm^{-1} corresponds to the protonated -OH of the Schiff base in complex-2 (**NS-2**). Medium band in the region 2988-2909 cm^{-1} correspond to the C-H stretching frequency. The band in the region 1074-1191 cm^{-1} corresponds to the ClO_4^-. Strong band at 1660 cm^{-1} corresponds to the C-N of the Schiff base**.**

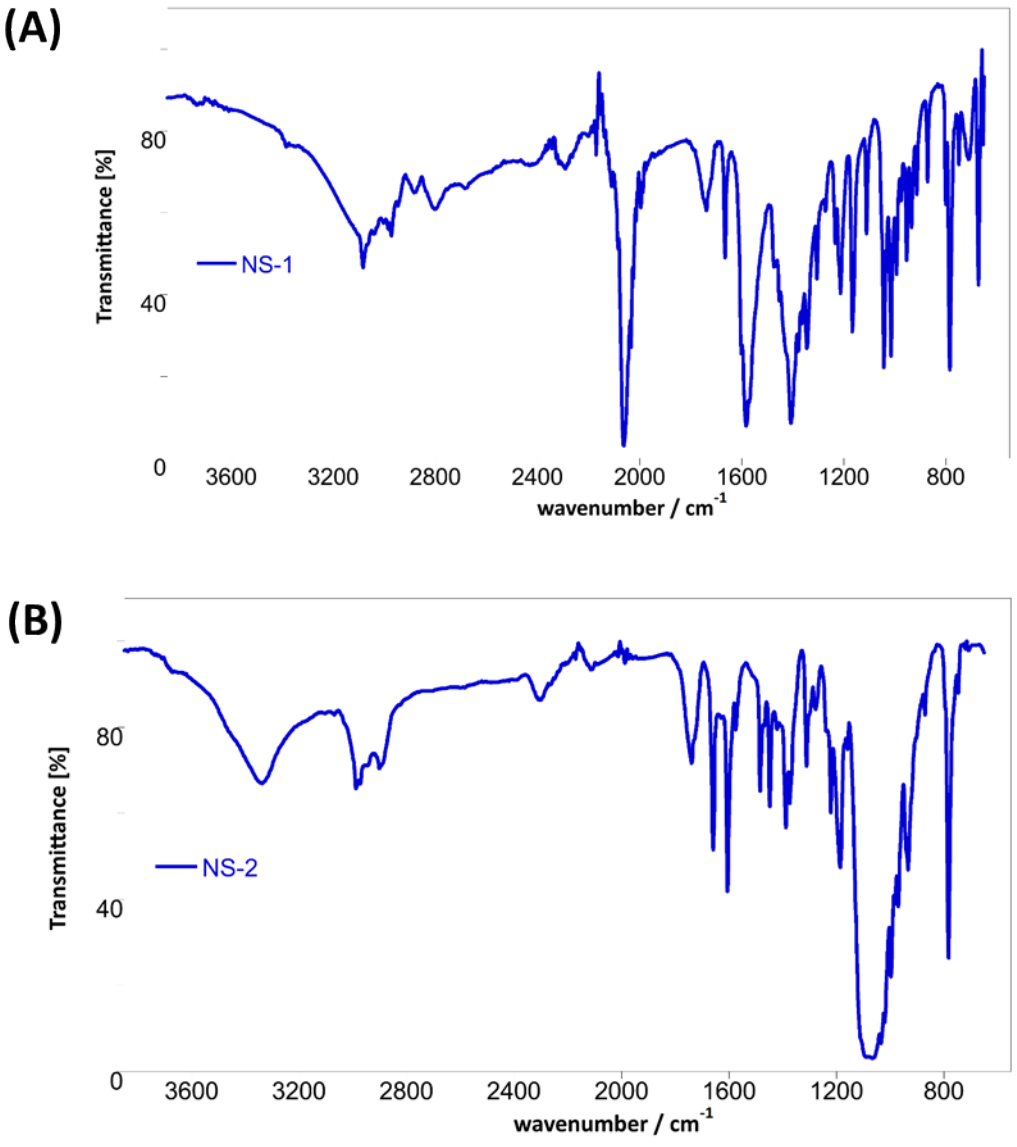


Figure S13: FT-IR spectra of the **(A) NS-1 (B) NS-2**

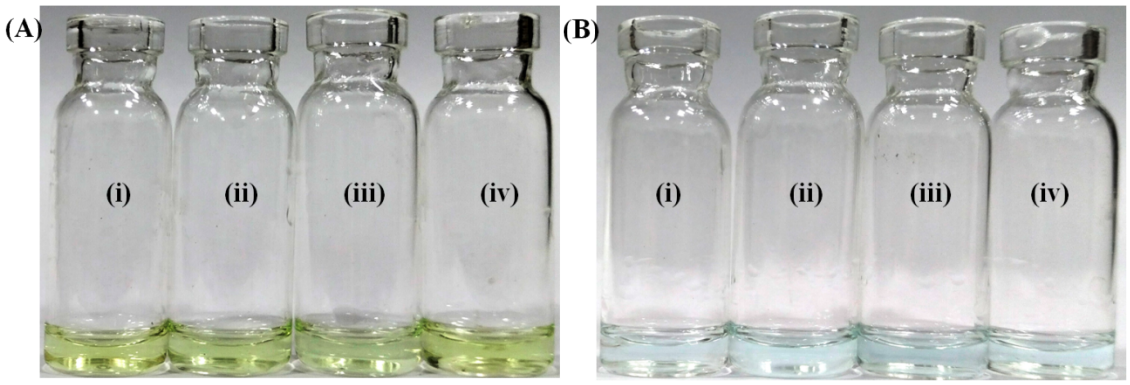


