Supporting Information

Green facile synthesis to develop nanoscale coordination polymers as lysosome targetable luminescent bioprobe

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Total number of Tables: 13

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NMR

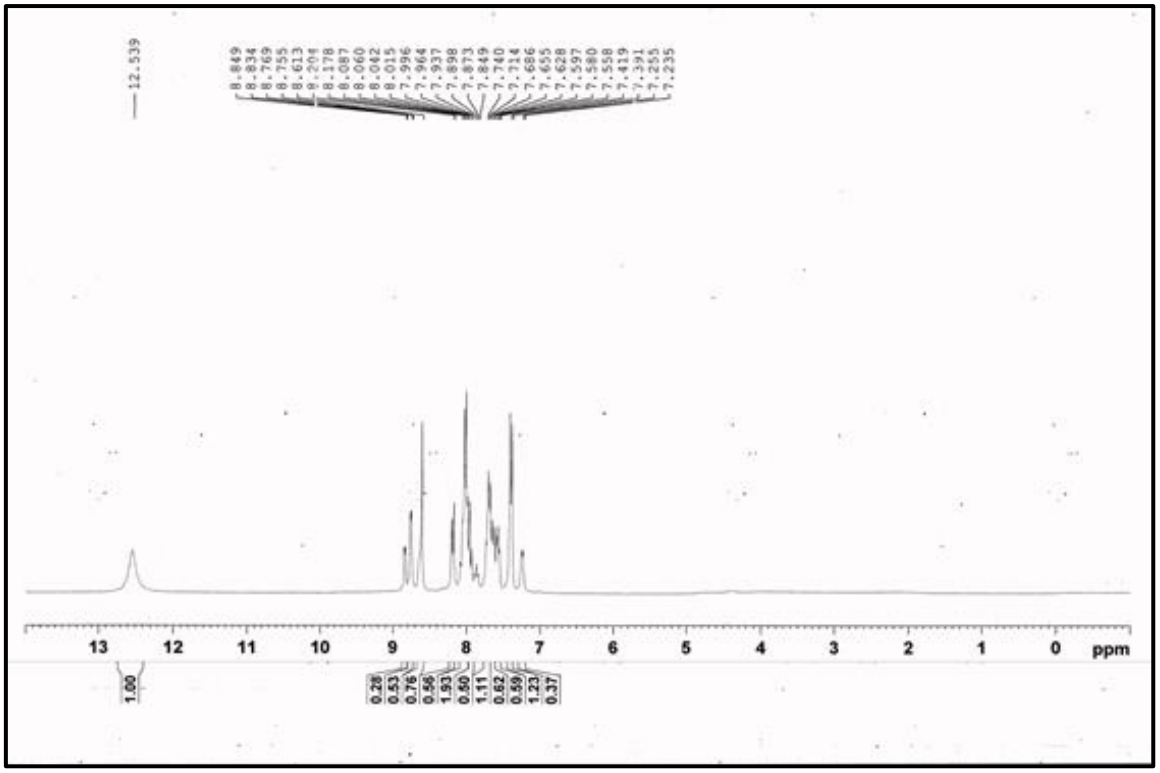


Fig. S1 ^{1}H NMR spectrum of the synthesized ligand (**HL**).

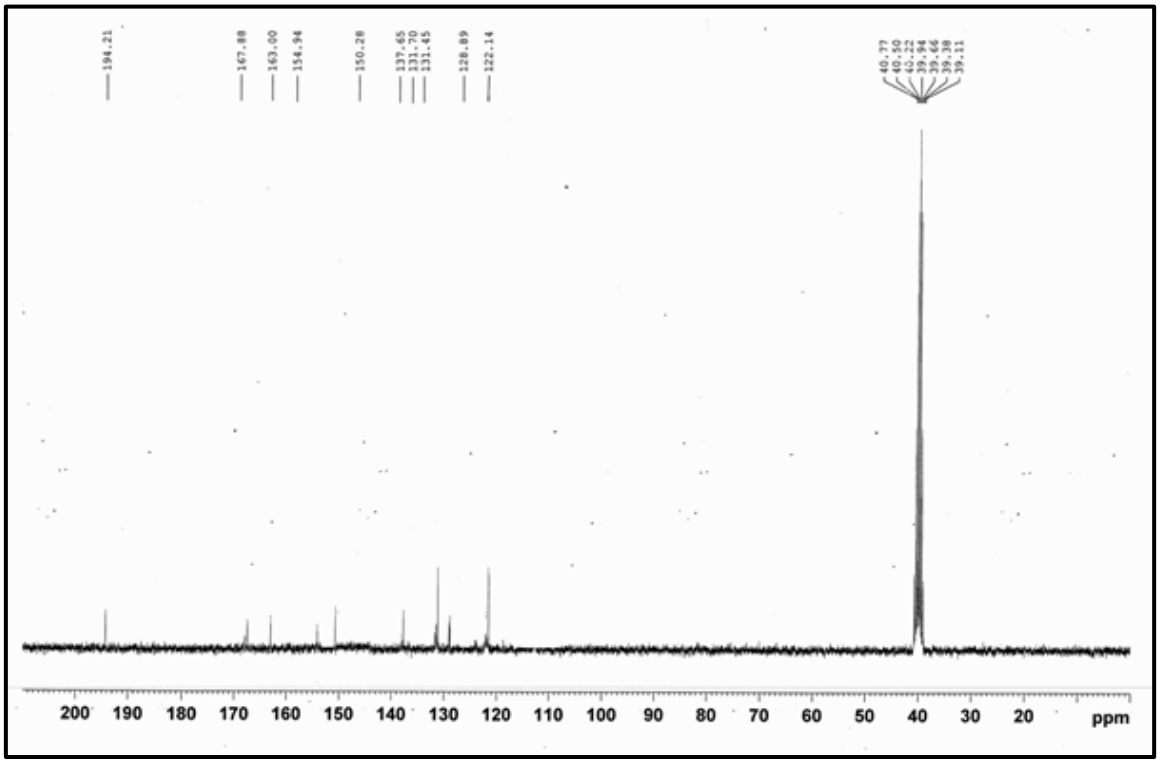


Fig. S2 ^{13}C NMR spectrum of the synthesized ligand (**HL**).

Mass

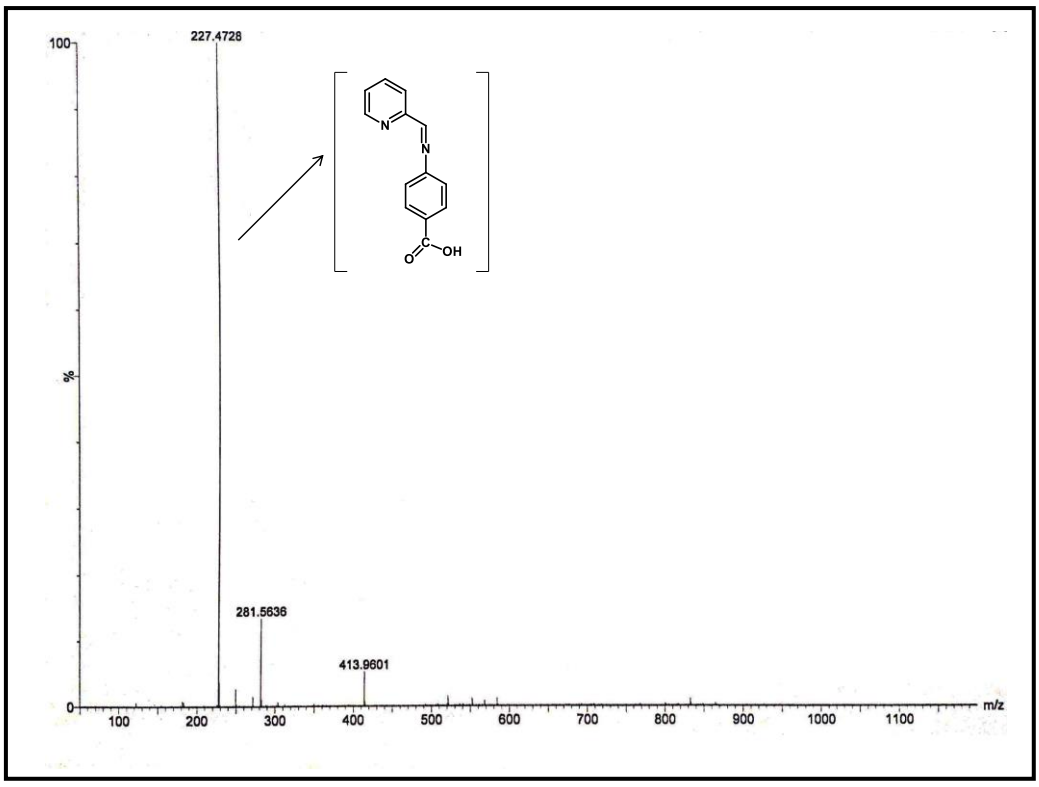


Fig. S3 ESI-MS spectrum of the synthesized ligand (**HL**).

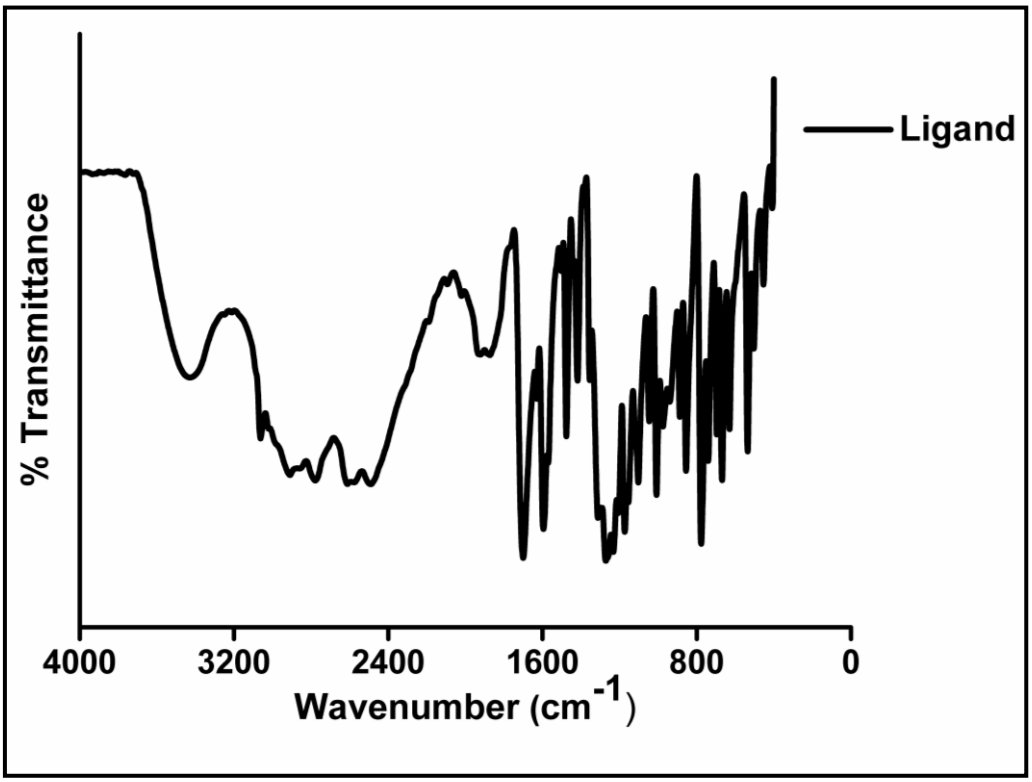


Fig. S4 FT-IR spectrum of as synthesized ligand (**HL**) at room temperature.

