Supplementary Information

Ultratrace level detection of Cu^{2+} in aqueous medium by novel Zn(II)-dicarboxylato – pyridyl coordination polymers and cell imaging with HepG2 cells.

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Figure S1. IR spectra of CP**1** and CP**1**+Cu(II) ion.
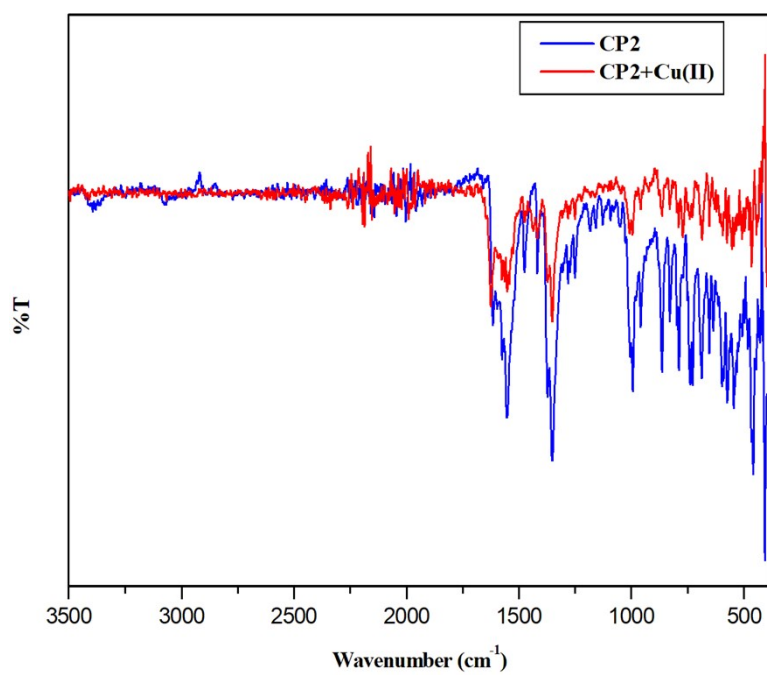
Figure S2. IR spectra of CP**2** and CP**2**+Cu(II) ion.

Table S1 Crystal data and refinement parameters for compound CP**1.**

Formula	$C_{19} H_{12} Cl N_3 O_5 Zn$
fw	461.19
crystsyst	triclinic
space group	*P -1*
a (Å)	9.0876(7)
b (Å)	10.0804(8)
c (Å)	11.7778(9)
α(deg)	66.626(2)
β(deg)	75.962(2)
γ (deg)	65.717(2)
V (Å^3)	898.68(12)
Z	2
D_{calcd}(g/cm^3)	1.704
μ(mm^{-1})	1.515
λ(Å)	0.71073
data[$I > 2\sigma(I)$]/params	3093/268
GOF on F^2	1.343
final *R* indices[$I > 2\sigma(I)$][a,b]	*R*1 = 0.0270 *wR*2 = 0.0990

[a]$R1 = \Sigma||F_o| \quad |F_c||/ \Sigma|F_o|$, [b]$wR2 = [\Sigma w(F_o^2 \quad F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

Table S2 Selected bond lengths and bond angles in CP**1.**

Zn(1) - O(1)	1.9870(19)	N(1) - Zn(1) - O(4)b	87.32(8)
Zn(1) - O(3)	2.082(2)	N(2) - Zn(1) - N(3)	75.55(8)
Zn(1) - N(1)	2.154(2)	N(2) - Zn(1) - O(4)b	82.66(7)
Zn(1) - N(2)	2.080(2)	N(3) - Zn(1) - O(4)b	86.46(8)
Zn(1) - N(3)	2.166(2)	Zn(1) - O(3) - C(1)	120.03(17)
Zn(1) - O(4)b	2.510(2)	C(4) - O(4) - Zn(1)a	122.45(18)
O(1) - Zn(1) - O(3)	100.39(8)	Zn(1) - N(1) - C(15)	115.47(17)
O(1) - Zn(1) - N(1)	110.65(8)	Zn(1) - N(1) - C(19)	125.85(16)

O(1) - Zn(1) - N(2)	163.19(8)	Zn(1) - N(2) - C(10)	119.84(16)
O(1) - Zn(1) - N(3)	95.85(8)	Zn(1) - N(2) - C(14)	118.93(16)
O(1) - Zn(1) - O(4)b	82.41(7)	Zn(1) - N(3) - C(5)	124.97(16)
O(3) - Zn(1) - N(1)	95.18(8)	Zn(1) - N(3) - C(9)	115.85(17)
O(3) - Zn(1) - N(2)	94.03(7)	N(1) - Zn(1) - N(3)	151.69(7)
O(3) - Zn(1) - N(3)	89.46(8)	N(1) - Zn(1) - N(2)	76.27(8)
O(3) - Zn(1) - O(4)b	175.29(8)		

a = x,-1+y,z   b = x,1+y,z

Table S3 Crystal data and refinement parameters for compound CP**2.**

Formula	$C_{21} H_{15} Cl N_3 O_5 Zn$,
fw	490.20
crystsyst	Triclinic
space group	$P\text{-}1$
a (Å)	8.697(5)
b (Å)	10.798(6)
c (Å)	13.165(7)
α(deg)	100.543(14)
β(deg)	105.004(14)
γ (deg)	113.587(14)
V (Å^3)	1035.5(10)
Z	2
D_{calcd}(g/cm^3)	1.572
μ(mm^{-1})	1.354
λ(Å)	0.71073
data[$I > 2\sigma(I)$]/params	3529/286
GOF on F^2	1.073
final R indices[$I > 2\sigma(I)$][a,b]	$R1 = 0.0766$ $wR2 = 0.2159$

Table S4 Selected bond lengths and bond angles in CP**2.**

Zn(1) - O(1)	1.961(4)	N(1) - Zn(1) - N(2)	74.7(2)
Zn(1) - O(3)	1.951(5)	N(1) - Zn(1) - N(3)	150.69(18)
Zn(1) - N(1)	2.211(6)	N(2) - Zn(1) - N(3)	76.2(2)
Zn(1) - N(2)	2.092(5)	Zn(1) - O(1) - C(19)	119.5(4)
Zn(1) - N(3)	2.174(7)	Zn(1) - O(3) - C(3)	115.4(4)
O(1) - Zn(1) - O(3)	98.53(18)	Zn(1) - N(1) - C(14)	116.1(4)
O(1) - Zn(1) - N(1)	92.3(2)	Zn(1) - N(1) - C(18)	125.6(4)
O(1) - Zn(1) - N(2)	132.83(19)	Zn(1) - N(2) - C(9)	117.8(4)
O(1) - Zn(1) - N(3)	104.9(2)	Zn(1) - N(2) - C(13)	119.9(4)
O(3) - Zn(1) - N(1)	105.0(2)	Zn(1) - N(3) - C(4)	126.3(5)
O(3) - Zn(1) - N(2)	128.6(2)	Zn(1) - N(3) - C(8)	115.4(5)
O(3) - Zn(1) - N(3)	95.8(2)	N(1) - Zn(1) - N(3)	150.69(18)

a = x,-1+y,z   b = x,1+y,z

(a)