Figure S14: Chromogenic changes of **(A) NS-1** and **(B) NS-2** in presence of **(i)** nitrate, **(ii)** sulfate, **(iii)** chloride and**(iv)** perchlorate salt of copper.

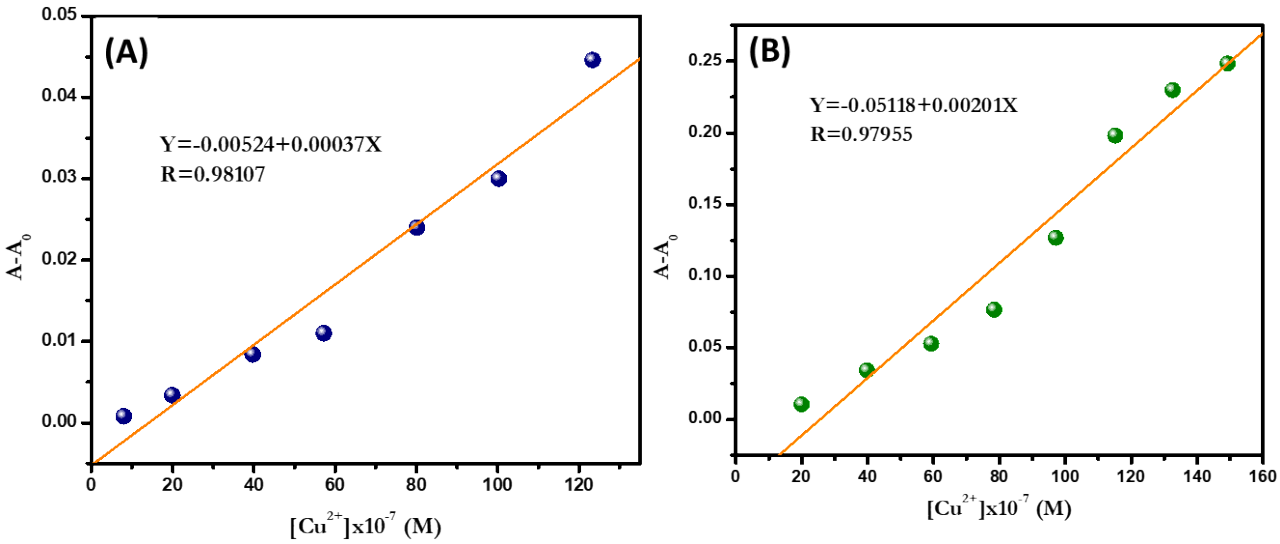


Figure S15: Change of absorbance at **(A)** 395 nm and **(B)** 295 nm as the linear function of the concentration of Cu^{2+} for the calculation of LOD for Cu^{2+} by **NS-1**and **NS-2** respectively.