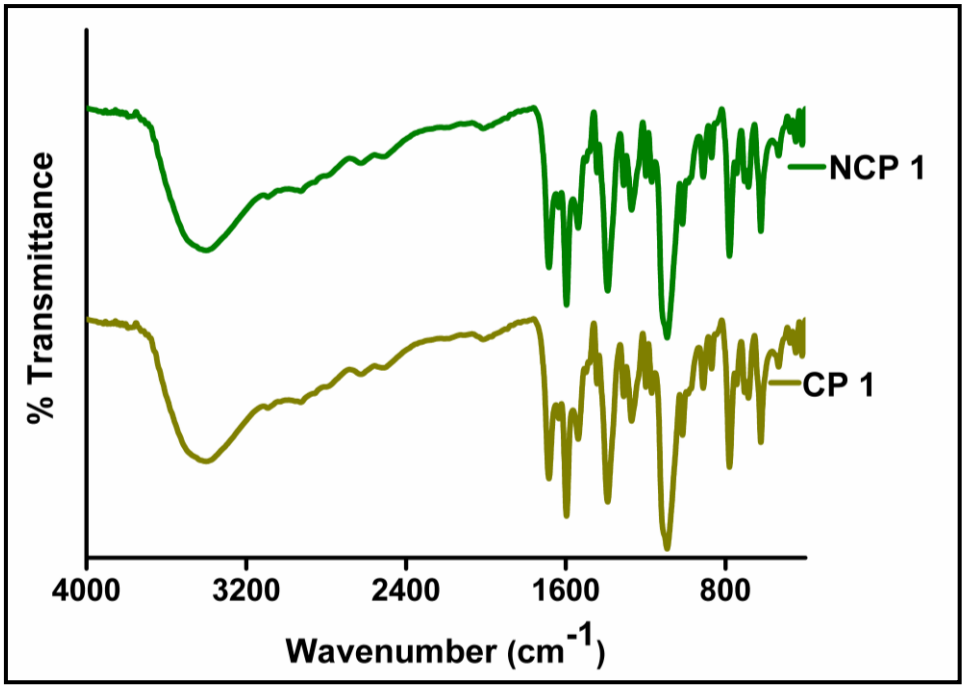


Fig. S5 FT-IR spectra of as synthesized **1** and nanoscale **1** at room temperature.

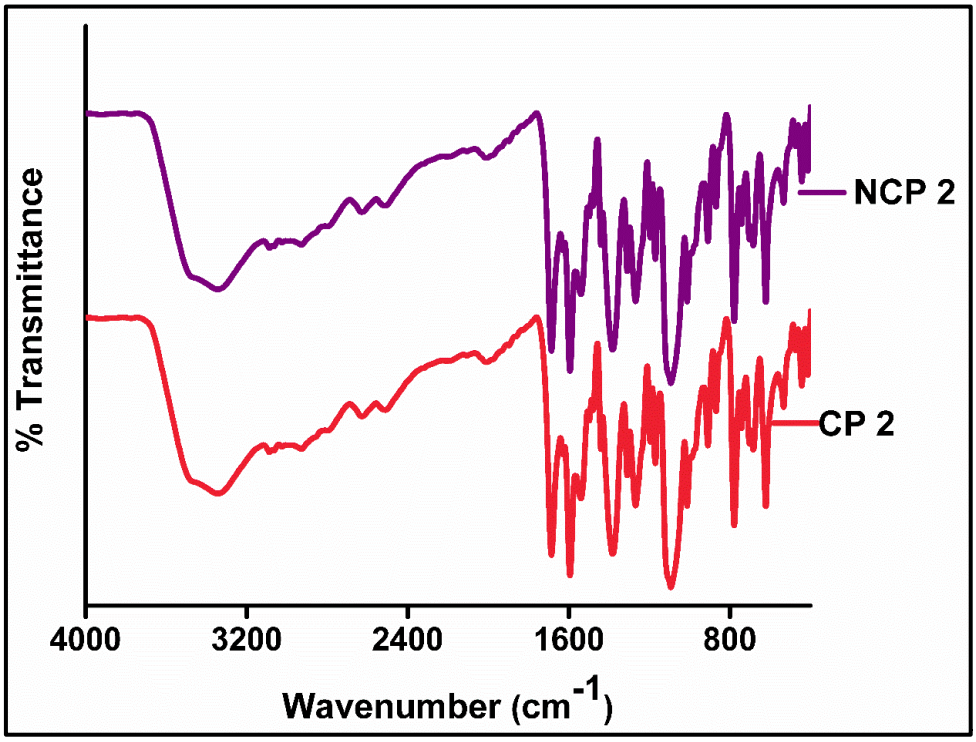


Fig. S6 FT-IR spectra of as synthesized **2** and nanoscale **2** at room temperature.

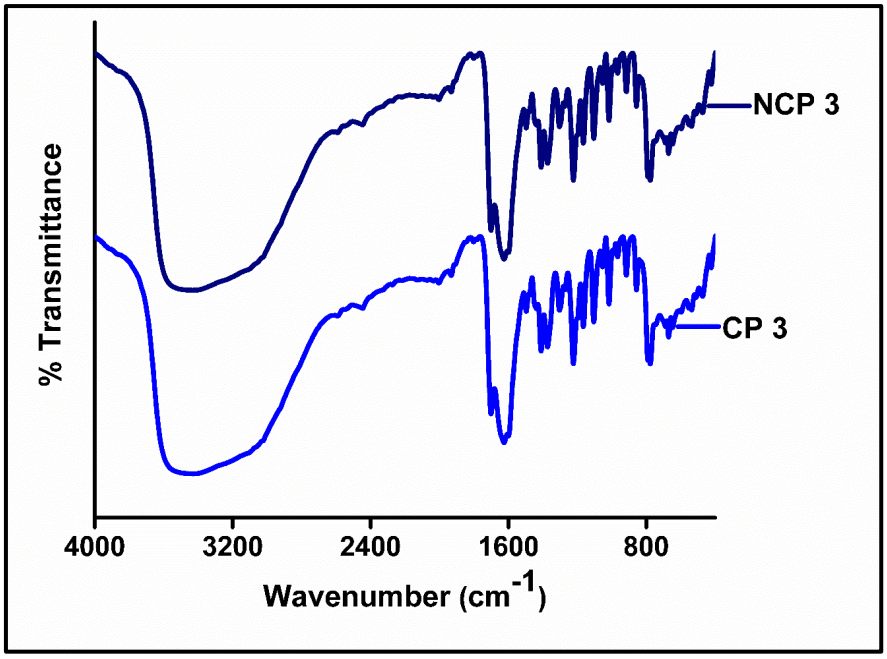


Fig. S7 FT-IR spectra of as synthesized **3** and nanoscale **3** at room temperature.

Table S1. Crystallographic parameters for Coordination polymers (**CP 1-3**)

Crystal Parameters	**CP1**	**CP2**	**CP3**
CCDC Number	2006521	2006522	2006523
Empirical formula	C_{26} H_{23}Cl Zn N_4 O_{10}	C_{26} H_{23}Cl Mn N_4 O_{10}	C_{26} H_{23}Cl Cu N_4 O_{10}
Formula weight	652.30	641.87	650.47
Crystal size/mm	0.36 × 0.30 × 0.28	0.39 × 0.28 × 0.23	0.35 × 0.26 × 0.15
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	Pbca	Pbca	Pbca
a/Å	19.430(6)	19.467(6)	19.3664(15)
b/Å	14.992(3)	14.876(3)	15.0082(12)
c/Å	18.642(6)	18.738(4)	18.5662(13)
α/°	90	90	90
β/°	90	90	90
γ/°	90	90	90
Volume/Å^3	5431(3)	5426(2)	5396.4(7)
Density	1.596	1.571	1.596
Z	8	8	8
F(000)	2672	2632	2664
μMo Kα/mm1 Mo Kα radiation/ CuKα radiation	0.202 λ=0.71073Å	0.202 λ=0.71073Å	0.202 λ=0.71073Å
Temperature/K	298(2)	298(2)	298(2)
R_{int}	0.0393	0.0411	0.0738
Range of h,k,l	-23 ≤ h ≤ 23, -17 ≤ k ≤ 17, -22 ≤ l ≤ 22	-24 ≤ h ≤ 24, -18 ≤ k ≤ 18, -23 ≤ l ≤ 23	-16≤ h ≤ 16, -12 ≤ k ≤ 12, -15 ≤ l ≤ 15
θmin/max/°	2.034/25.145	2.727/26.399	2.433/17.405
Reflections collected/unique/observed [I>2σ(I)]	109587/4829/3484	84755/5554/4562	33565/1652/1267
Data/restraints/ parameters	4829/5/431	5554/6/394	1652/560/412
Goodness of fit on F2	1.052	1.053	1.207
Final $R_{indices}$[I>2σ(I)]	R_1 = 0.0393, wR_2 = 0.0769	R_1 = 0.0411, wR_2 = 0.1144	R_1 = 0.0738, wR_2 = 0.1973
$R_{indices}$(all data)	R_1 = 0.0668, wR_2 = 0.0879	R_1 = 0.0521, wR_2 = 0.1252	R_1 = 0.1034, wR_2 = 0.2436

Crystallographic morphological representation of all the CPs

All the Molecular pictures were prepared with program DIAMOND.[1S]