(b)
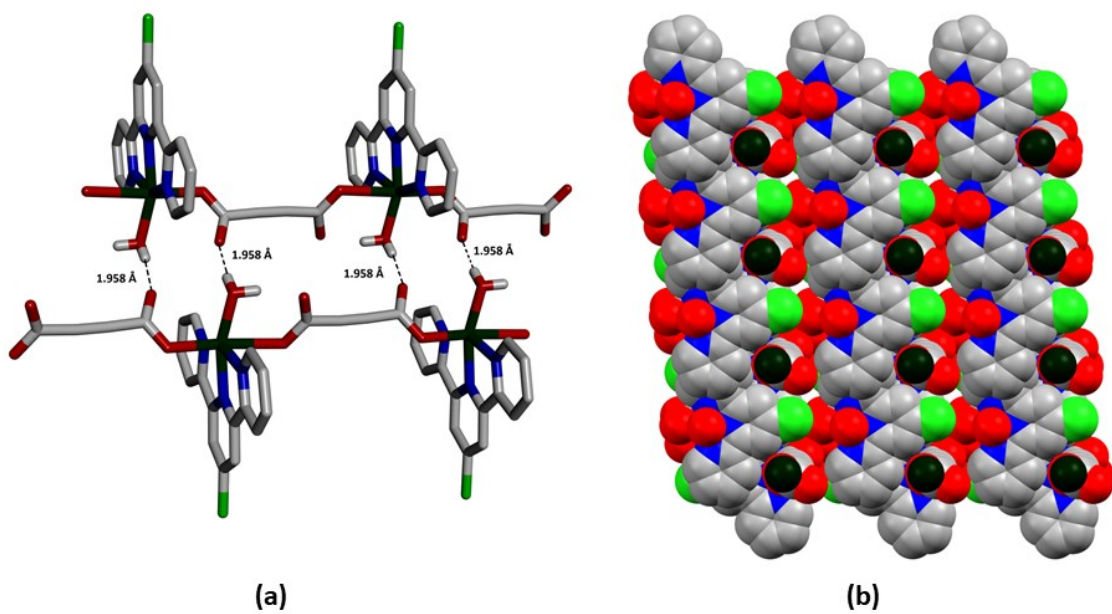
Figure S3. (a) H-bonding interaction between water and adc^{2-} ion in CP**1**. **(b)** spell field model of CP**1.**
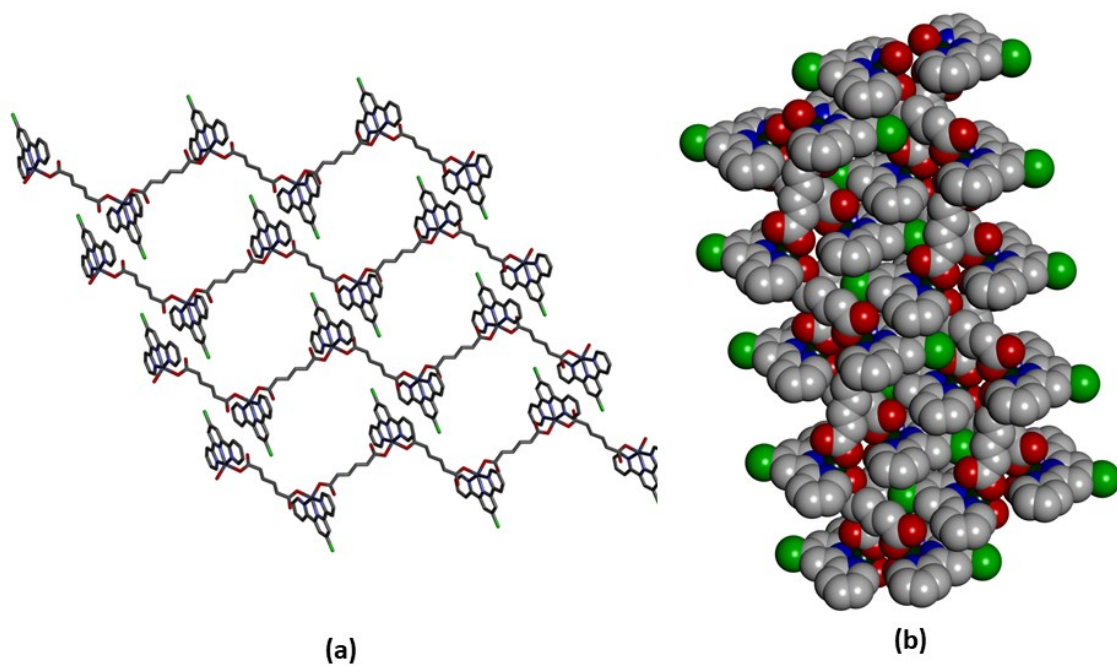

(a)

(b)