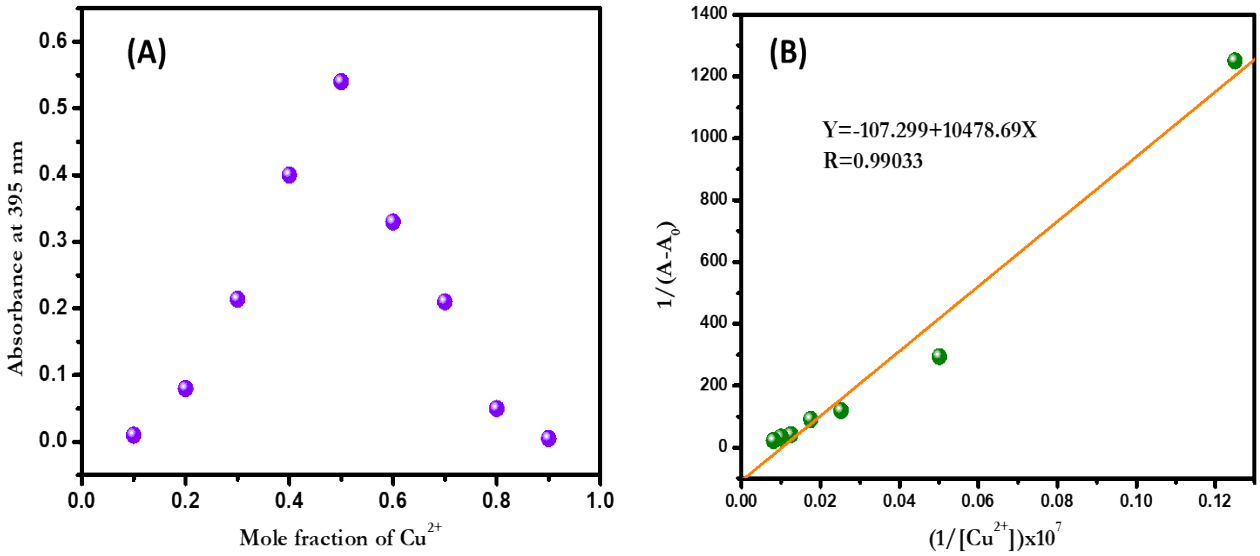


Figure S16: (A) Job's plot of **NS-1** with Cu^{2+} for the stoichiometry determination monitoring the change of absorbance at 395 nm **(B)** Benesi–Hildebrand plot for absorbance of Cu^{2+} with **NS-1** for the association constant determination.

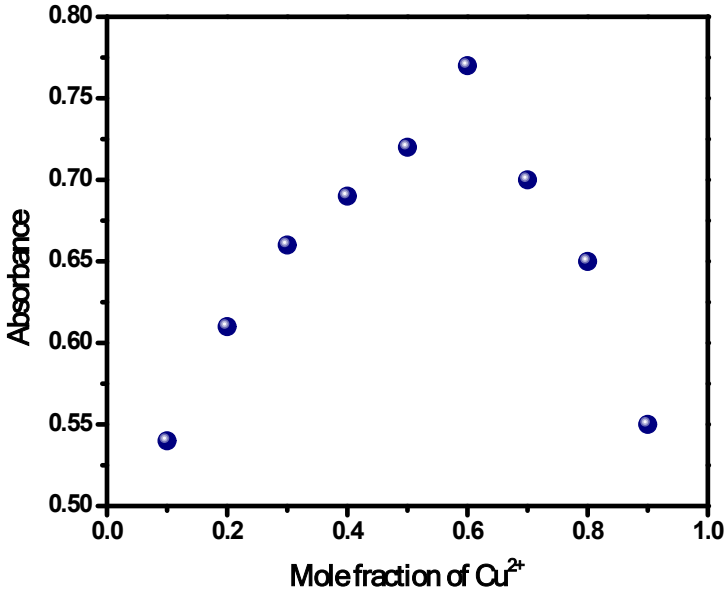


Figure S17: Job's plot of **NS-2** with Cu^{2+} for the stoichiometry determination monitoring the change of absorbance at 295 nm.