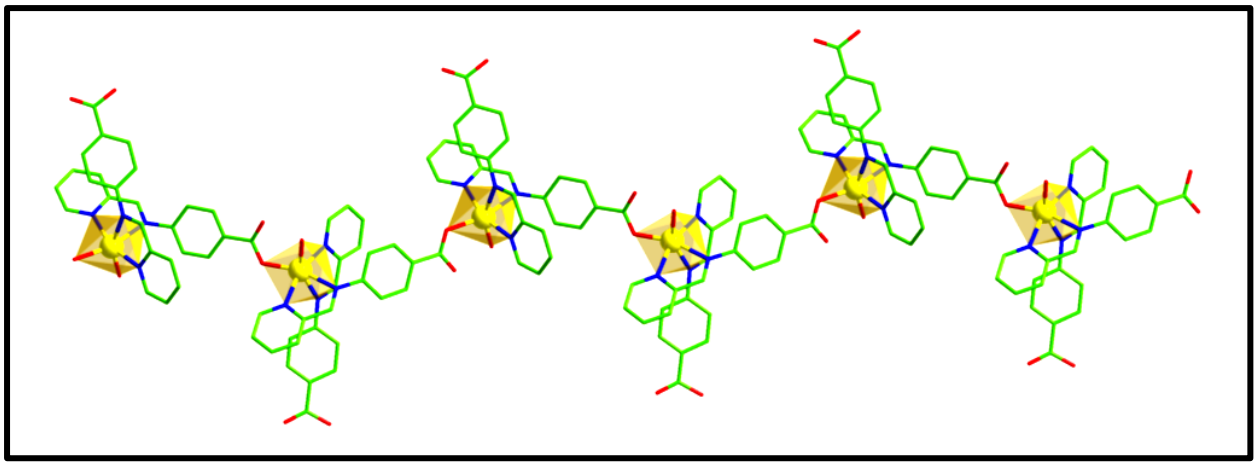


Fig. S8 1D polymeric chain of **CP 1** with the polyhedral view around central Zn.

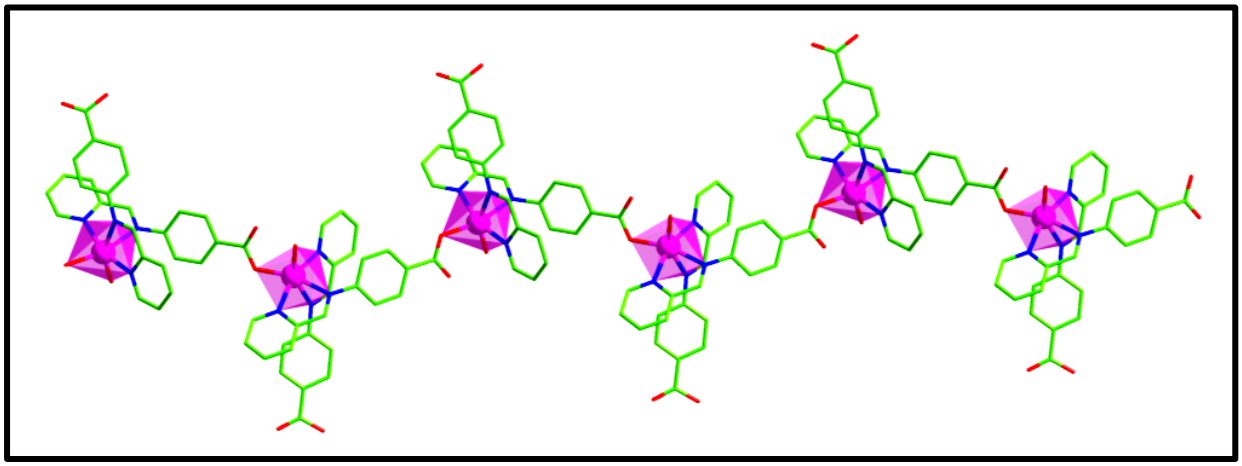


Fig. S9 1D polymeric chain of **CP 2** with the polyhedral view around central Mn.

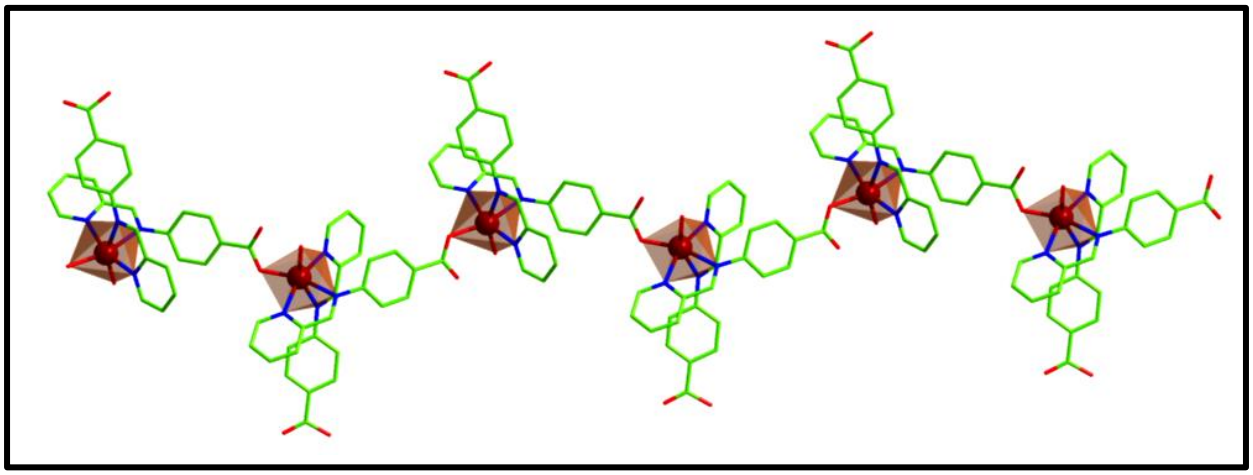


Fig. S10 1D polymeric chain of **CP 3** with the polyhedral view around central Cu.

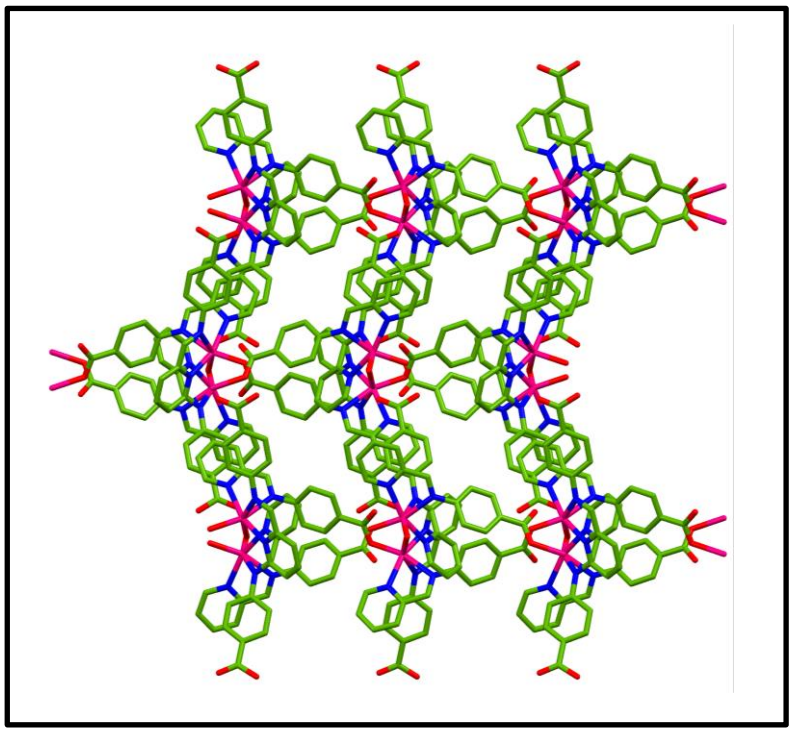


Fig. S11 Crystal packing of **CP 2** around along crystallographic ‘a’ axis.

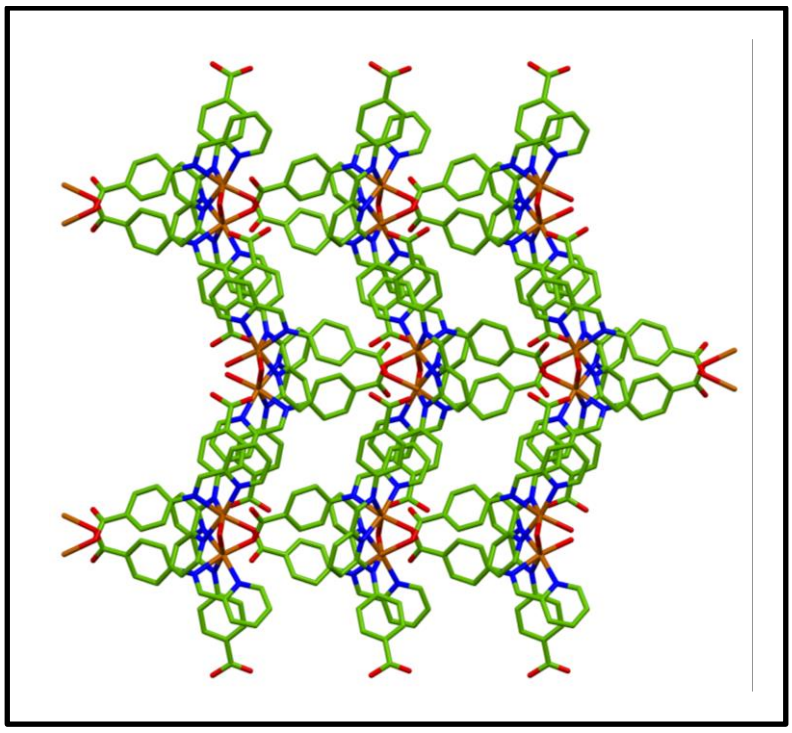
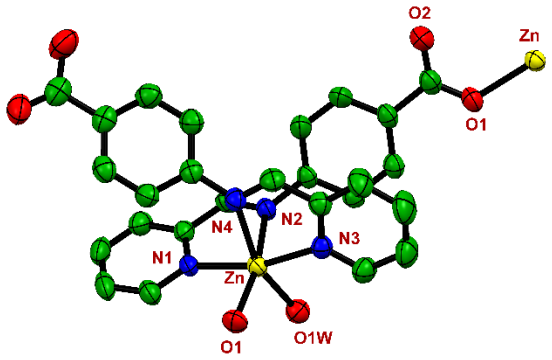
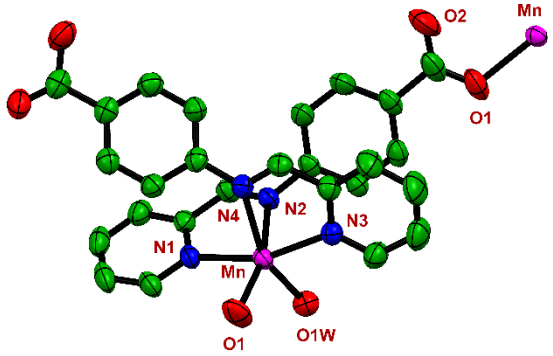
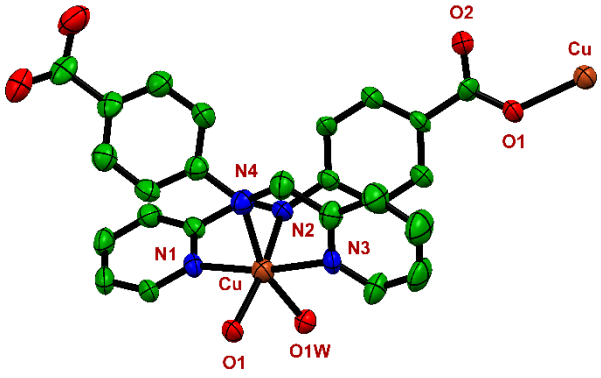


Fig. S12 Crystal packing of **CP 3** around along crystallographic ‘a’ axis.