Figure S4. (a) Supramolecular aggregate of 1D coordination polymer. **(b)** Spell field model of CP**2**.
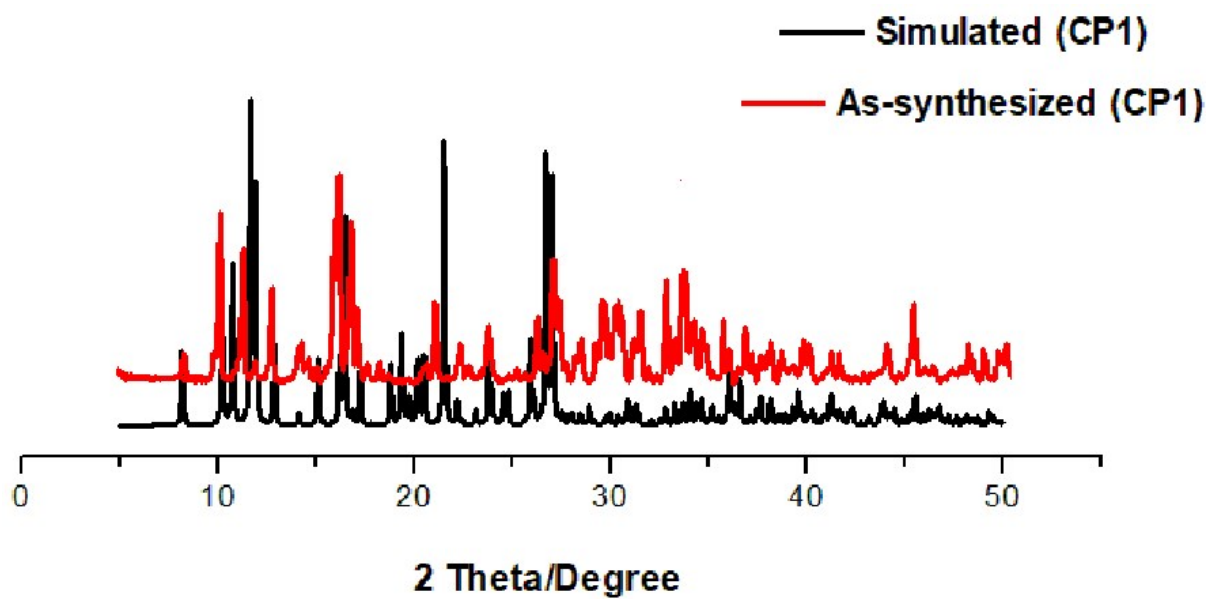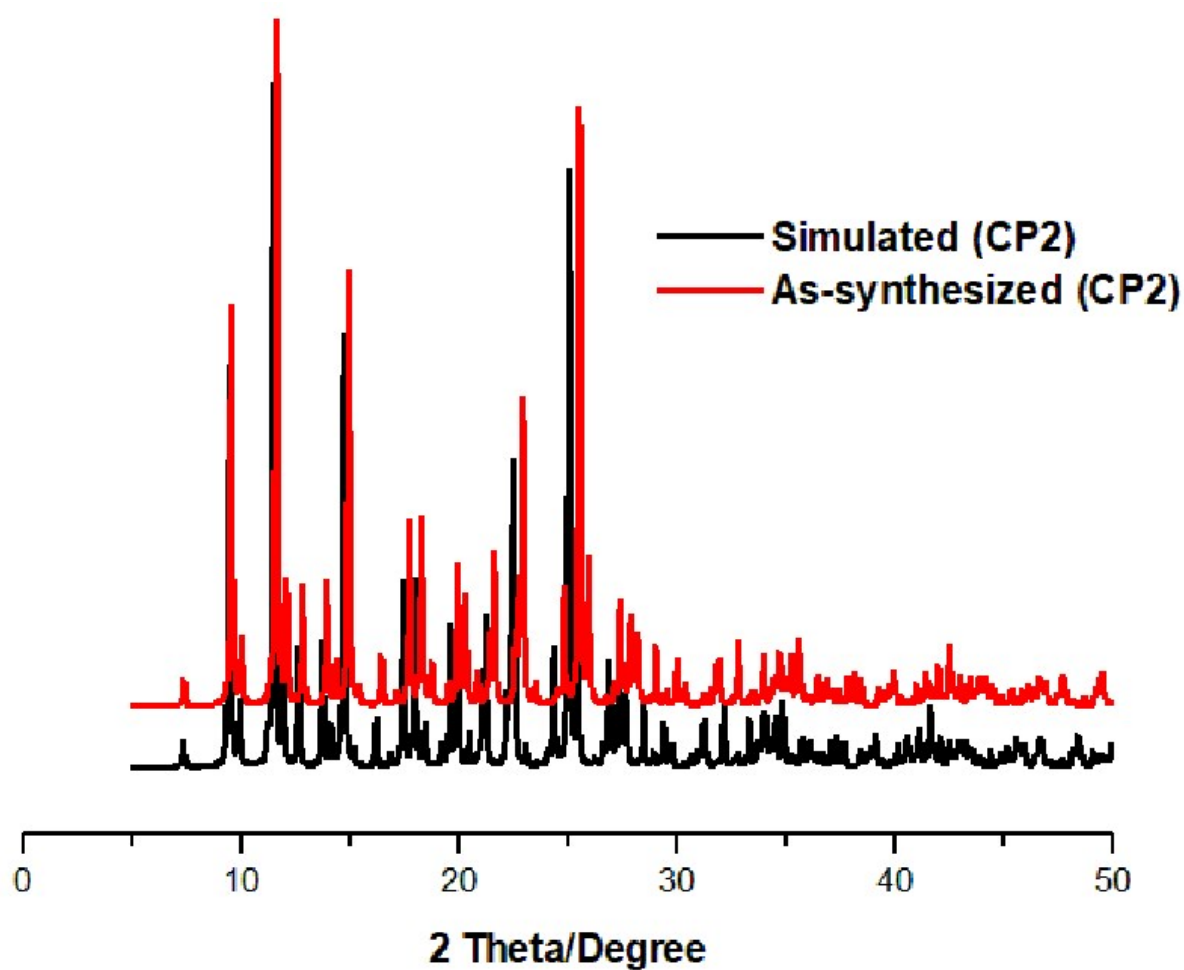
Figure S5. Powder X-ray Diffraction analysis of CP**1.**

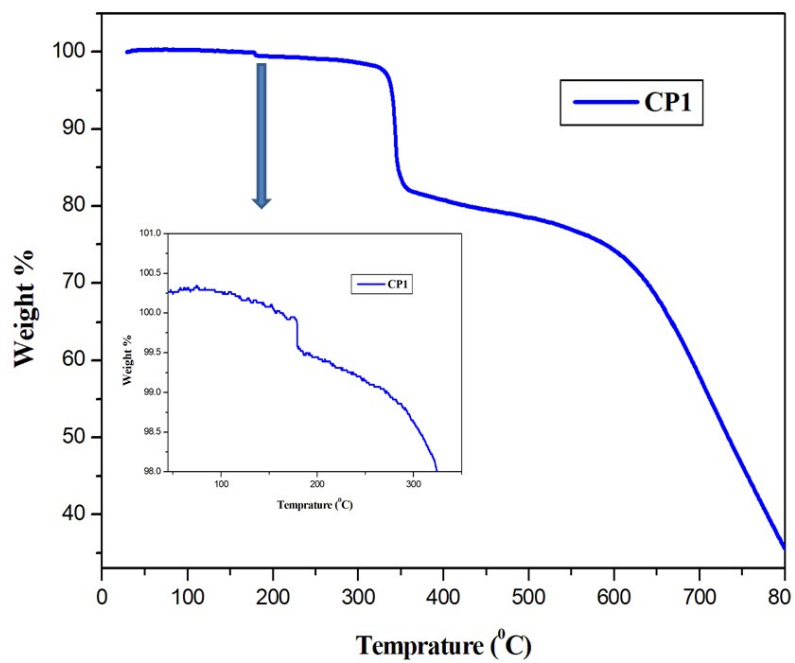**Figure S6.** Powder X-ray Diffraction analysis of CP**2**.
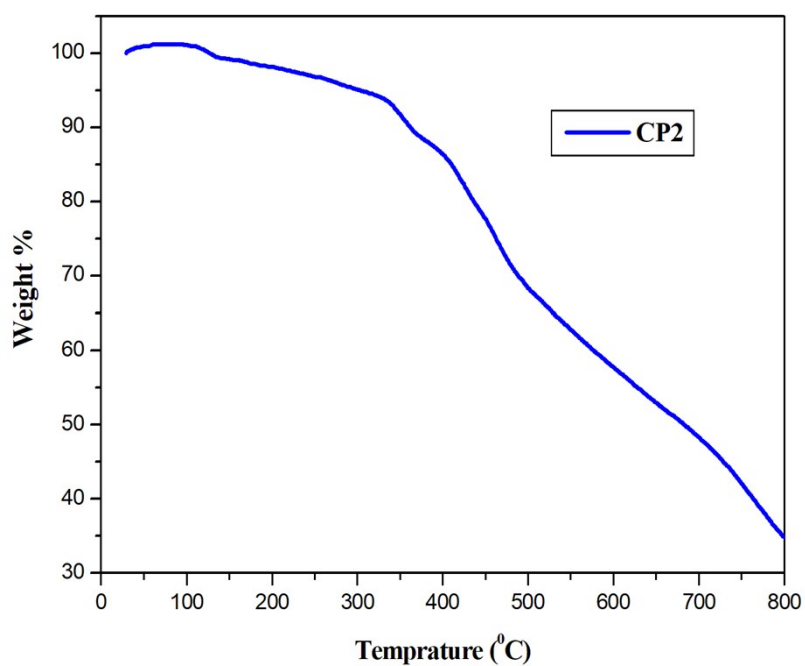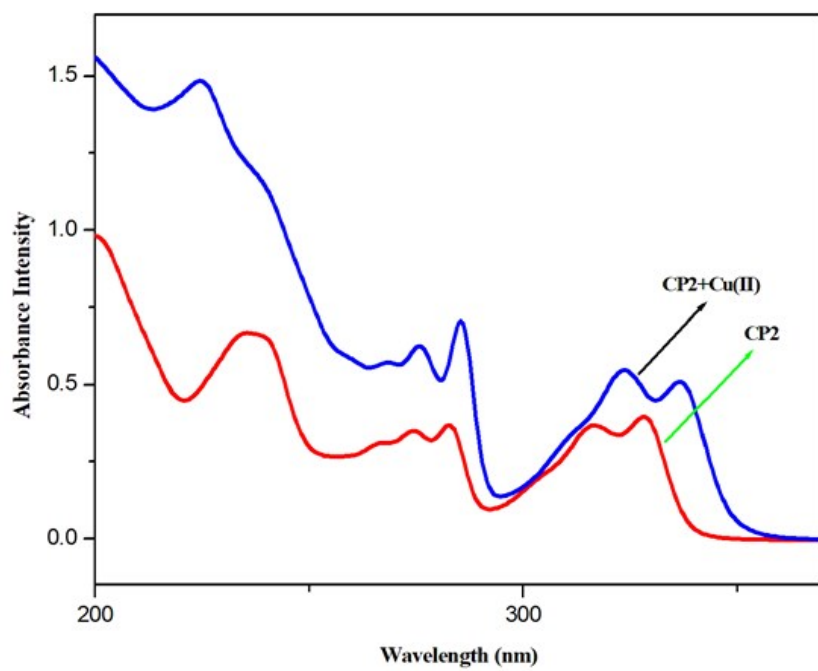
Figure S7. Thermogravimetric analysis (TGA) of CP**1**.

