

Ambient Complexation Reaction of Zinc Acetate and Ascorbic Acid Leads to a New Form of Nanoscale Particles with Emergent Optical Properties

Srestha Basu^{a\$}, Archismita Hajra^{b\$} and Arun Chattopadhyay^{a,b*}

^{\$}Equal Contribution

^aDepartment of Chemistry, Indian Institute of Technology Guwahati,
Guwahati 781039, India

^b Centre for Nanotechnology, Indian Institute of Technology Guwahati,
Guwahati 781039, India

E-mail: arun@iitg.ac.in

Electronic Supplementary Information

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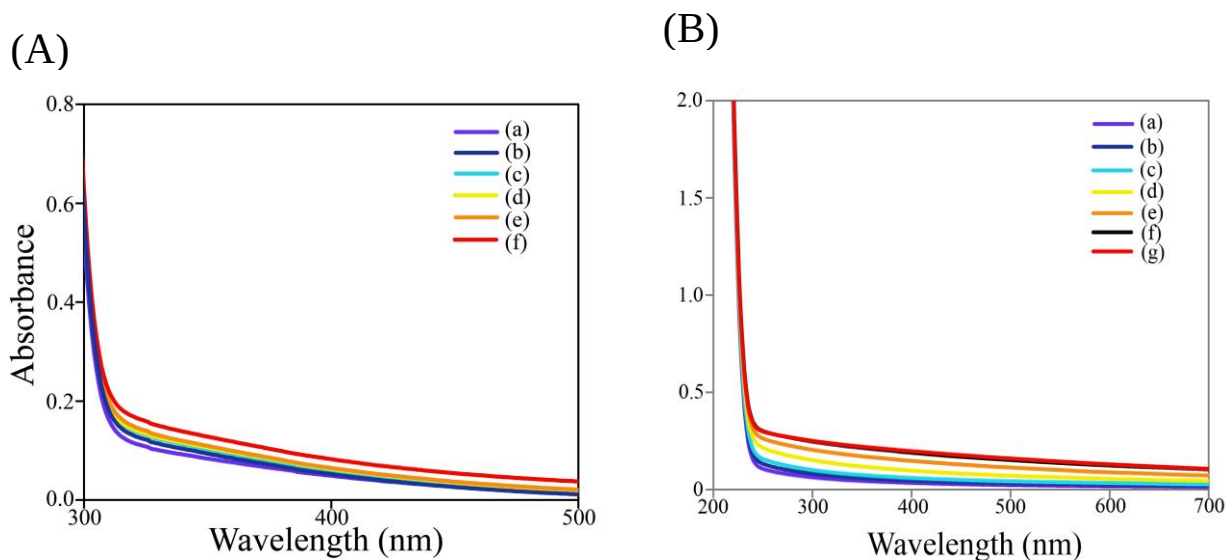


Fig. S1 (A) UV-absorbance spectra of ascorbic acid acquired at (a) 0 min, (b) 10 min, (c) 20 min, (d) 40 min, (e) 50 min, and (f) 60 min. **(B)** UV-absorbance spectra of zinc acetate at (a) 0 min, (b) 10 min, (c) 20 min, (d) 30 min, (e) 40 min, (f) 50 min and (g) 60 min. Here 0 min refers to the time when zinc acetate and ascorbic acid were mixed.

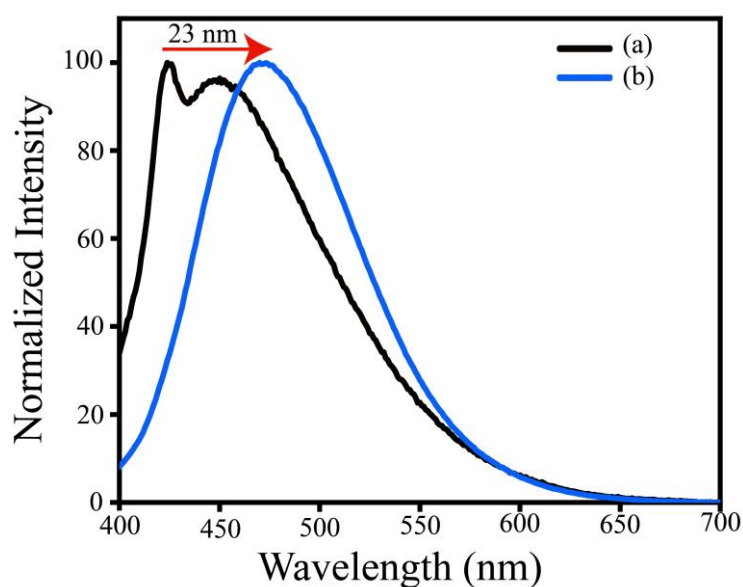


Fig. S2 Normalized emission spectra of (a) ascorbic acid and (b) reaction mixture of zinc acetate dihydrate and ascorbic acid. The excitation wavelength was set at 371 nm.