Table S2: Mode of coordination of the synthesized ligand [4-[(Pyridin-2-ylmethylene)-amino]-benzoic acid]

Coordination Polymer (CP)	ORTEP view	Coordination mode
1		**One ligand (LH) acts as chelating η2 (through the pyridyl and the imine "N" donors), the other is deprotonated (L−) and has a μ3:η2- η1 coordination mode (through the pyridyl and the imine "N" donors and one carboxylate "O") bridging the metals to give origin to a rippled chain.**
2		**Coordination mode of then ligands in CP 2 is same as the coordination modes of the ligand in CP 1**
3		**Coordination mode of the ligands in CP 2 is same as the coordination modes of the ligand in CP 1**

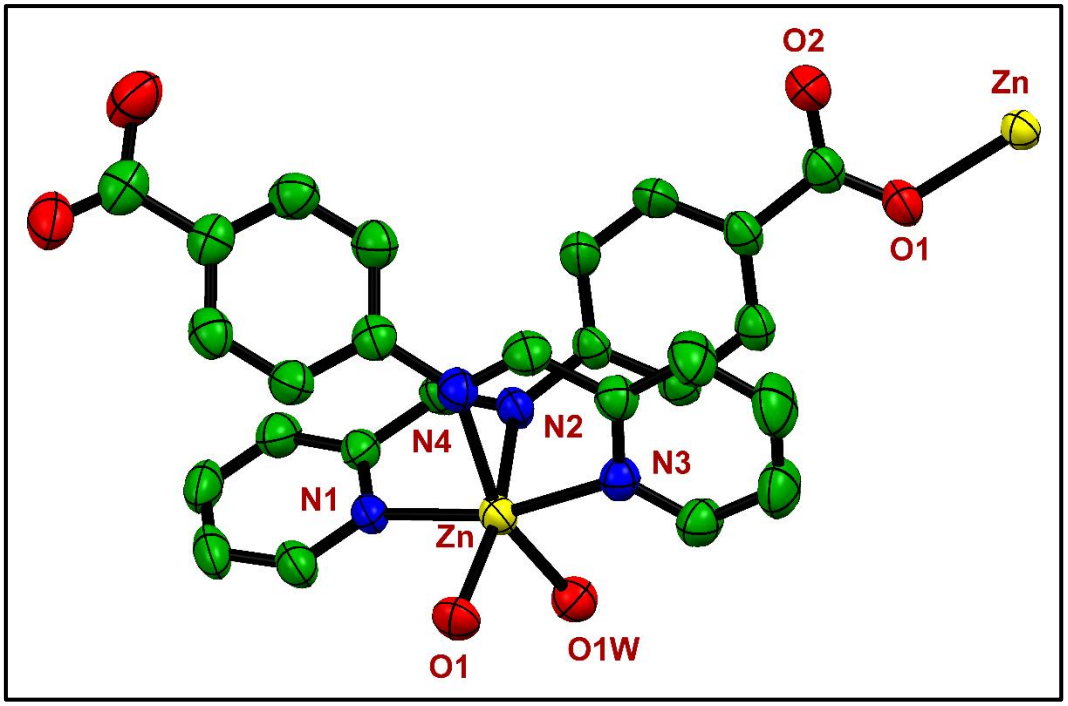


Fig. S13 ORTEP plot of coordination polymer **1** (**CP 1**) with 50% ellipsoid probability. C atoms are not leveled and indicated by green coloration. H atoms and solvents are not shown for the clarity purpose.

Table S3 (A): Selected Bond Angles (°) of **CP 1**

O1-Zn-O1W	96.57(9)	O1W-Zn-N4	159.19(9)
O1-Zn-N1	91.70(9)	N1-Zn-N2	75.70(9)
O1-Zn-N2	167.28(9)	N1-Zn-N3	165.17(9)
O1-Zn-N3	98.07(9)	N1-Zn-N4	91.07(9)
O1-Zn-N4	101.58(9)	N2-Zn-N3	94.63(9)
O1W-Zn-N1	98.52(9)	N2-Zn-N4	80.70(9)
O1W-Zn-N2	83.82(9)	N3-Zn-N4	76.10(9)
O1W-Zn-N3	91.46(9)		

Table S3 (B): Selected Bond Lengths (Å) of **CP 1**

Zn-O1	2.038(2)
Zn-O1W	2.157(3)
Zn-N1	2.136(2)
Zn-N2	2.233(2)
Zn-N3	2.123(2)
Zn-N4	2.267(3)

Table S4: Hydrogen Bonding Parameters of **CP 1**

D-H⋯A	**D-H(Å)**	**H⋯A(Å)**	**D⋯A(Å)**	**<D-H⋯ A(°)**	**Symmetry**
O1W -- H11W .. O4	0.83(4)	2.02(4)	2.808(4)	158(4)	x, y, z
O1W -- H12W .. O2	0.84(4)	1.82(4)	2.634(3)	163(4)	x, y, z
O2W -- H20A .. O2	0.88(3)	2.07(3)	2.923(5)	164(2)	1/2+x, y,3/2-z
O2W -- H20B .. O83	0.87(3)	2.05(3)	2.883(16)	159(6)	-1/2+x, y,3/2-z
O3 -- H31 .. O2W	1.05(6)	1.57(6)	2.594(4)	167(4)	x, y, z
C1 -- H1 .. O1	0.93	2.59	3.135(4)	118.0	x, y, z
C19 -- H19 .. O82	0.93	2.57	3.497(16)	179.0	-1/2+x, y, 3/2-z
C22 -- H22 .. O3	0.93	2.41	2.728(5)	100.0	x, y, z
C25 -- H25 .. O81	0.93	2.60	3.375(14)	141.0	x, y, z

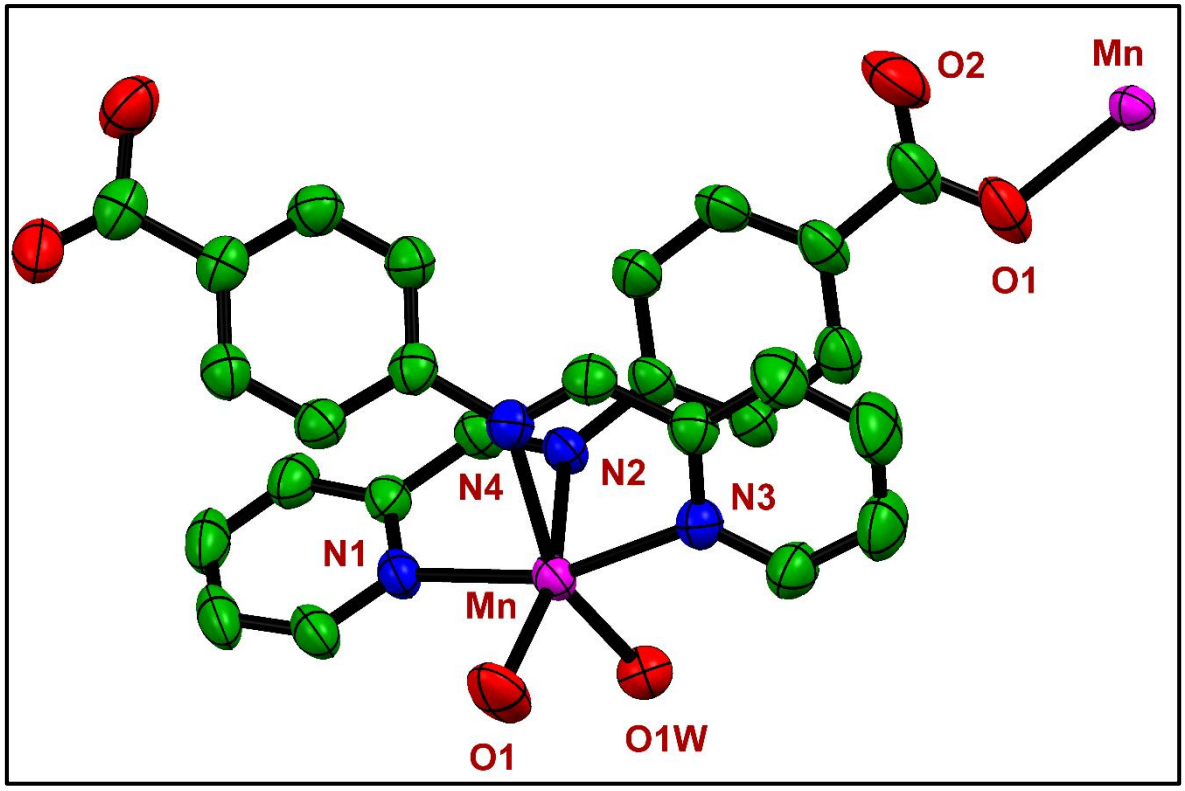


Fig. S14 ORTEP plot of coordination polymer **2** (**CP 2**) with 50% ellipsoid probability. C atoms are not levelled and indicated by green coloration. H atoms and solvents are not shown for the clarity purpose.