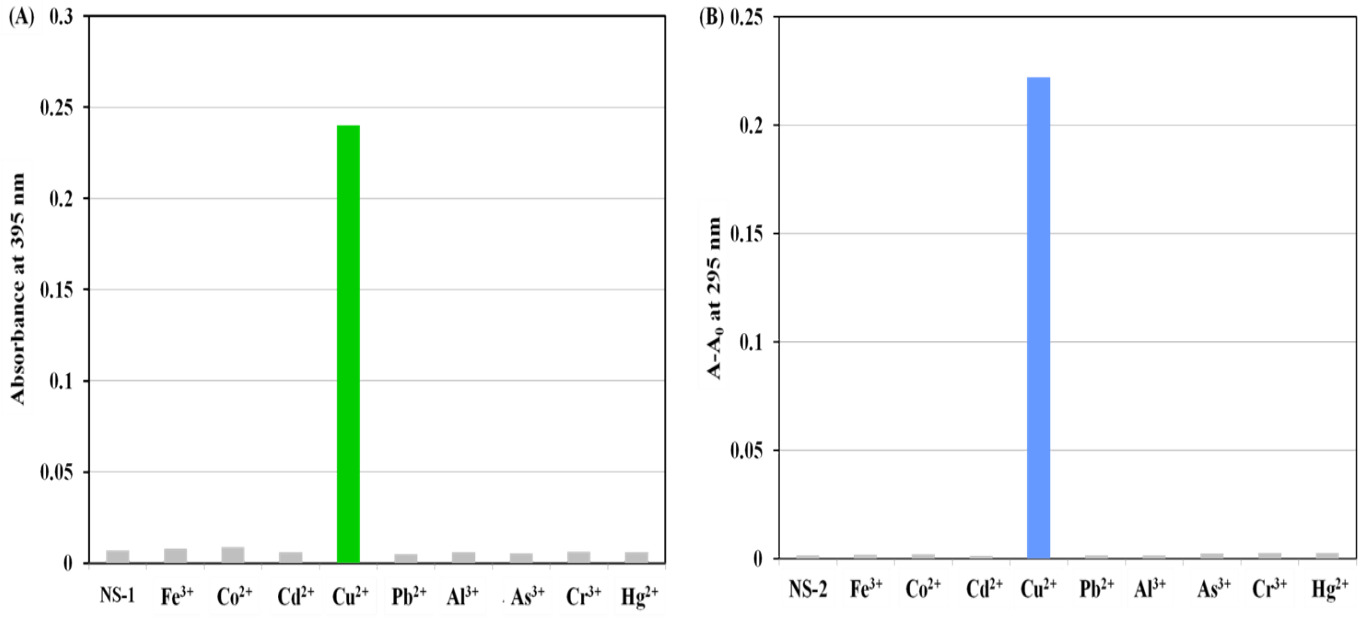


Figure S18: Selectivity of **(A) NS-1** and **(B) NS-2** toward Cu^{2+}.