Figure S8. Thermogravimetric analysis (TGA) of CP**2**.
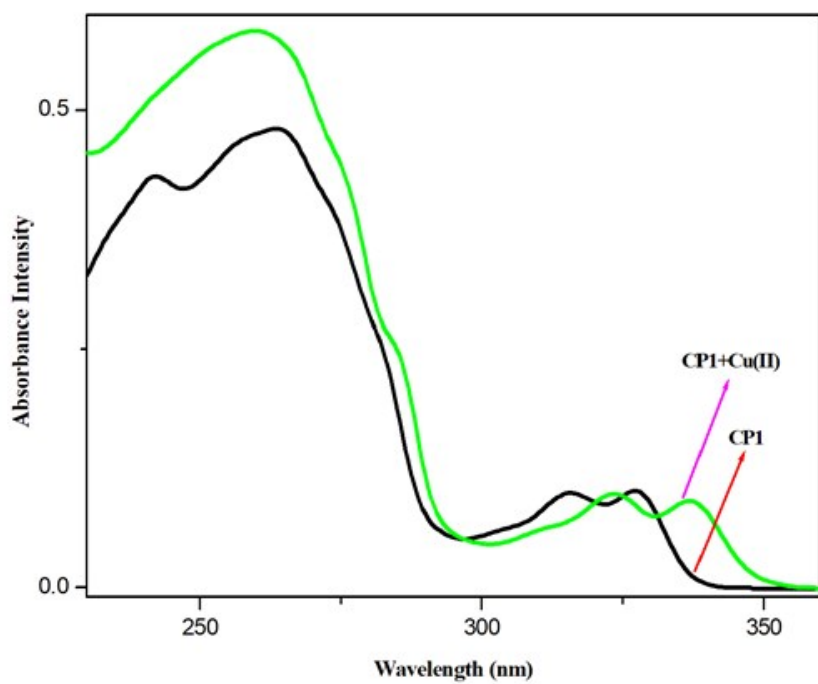
Figure S9. UV Visible spectrum of CP**1** and CP**1**+Cu(II) in aqueous medium.

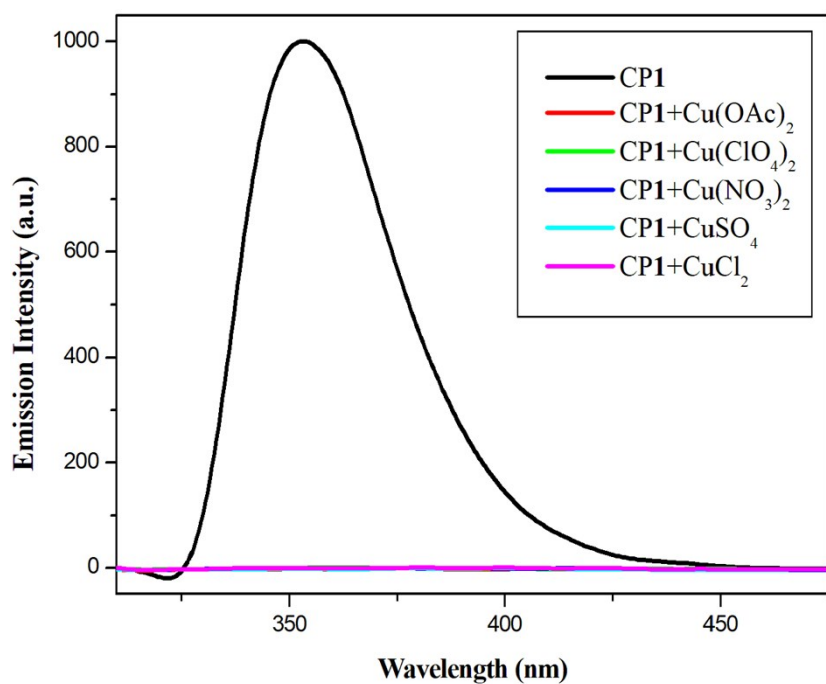**Figure S10.** UV Visible spectrum of CP**2** and CP**2**+Cu(II) in aqueous medium.