Table S5 (A): Selected Bond Angles (°) of **CP 2**

O1-Mn-O1W	101.47(9)	O1W-Mn-N4	155.27(8)
O1-Mn-N1	91.21(8)	N1-Mn-N2	72.29(7)
O1-Mn-N2	163.40(8)	N1-Mn-N3	161.04(7)
O1-Mn-N3	101.60(8)	N1-Mn-N3	90.85(7)
O1-Mn-N4	101.13(9)	N2-Mn-N3	94.04(7)
O1W-Mn-N1	98.59(7)	N2-Mn-N4	78.00(7)
O1W-Mn-N2	83.17(7)	N3-Mn-N4	73.11(7)
O1W-Mn-N3	92.56(7)		

Table S5 (B): Selected Bond Lengths (Å) of **CP 2**

Mn-O1	2.088(2)
Mn-O1W	2.214(2)
Mn-N1	2.255(2)
Mn-N2	2.318(2)
Mn-N3	2.234(2)
Mn-N4	2.339(2)

Table S6: Hydrogen Bonding Parameters of **CP 2**

D-H⋯A	**D-H(Å)**	**H⋯ A(Å)**	**D ⋯A(Å)**	**<D-H ⋯ A(°)**	**Symmetry**
O1W -- H11A .. O4	0.77(4)	2.03(4)	2.794(3)	174(3)	1-x,1/2+y,3/2-z
O1W -- H12A .. O2	0.84(4)	1.92(4)	2.617(3)	148(4)	x, y, z
O2W -- H20W .. O2	0.88(3)	2.25(3)	3.088(5)	159(2)	1-x,1/2+y,3/2-z
O2W -- H21W .. O93	0.87(3)	2.14(3)	2.969(6)	158(4)	1-x,1-y,1-z
O3 -- H31 .. O2W	0.92(2)	1.69(2)	2.592(3)	167(4)	x, y, z
C9 -- H9 .. O2	0.9300	2.45	2.768(4)	100.0	x, y, z
C19 -- H19 .. O92	0.9300	2.48	3.413(4)	176.0	1-x,1-y,1-z
C22 -- H22 .. O3	0.9300	2.40	2.717(3)	100.0	x, y, z
C25 -- H25 .. O91	0.9300	2.52	3.313(5)	143.0	x, y, z

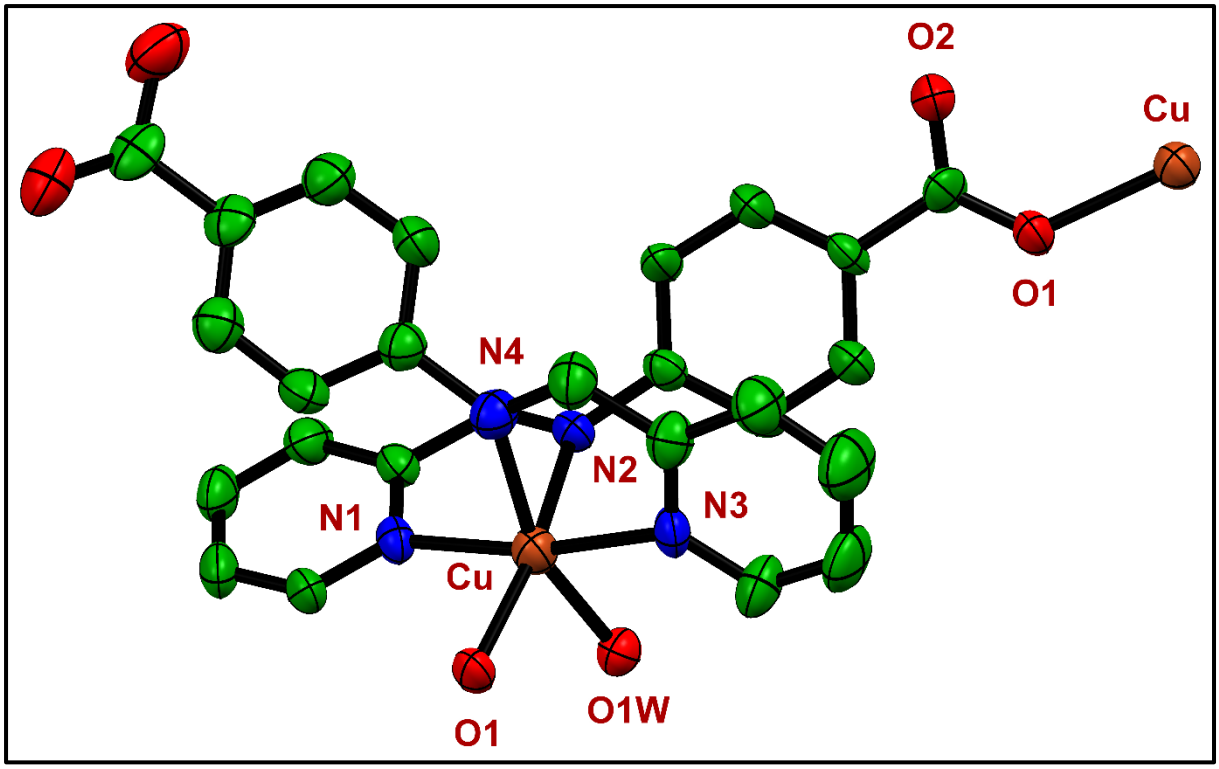


Fig. S15 ORTEP plot of coordination polymer **3** (**CP 3**) with 50% ellipsoid probability. C atoms are not levelled and indicated by green coloration. H atoms and solvents are not shown for the clarity purpose.

Table S7 (A): Selected Bond Angles (°) of **CP 3**

O1-Cu -O1W	94.1(4)	O1W-Cu-N4	160.7(4)
O1-Cu-N1	91.8(5)	N1-Cu-N2	77.2(5)
O1-Cu-N2	168.6(4)	N1-Cu-N3	169.6(5)
O1-Cu-N3	94.5(5)	N1-Cu-N4	92.9(5)
O1-Cu-N4	101.6(5)	N2-Cu-N3	96.9(5)
O1W-Cu-N1	97.8(4)	N2-Cu-N4	82.1(5)
O1W-Cu-N2	84.6(4)	N3-Cu-N4	77.7(5)
O1W-Cu-N3	90.1(4)		

Table S7 (B): Selected Bond Lengths (Å) of **CP 3**

Cu -O1	2.052(10)
Cu-O1W	2.110(10)
Cu-N1	2.124(12)
Cu-N2	2.164(12)
Cu-N3	2.154(12)
Cu-N4	2.178(13)

Table S8: Hydrogen Bonding Parameters of **CP 3**

D-H⋯A	**D-H(Å)**	**H⋯ A(Å)**	**D ⋅⋅ A(Å)**	**<D-H ⋯ A(°)**	**Symmetry**
O1W – H1WA .. O2	0.85	1.87	2.619(14)	146.1	x, y, z
O1W -- H1WB .. O4	0.85	1.98	2.827(16)	175.5	1-x, -1/2+y, 3/2-z
O2W -- H2WB .. O2	0.85	2.09	2.84(2)	146.7	1-x, 1/2+y, 3/2-z
O3 -- H3.. O2W	0.82	1.80	2.607(19)	169.0	x, y, z
O2 -- H2WB .. O94	0.85	2.04	2.73(4)	137.0	1/2+x, +y, 3/2-z
C9 -- H9.. O82	0.93	2.57	3.47(4)	163.0	-1/2+x, y, 3/2-z
C19 -- H19 .. O91	0.93	2.48	3.40(2)	174.0	-1/2+x, y, 3/2-z
C21 -- H2 .. O82	0.93	2.42	3.23(4)	146.0	x, y, z
C24 -- H24 .. O3	0.93	2.38	2.71(2)	101.0	x, y, z

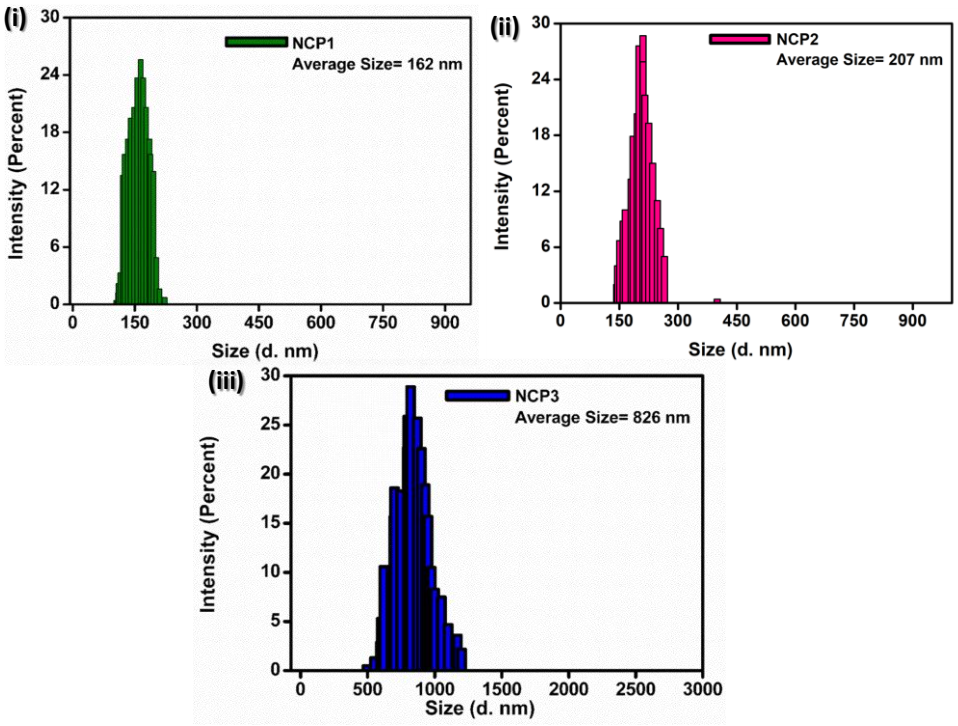


Fig. S16 DLS data of DMSO dispersed solution of all the **NCP**s: (i) **NCP 1**, (ii) **NCP 2** and (iii) **NCP 3**.