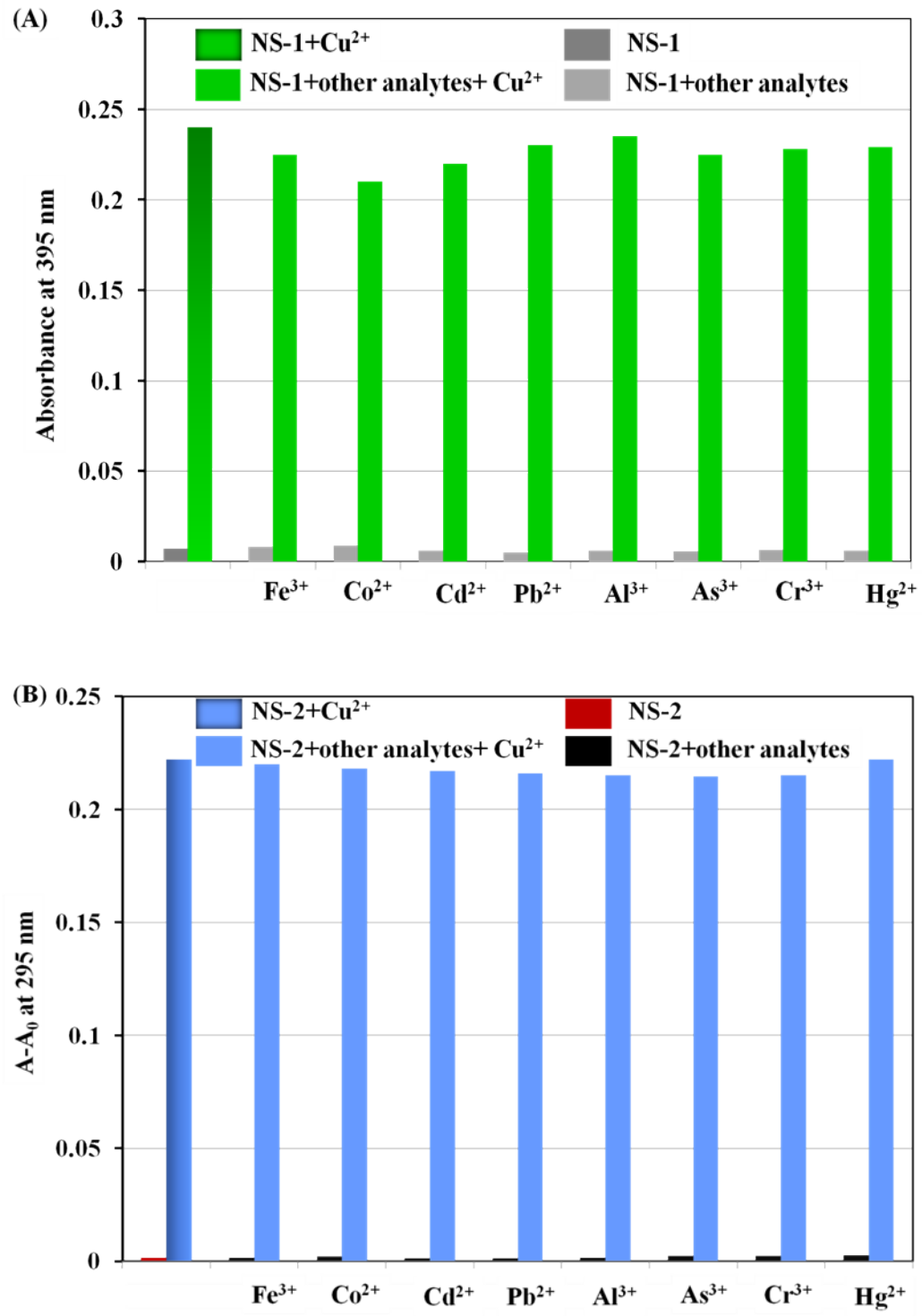


Figure S19: Cross-interference studies of **(A) NS-1** and **(B) NS-2** toward Cu^{2+}in presence of other competing cations in similar environment.

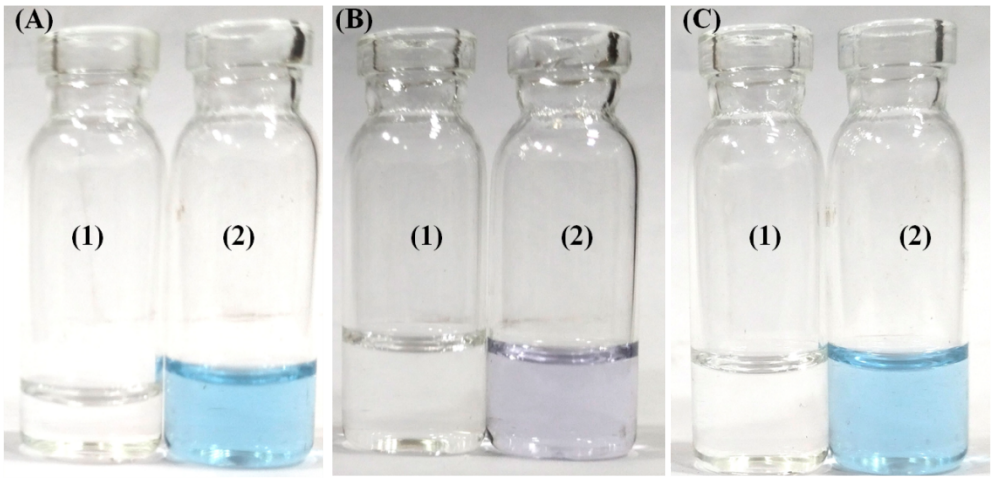


Figure S20: Naked eye chromogenic changes of **(A) (1)** pyridine-2-aldehyde**, (2)** pyridine-2-aldehyde**+**Cu^{2+}, **(B) (1)** 2-amino-2 methyl-1-propanol**, (2)** 2-amino-2 methyl-1-propanol **+**Cu^{2+} and **(C) (1)** in-situ generated ligand **(2)** in-situ generated ligand**+**Cu^{2+}.