Figure S11. Emission Intensity of CP**1** in presence of different Cu salts.
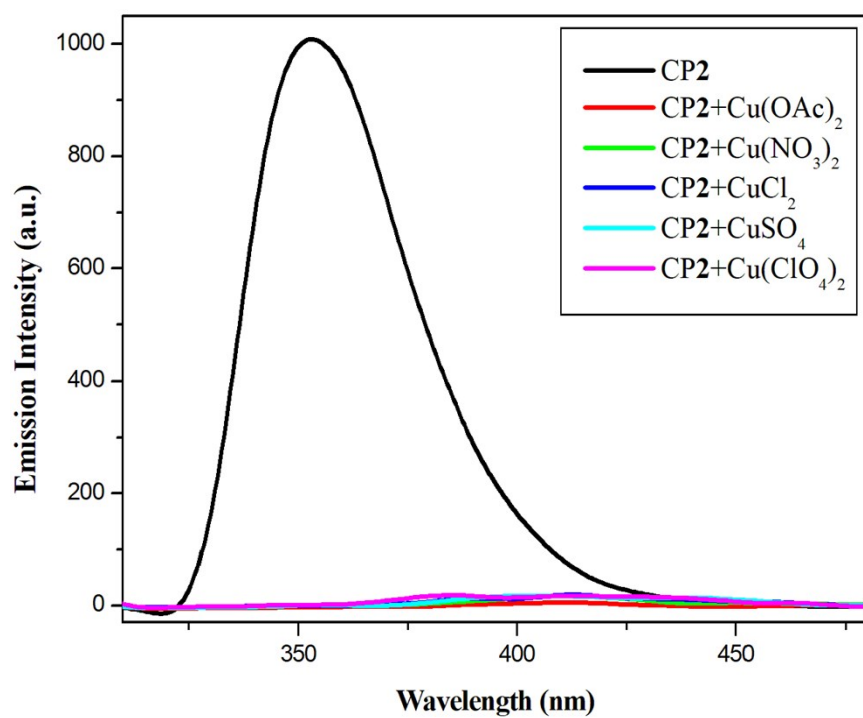

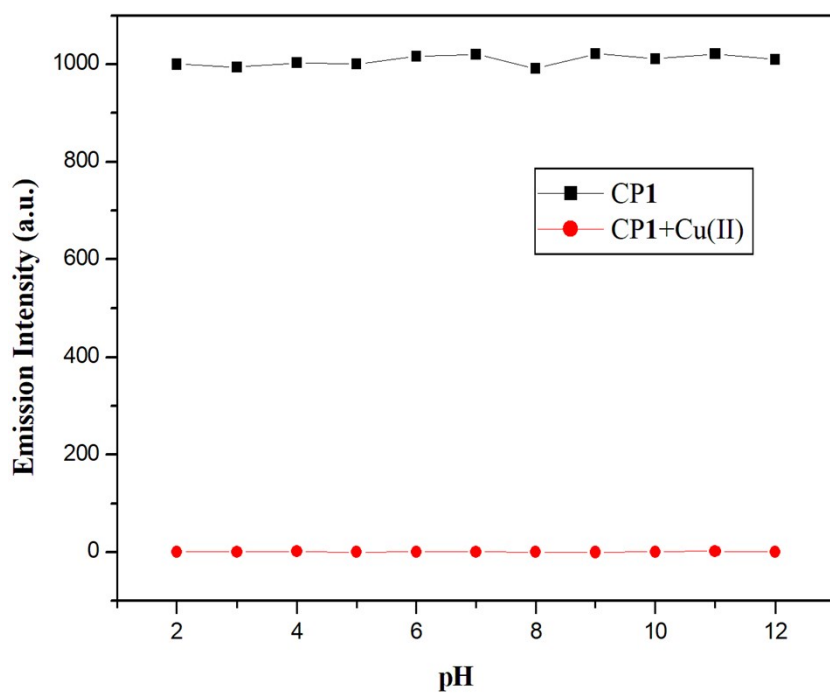**Figure S12.** Emission Intensity of CP**2** in presence of different Cu salts.

Figure S13. Emission Intensity of CP**1** and CP**1** in presence of Cu(II) ion at different pH.
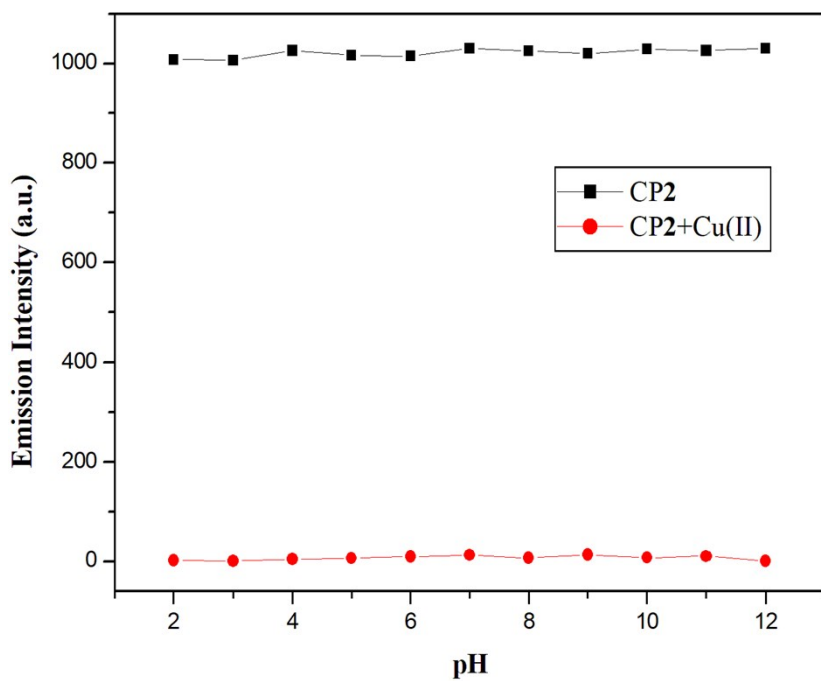