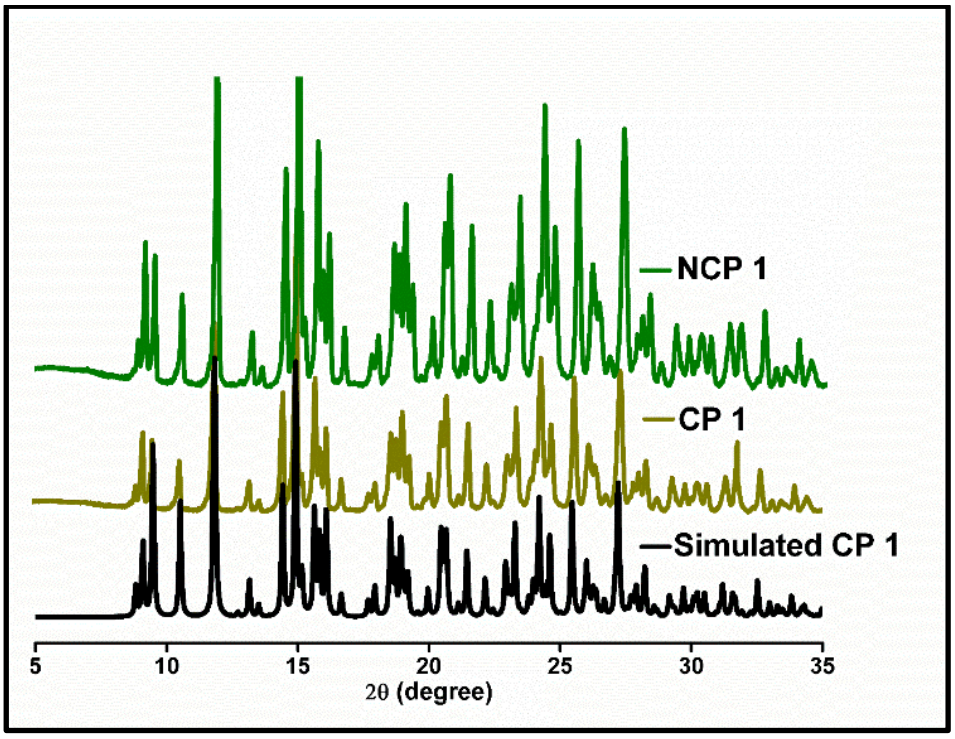


Fig. S17 PXRD pattern of simulated **1**, as synthesized **1** and nanoscale **1** collected under air.

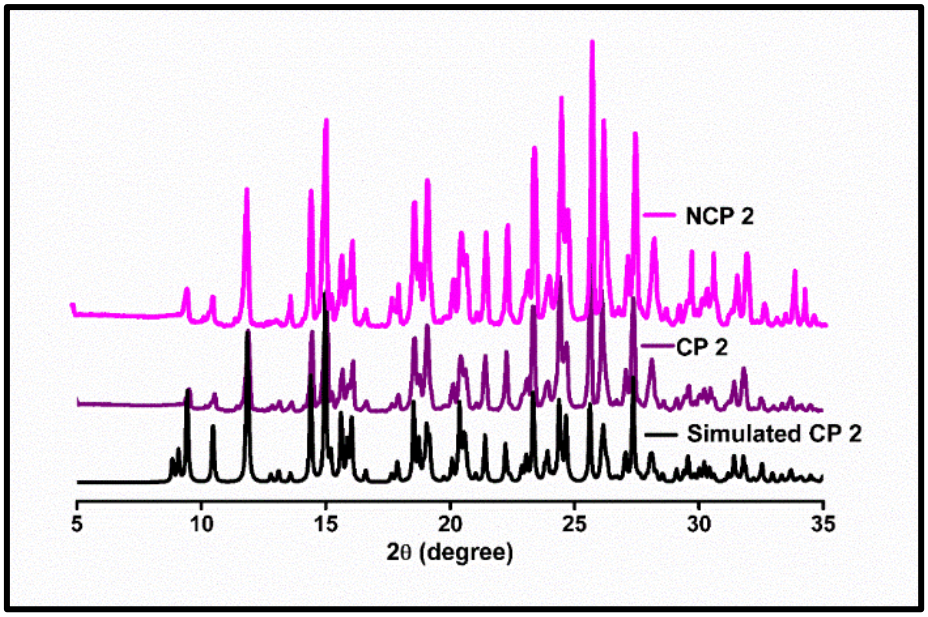


Fig. S18 PXRD pattern of simulated **2**, as synthesized **2** and nanoscale **2** collected under air.

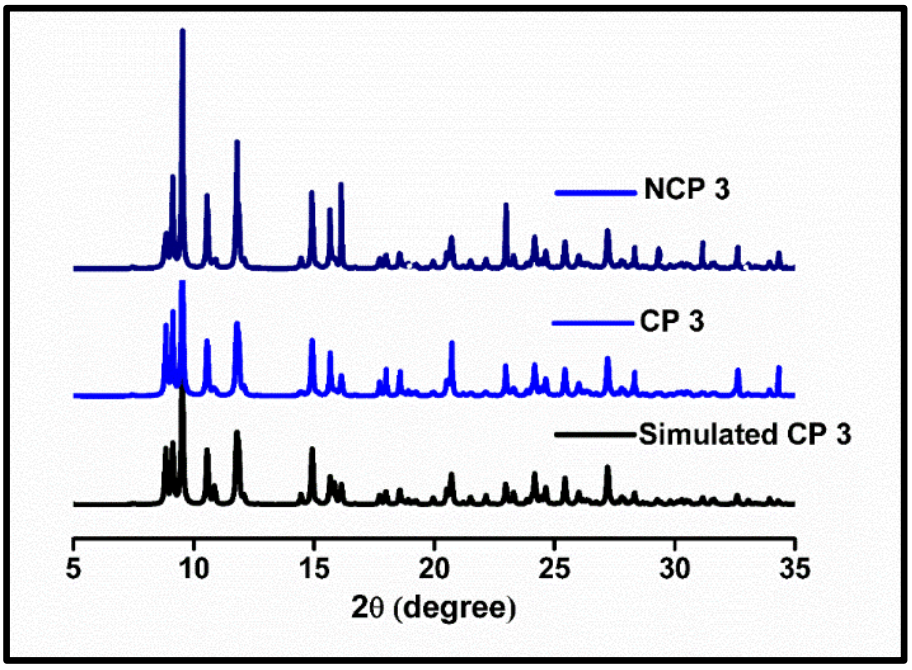
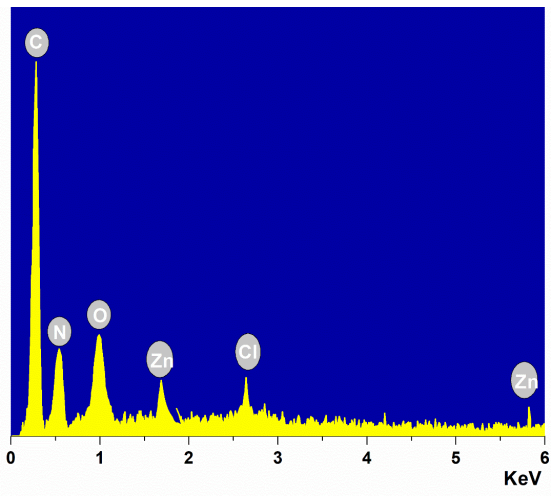


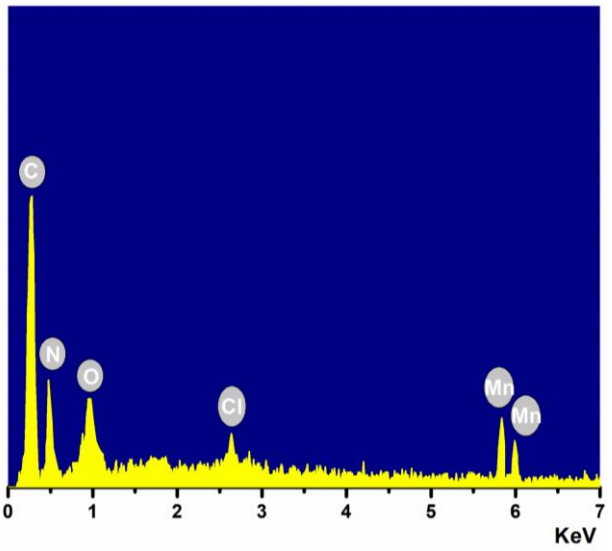
Fig. S19: PXRD pattern of simulated **3**, as synthesized **3** and nanoscale **3** collected under air.

Energy Dispersive X-ray analysis



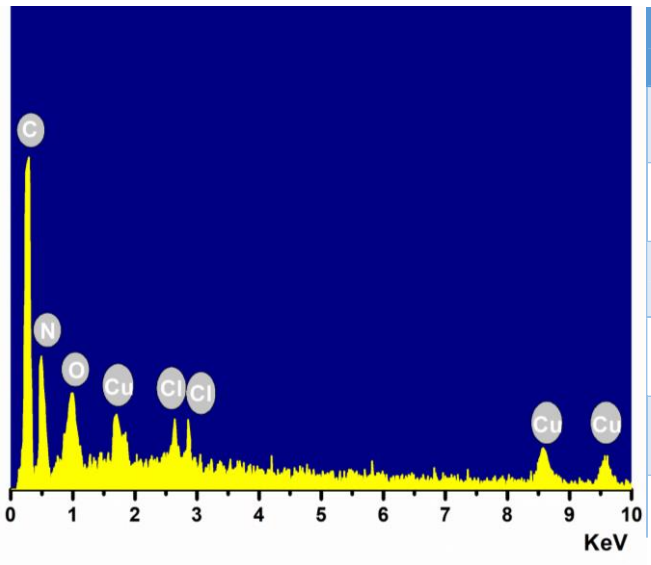
Element	Weight%	Atomic%
C K	90.17	95.37
O K	4.10	3.26
N K	4.49	0.90
Cl K	1.14	0.45
Zn K	0.11	0.02
Totals	100.00	100.00

Fig. S20 EDX data of **NCP 1**.



Element	Weight%	Atomic%
C K	62.64	84.84
O K	15.85	9.61
N K	16.76	4.38
Cl K	1.96	0.90
Mn K	2.79	0.71
Totals	100.00	100.00

Fig. S21 EDX data of **NCP 2**.



Element	Weight%	Atomic%
C K	50.44	82.64
O K	10.70	4.46
N K	20.92	8.54
Cl K	3.00	1.94
Cu K	14.94	10.86
Totals	100.00	100.00

Fig. S22 EDX data of **NCP 3**.