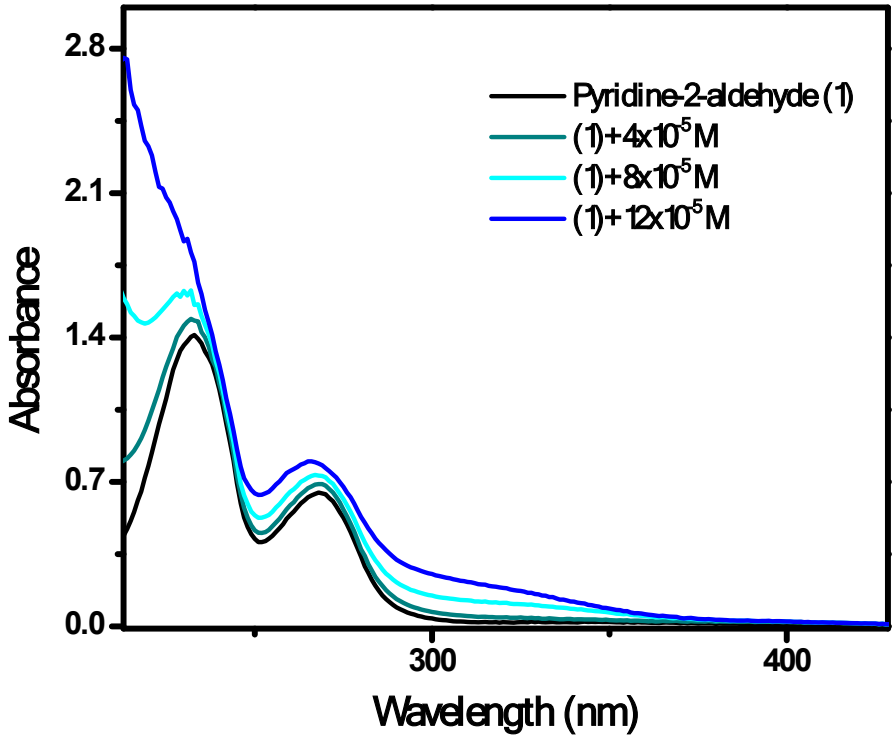


Figure S21: UV-Vis spectral change of pyridine-2-aldehyde in presence of Cu^{2+}

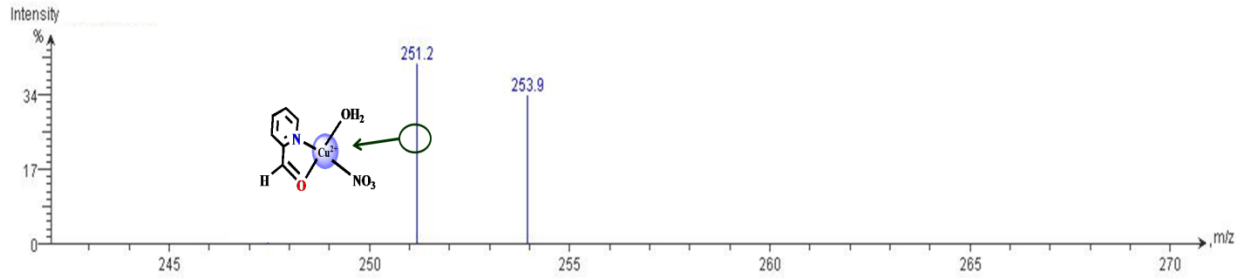


Figure S22: ESI-MS data of **NS-2** after interaction with Cu^{2+}.

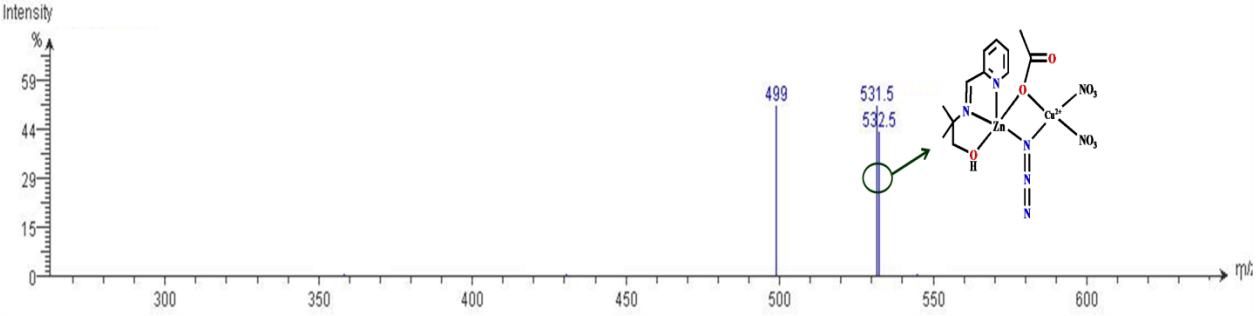


Figure S23: ESI-MS data of **NS-1** after interaction with Cu^{2+}.