Figure S14. Emission Intensity of CP**1** and CP**1** in presence of Cu(II) ion at different pH.
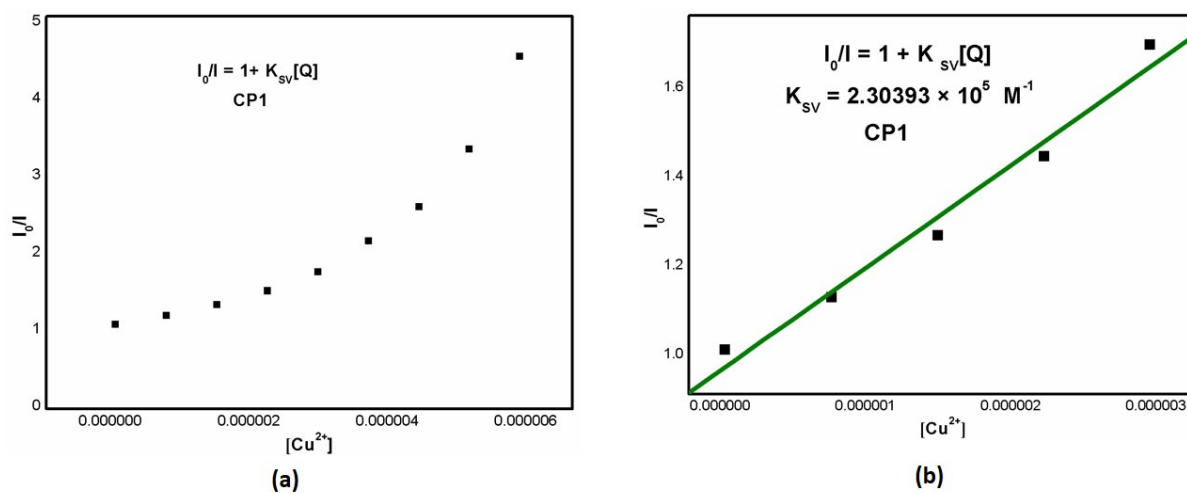
Figure S15. (a) Stern-Volmer plot of CP**1. (b)** Stern-Volmer plot of CP**1** at lower range of quencher $[Cu^{2+}]$ (in M) concentration.
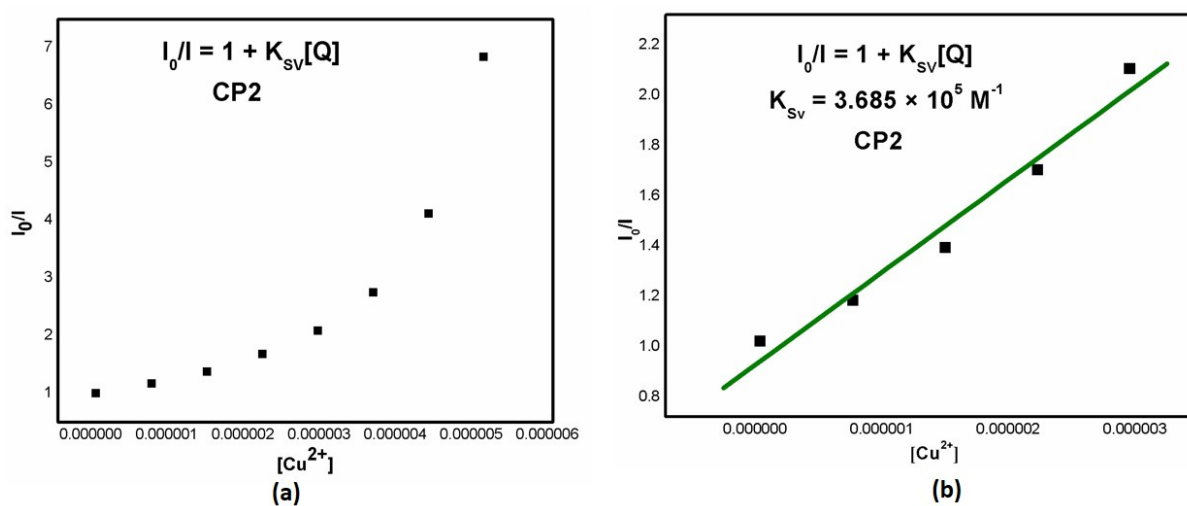

Figure S16. Stren-Volmer plot of CP**2. (b)** Stern-Volmer plot of CP**2** at lower range of quencher $[Cu^{2+}]$ (in M) concentration.
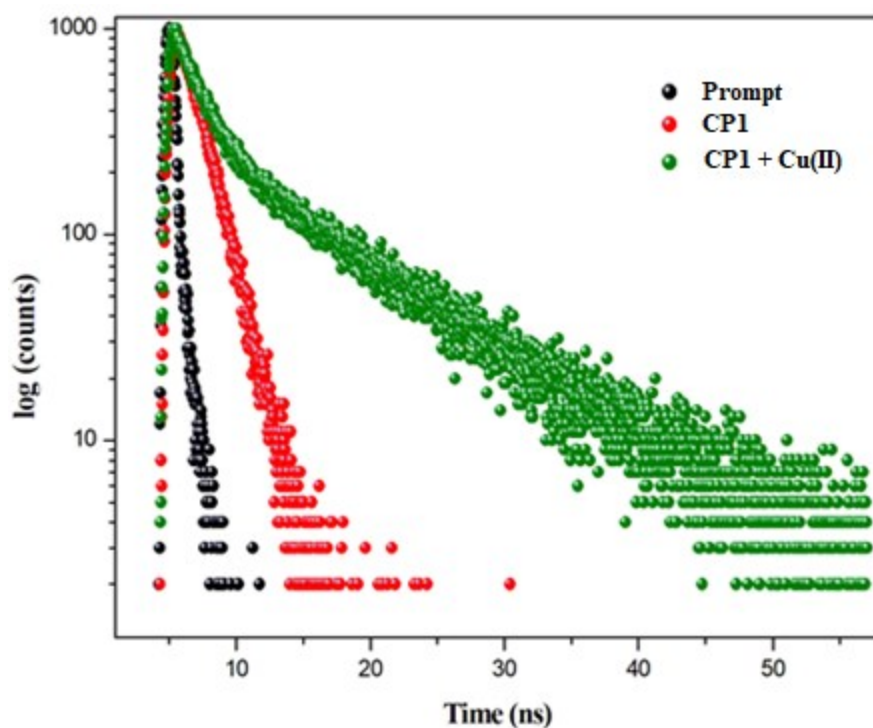
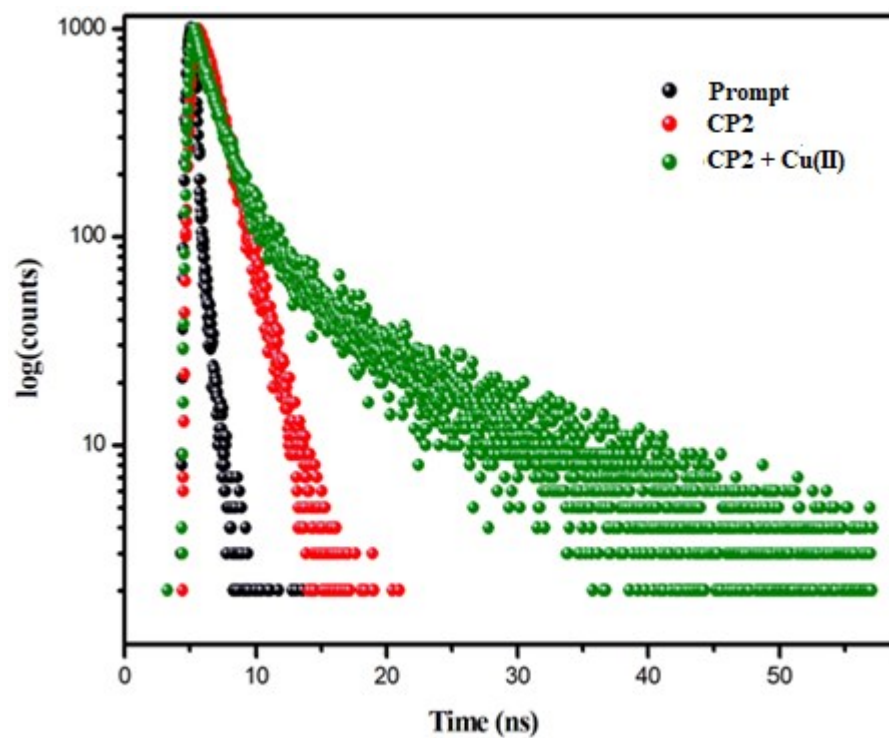**Figure 17** Excited state decay profile of prompt, CP**1** and Cu^{2+} ion with CP**1** in aqueous medium.