UV-visible spectral studies

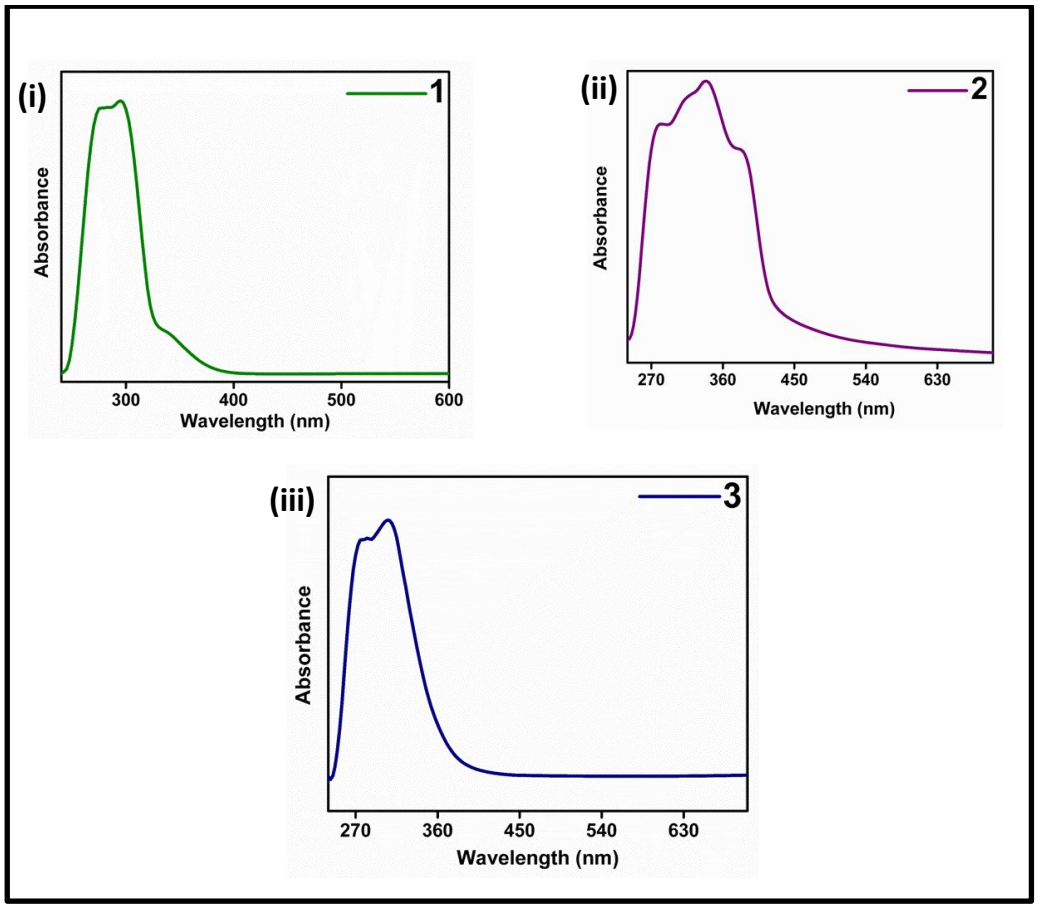


Fig. S23 UV-visible spectral data plot for all the **NCP**s (i) **1**, (ii) **2** and (iii) **3** respectively.

Calculation of Quantum Yield (Φ)

Quinine sulfate solution (dissolved in 0.5M H_2SO_4) is taking as a reference to calculate the fluorescence quantum yield.

Quantum Yield (Φ) = Φ_R ($I \times A_R \times \eta^2 / I_R \times A \times \eta_R^2$) (Subscript R represent the reference Quinine Sulfate) (Subscript R represent the reference Quinine Sulfate)

$\Phi_R = \Phi_{emi} = 0.546$, $\lambda_{emi} = 345$ nm at 25ºC

A = Optical density.

I = Integrated emission intensity.

η = Refractive index. For DMSO and H_2O η = 1.479 and 1.333.

Table S9: The calculation of Quantum Yield of all the NCPs

Solution under experiment	Integrated emission intensity (I)	Optical density (A)	Quantum Yield (Φ)
Quinine sulfate in 0.5M H_2SO_4	6.2×10^8	0.077	0.5460
NCP1	0.68×10^7	0.038	0.015
NCP2	0.19×10^7	0.020	0.008
NCP3	0.60×10^6	0.017	0.003

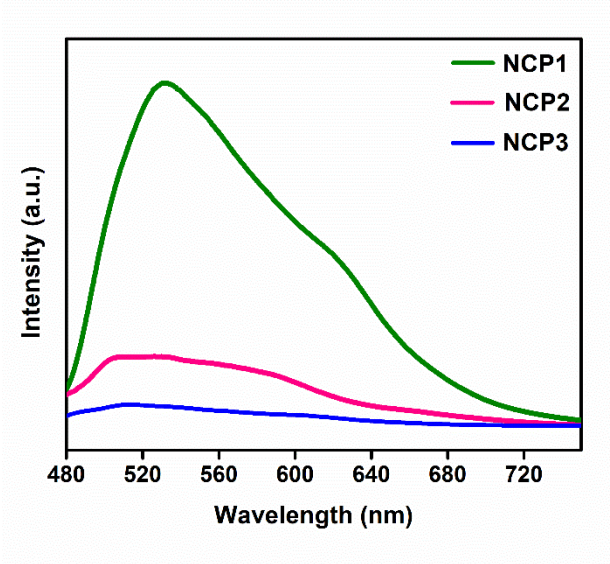


Fig. S24 Comparative solid-state fluorescence spectral study of all the **NCP**s.

Limit of detection (LOD) calculation in PBS buffer medium

The detection limit of **NCP 1** was calculated using the conventional.

formula:

$$\mathbf{LOD = (3\sigma/m)}$$

Where, the standard deviation (**σ**) was calculated via the measurement of five successive fluorescence intensities. The slope (**m**) obtained by plotting the emission intensity of complexes.

Table S10: LOD calculation

NCP 1	σ	m	LOD
	2.30	**21.17**	**0.325**

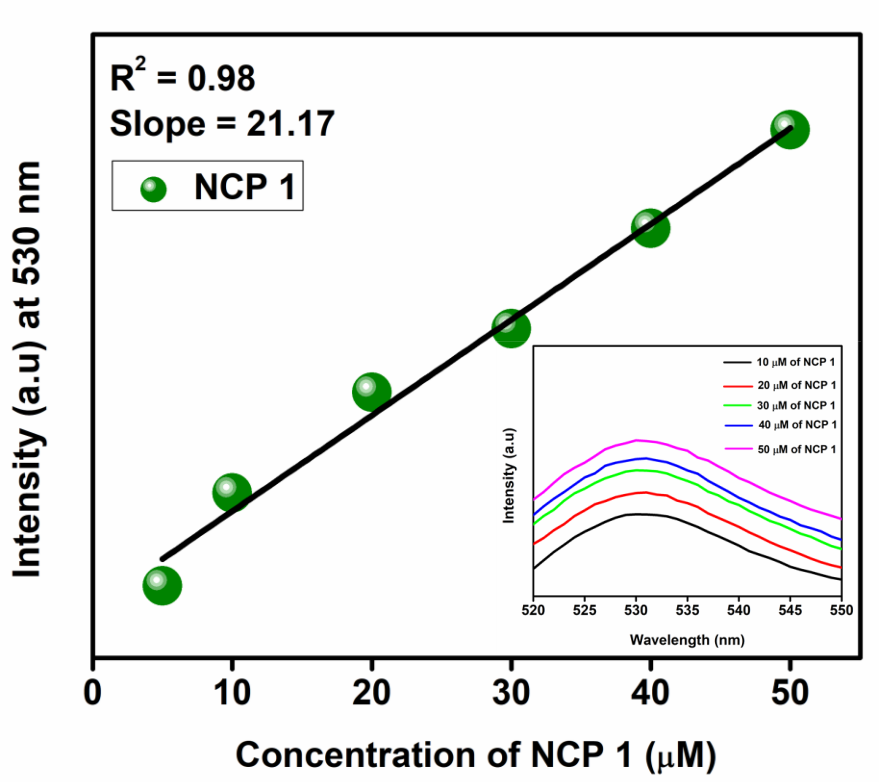


Fig. S25 Intensity vs. concentration plot for **NCP 1** in PBS buffer solution in inset fluorescence spectral changes plot for **NCP 1** in PBS buffer medium maintaining the lysosomal acidic pH.

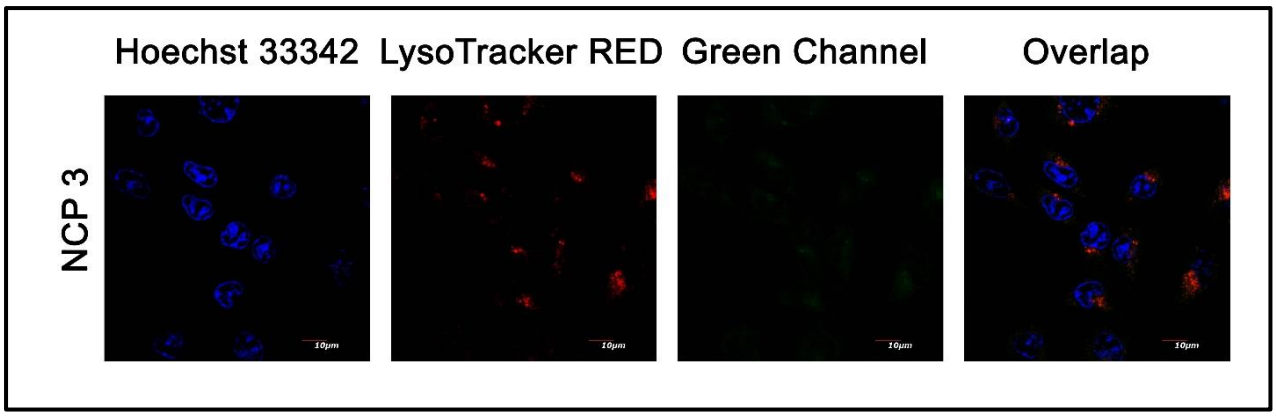


Fig. S26 Confocal images of A549 cells incubated with **NCP 3** and Lyso-Tracker Red indicating the colocalization. Red channel emission was collected in the range of 580−620 nm whereas Green channel emission was collected in the range of 500−530 nm.