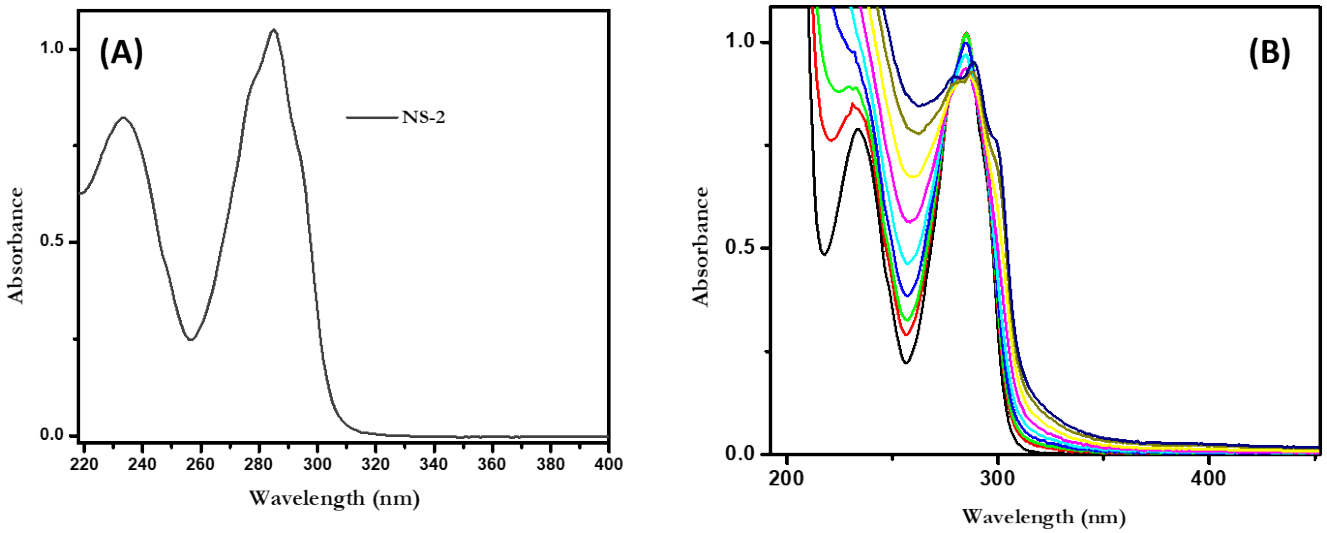


Figure S24: (A) UV-Vis absorption spectrum of **NS-2** (100 µM) in acetonitrile (B) UV-Vis spectral alteration of 10 µM **NS-2** in acetonitrile in presence of 10 µM Cu^{2+}spiked human urine sample.

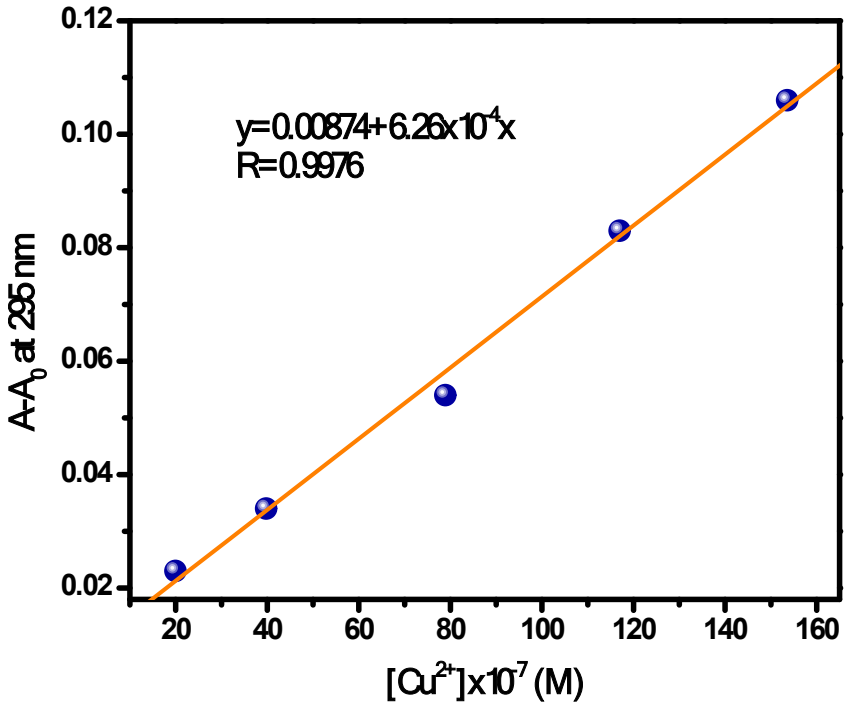


Figure S28: Change of absorbance at 295 nm as the linear function of the concentration of Cu^{2+} for the calculation of LOD of **NS-2** toward Cu^{2+}in human urine sample.