Figure S18 Excited state decay profile of prompt, CP**1** and Cu^{2+} ion with CP**1** in aqueous medium.
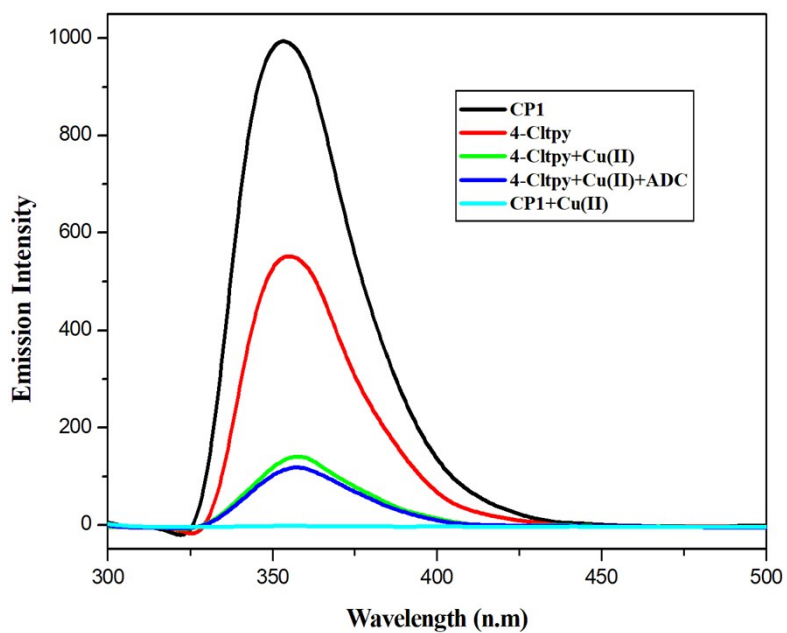
Figure S19 Emission intensity of CP**1** , constitute materials of CP**1** and their intensity change in presence of Cu(II) ion.
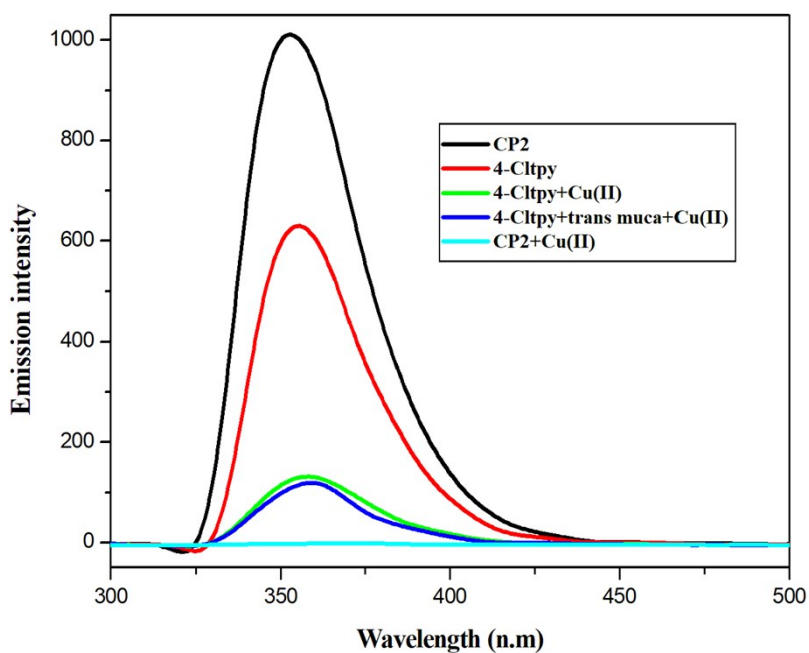

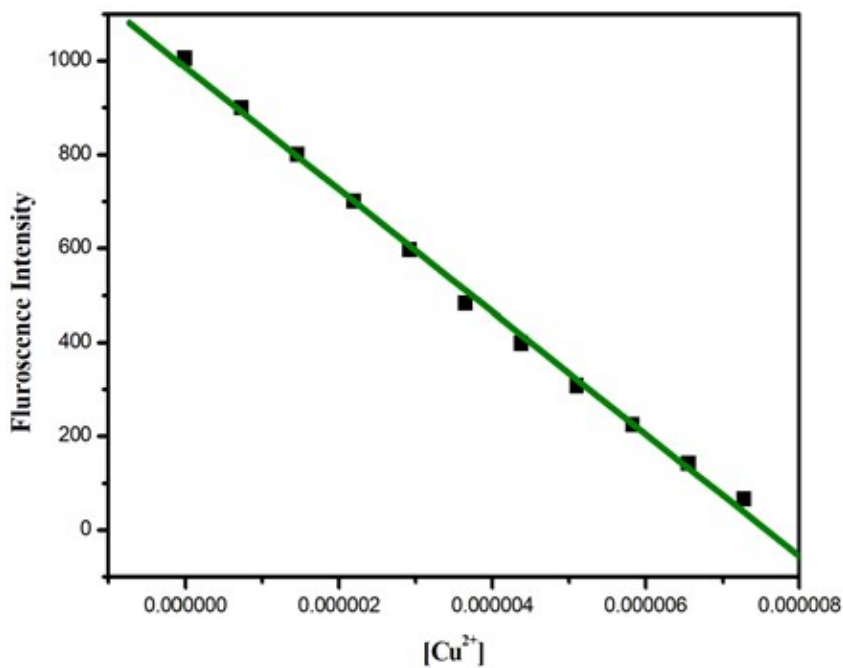**Figure S20** Emission intensity of CP**2** , constitute materials of CP**2** and their intensity change in presence of Cu(II) ion.

Figure S21 The linear dynamic response of **CP1** for Cu^{2+} ion and the determination of the limit of detection(LOD) of Cu^{2+} ion.
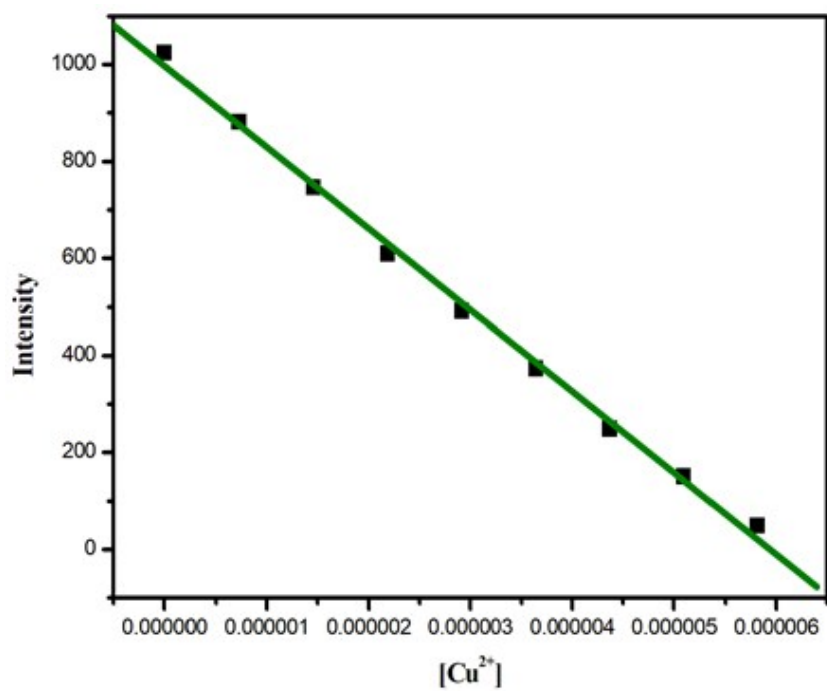