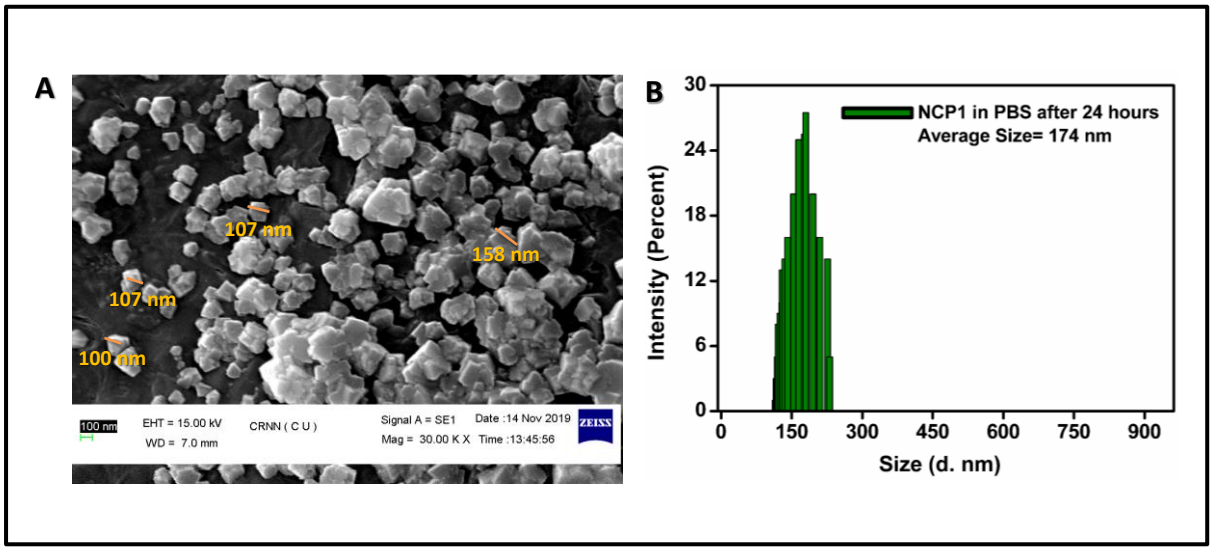


Fig. S27 (A) SEM image of **NCP 1** which is sonicated with PBS buffer solution for 24 h, (B) DLS data of PBS buffer dispersed solution of the **NCP 1** for 24 h.

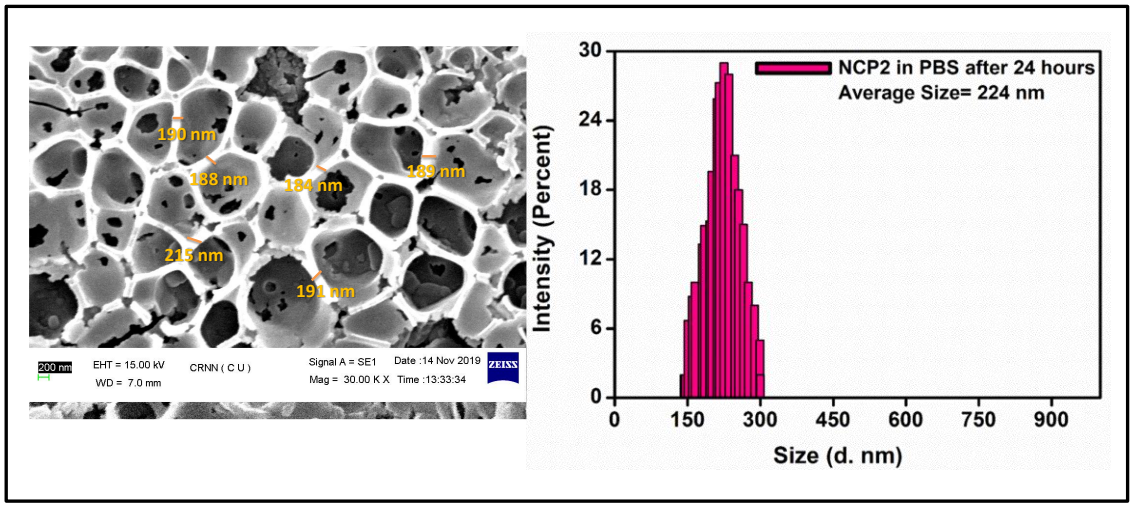


Fig. S28 (A) SEM image of **NCP 2** which is sonicated with PBS buffer solution for 24 h, (B) DLS data of PBS buffer dispersed solution of the **NCP 2** for 24 h.

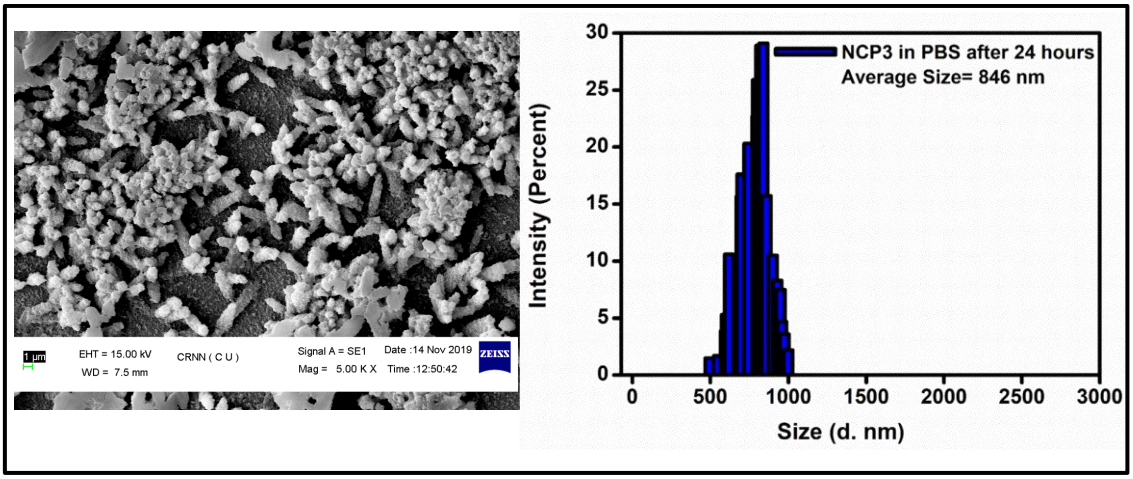


Fig. S29 (A) SEM image of **NCP 3** which is sonicated with PBS buffer solution for 24 h, (B) DLS data of PBS buffer dispersed solution of the **NCP 3** for 24 h.

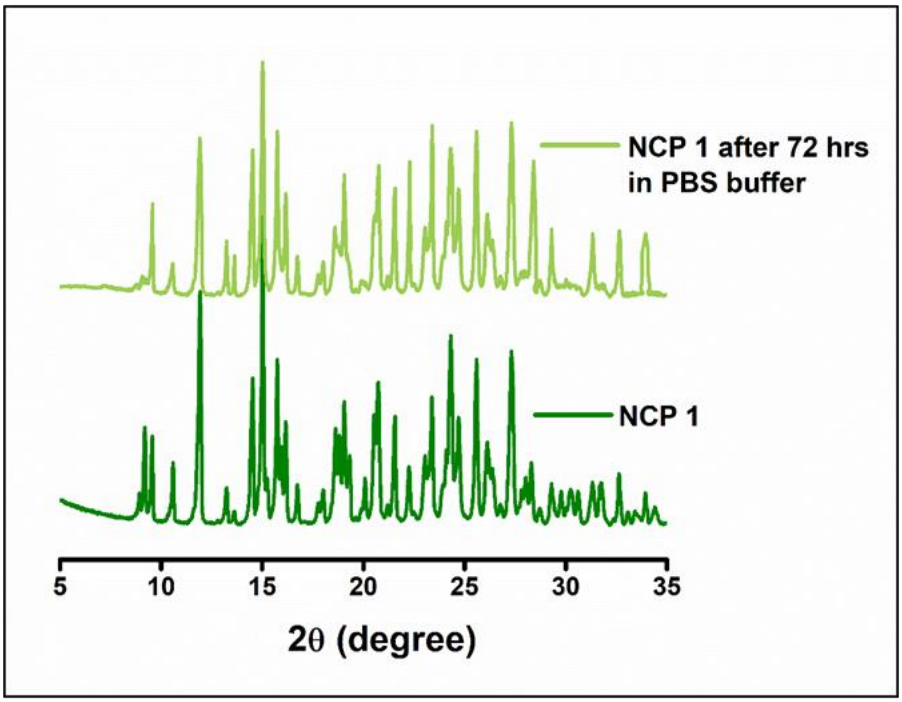


Fig. S30 PXRD pattern of **NCP 1** after 72 hours dispersion in PBS.

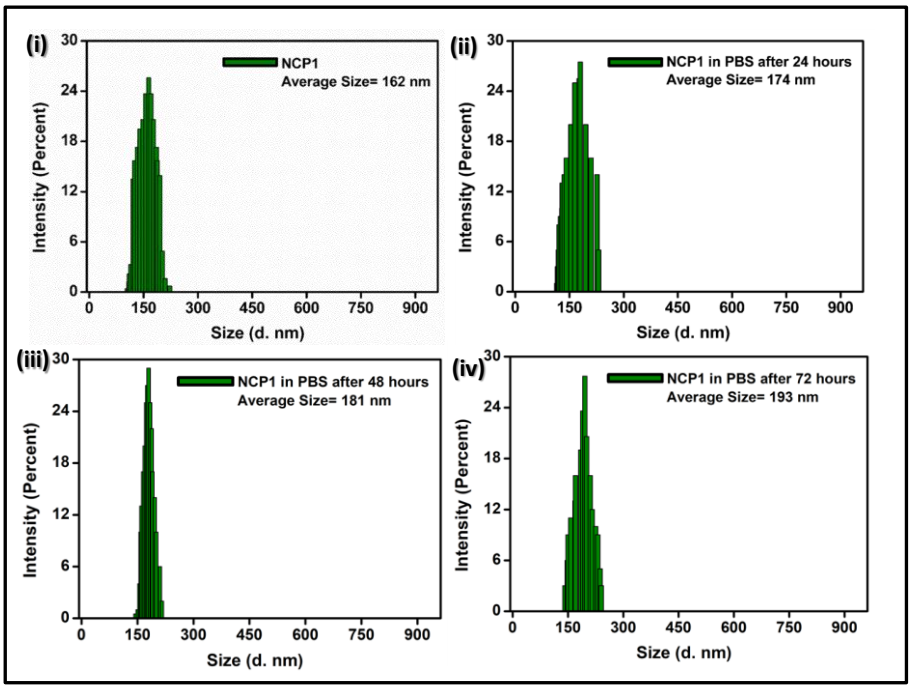


Fig. S31 DLS data of PBS buffer dispersed solution of **NCP 1** (maintaining acidic pH) for: a) as dispersed, b) after 24 hours, c) after 48 hour after 48 hours, d) after 72 hours of dispersion.

References

1S K. Brandenburg and H. Putz, Cryst. Impact Bonn, Ger.