Table S12: Comparative literature survey of the recently developed complex based chemosensors for the detection of Cu^{2+}

Entry	**Solvent Medium**	**LOD**	**Solid state detection**	**Detection from real field sample**	**Cu^{2+} detection from human urine: A potential biomarker sensor for Wilson's disease diagnosis**	***Ref.***
1.	H_2O/DMSO =9/1 (v/v)	4.6 nM	No	No	No	X1
2.	Buffer solution	77 nM	No	Yes	No	X2
3.	HEPES-buffer	2.77 µM	No	No	No	X3
4.	H_2O with 0.5% DMSO	6.1 µM	Yes	Yes	No	X4
5.	H_2O/EtOH (7: 3 v/v)	-	No	Yes	No	X5
6.	HEPES buffered (pH 7.0, 10 mM)	-	No	No	No	X6

	water					
7.	THF/H_2O, (1/1, v/v)	8.95×10^{-8} M	Yes	Yes	No	X7
8.	CH_3CN:H_2O = 7:3 v/v	1.53 µM	No	No	No	X8
9.	H_2O	20 µM	Yes	Yes	No	X9
10.	Acetonitrile -water (1:1)	0.03 µM	Yes	Yes	No	X10
11.	CH_3CN	0.08 µM	No	No	No	X11
12.	(HEPES:CH3 CN (1:1), pH 7.4	5 nM	No	Yes	No	X12
13.	CH_3CN–H_2O solution (4:1, v/v)	-	No	No	No	X13
14.	MeCN/ H_2O (9/1)	-	No	No	No	X14
15.	**H_2O**	**NS-1: 48.6 fM NS-2: 2.4 µM**	**Yes**	**Yes**	**Yes**	**Present work**

References:

X1 Y.W. Sie, C.F. Wan, A.T. Wu, ***RSC Adv***.,2017, **7**, 2460-2465.

X2 N. Wang, Y. Liu, Y. Li, Q. Liu, M. Xie, ***Sens. Actuators B Chem.,*** 2018**, *255***, 78-86.

X3 Y. Fu, Q. C. Feng, X. J. Jiang, H. Xu, M. Li, S. Q. Zang, ***Dalton Trans.,*** 2014**, 43**, 5815-5823.

X4 Y.W. Sie, C.L. Li, C.F. Wan, J.H. Chen, C.H. Hu, H. Yan, A.T. Wu, ***Inorg. Chim. Acta***, 2017, **467**, 325-329.

X5 M.A. Wani, N. Thakur, M.D. Pandey, R. Pandey, ***New J. Chem.***, 2017, **41**,10000-10008.

X6 M. G. Choi, S. Cha, H. Lee, H. L. Jeon, S. K. Chang, ***Chem. Commun***., 2009, 7390-7392.

X7 L. Hou, X. Kong, Y. Wang, J. Chao, C. Li, S. Dong, y. Wang, S. Shuang, ***J. Mater. Chem. B***, 2017, **5**, 8957-8966.

X8 A. K. Mahapatra, S. Mondal, S. K. Manna, K. Maiti, R. Maji, M. R. Uddin, S. Mandal, D. Sarkar, T. K. Mondal, D. K. Maiti***, Dalton Trans***., 2015, 44, 6490-6501.

X9 Z. Quing, Z. Mao, T. Qing, X. He, Z. Zou, D. He, H. Shi, J. Huang, J. Liu, K. Wang, ***Anal. Chem.,*** 2014**, 86**, 11263−11268.

X10 N. Dey, J. Kulhanek, F. Bures, S. Bhattacharya, ***J. Org. Chem***., 2019, **84**, 1787–1796.

X11 X. He, J. Zhang, X. Liu, L. Dong, D. Li, H. Qiu, S. Yin, ***Sens. Actuators B Chem***., 2014, **192**, 29-35.

X12 A. Kumar, S. Kumar, P. S. Chae, ***Dyes and Pigm***., 2020, **181**, 108522.

X13 Y. Yang, C. Gao, B. Li, L. Xu, L. Duan, ***Sens. Actuators B Chem***., 2014, 199, 121-126.

X14 S. Malkondu, S. Erdemir, ***Tetrahedron***, 2014, **70**, 5494-5498.