Figure S22 The linear dynamic response of **CP2** for Cu^{2+} ion and the determination of the limit of detection (LOD) of Cu^{2+} ion.
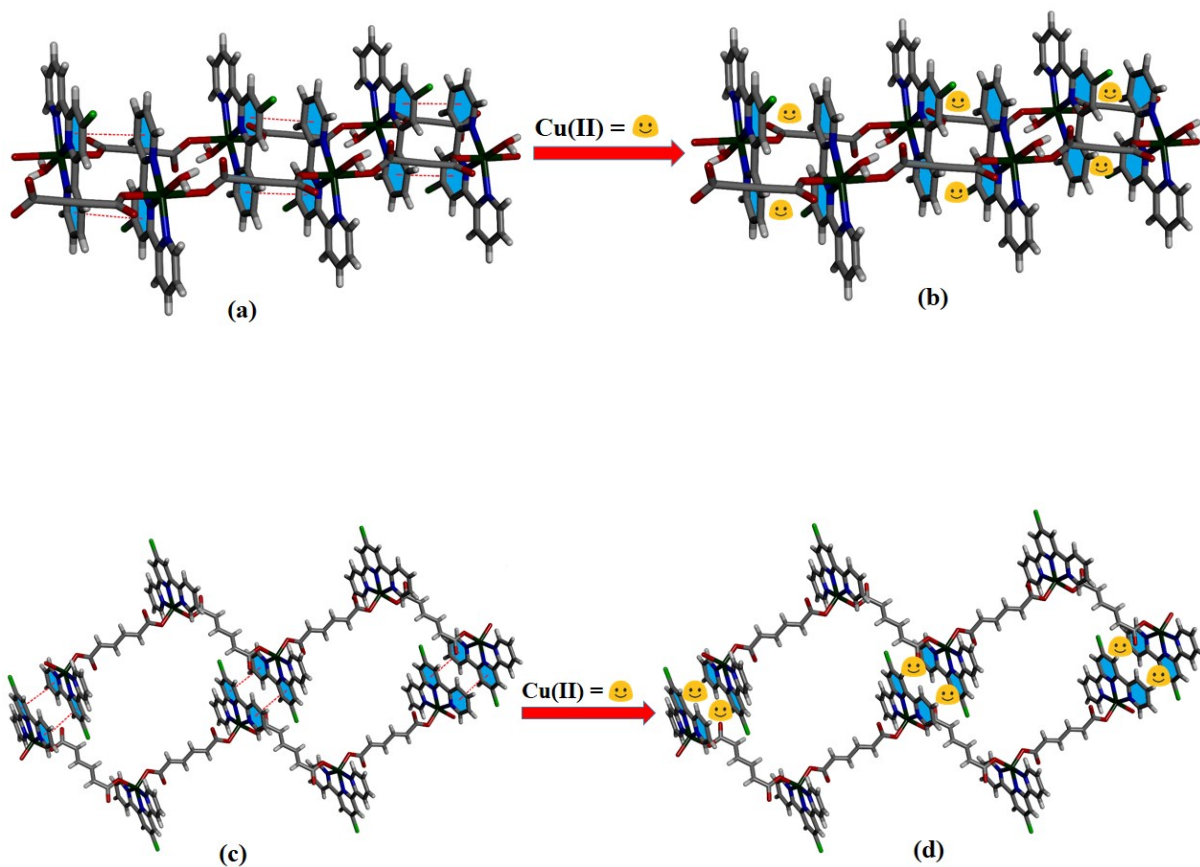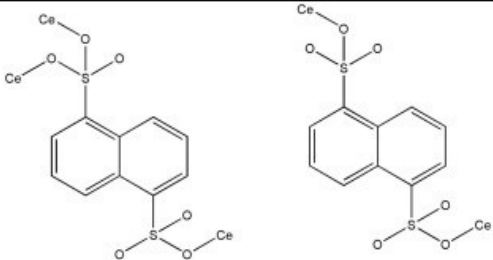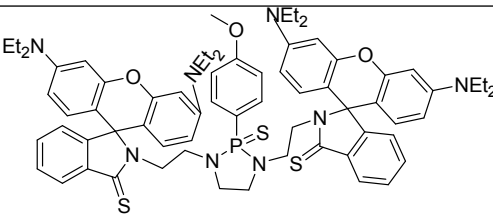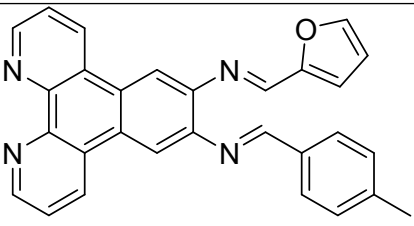
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Figure S23. (a) $\pi\cdots\pi$ interaction between CP**1** moiety, **(b)** interaction between Cu(II) and CP**1**, **(c)** $\pi\cdots\pi$ interaction between CP**2** moiety, **(d)** interaction between Cu(II) and CP**2**.

Table S5 Comparison data for Cu^{2+} ion sensor.

Sl. No.	Ligand	Selectivity (LOD)	Solvent	Live Cell Imaging	Reference
1.		3.0 μM.	Water	No	1.
2.	SSA/AMP-Tb, 5-sulfosalicylic acid (SSA), adenosine monophosphate (AMP) and terbium ion (Tb3+),	0.3 μM	HEPES buffer (0.1 M, pH 7.4)	No	2.
3.		0.01 μM.	MeCN	No	3.
4.		0.45 μM.	MeOH	No	4.
5.	CP**1** and CP**2**	0.14 μM and 0.06 μM respectively.	Water	Yes	**This Work**

Reference:

1. S. Geranmayeh, M. Mohammadnejad and S. Mohammadi, *Ultrason. Sonochem*, 2018, **40**, 453-459.
2. P. Huang, F. Wu and L.Mao, *Anal. Chem*. 2015, **87**, 6834-6841.
3. H. She, F. Song, J. Xu, X. Xiong, G. Chen,; J. Fan, S. Sun and X. Peng, *Chem. Asian J.* 2013, **8**, 2762-2767.
4. G. V. Vaidyanathan and U. B. Nair, *Dalton Trans*. 2012, **41**, 5769-5773.