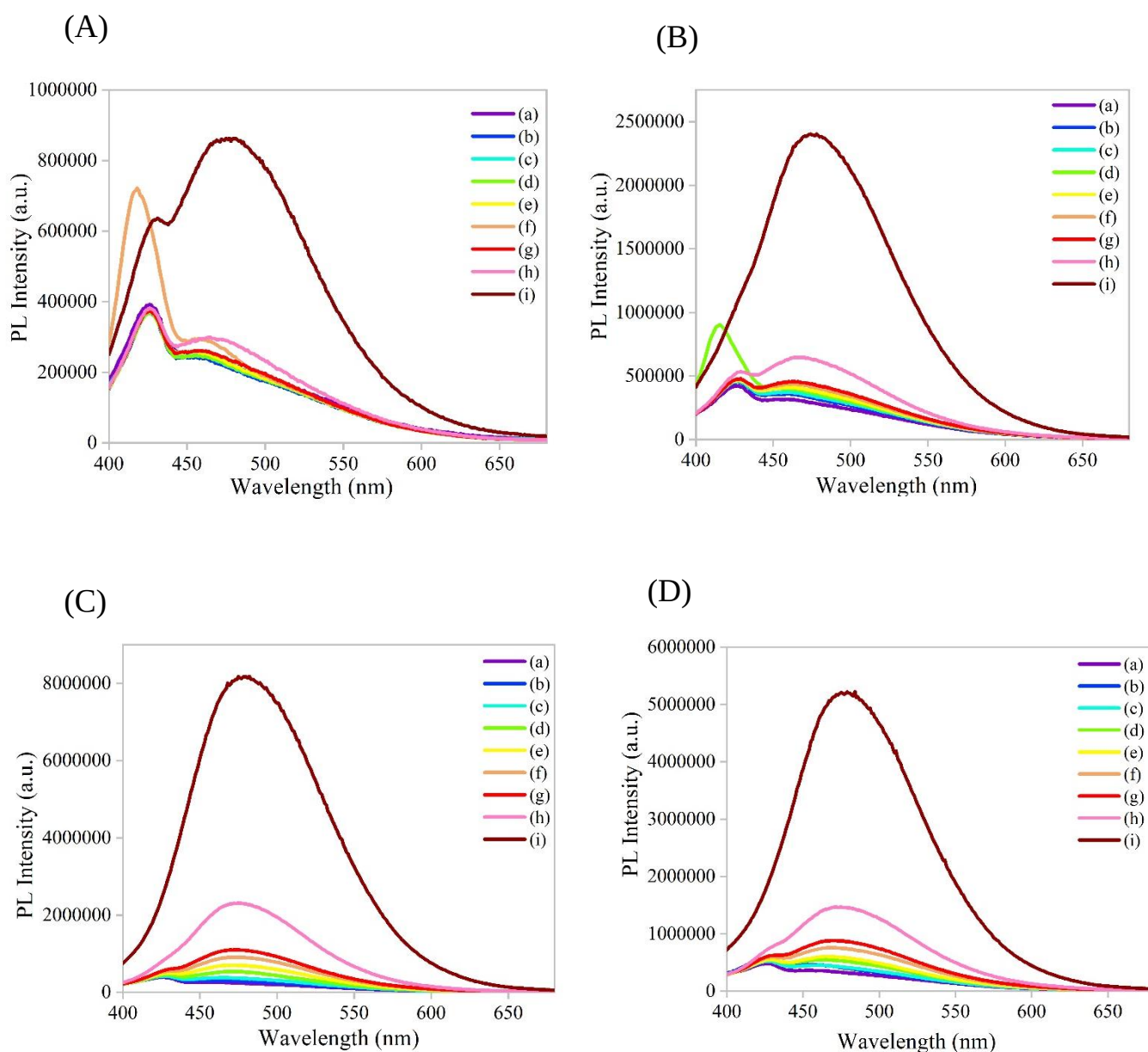


Fig. S3 (A) Emission spectra of the reaction mixture containing ascorbic acid and ~ 20 mg zinc acetate at (a) 0 min, (b) 10 min, (c) 20 min, (d) 30 min, (e) 40 min, (f) 50 min, (g) 60 min, (h) 120 min, and (i) 12 h. (B) Emission spectra of the reaction mixture containing ascorbic acid and ~ 100 mg zinc acetate at (a) 0 min, (b) 10 min, (c) 20 min, (d) 30 min, (e) 40 min, (f) 50 min, (g) 60 min, (h) 120 min, and (i) 12 h. (C) Emission spectra of the reaction mixture containing ascorbic acid and ~ 200 mg zinc acetate at (a) 0 min, (b) 10min, (c) 20 min, (d) 30 min, (e) 40 min, (f) 50 min, (g) 60 min, (h) 120 min, and (i) 12 h. (D) Emission spectra of the reaction mixture containing ascorbic acid and ~ 300 mg zinc acetate at (a) 0 min, (b) 10min, (c) 20 min, (d) 30 min, (e) 40 min, (f) 50 min, (g) 60 min, (h) 120 min, and

(i) 12 h. The excitation wavelength was set at 371 nm Here 0 min refers to the time when zinc acetate and ascorbic acid were mixed.

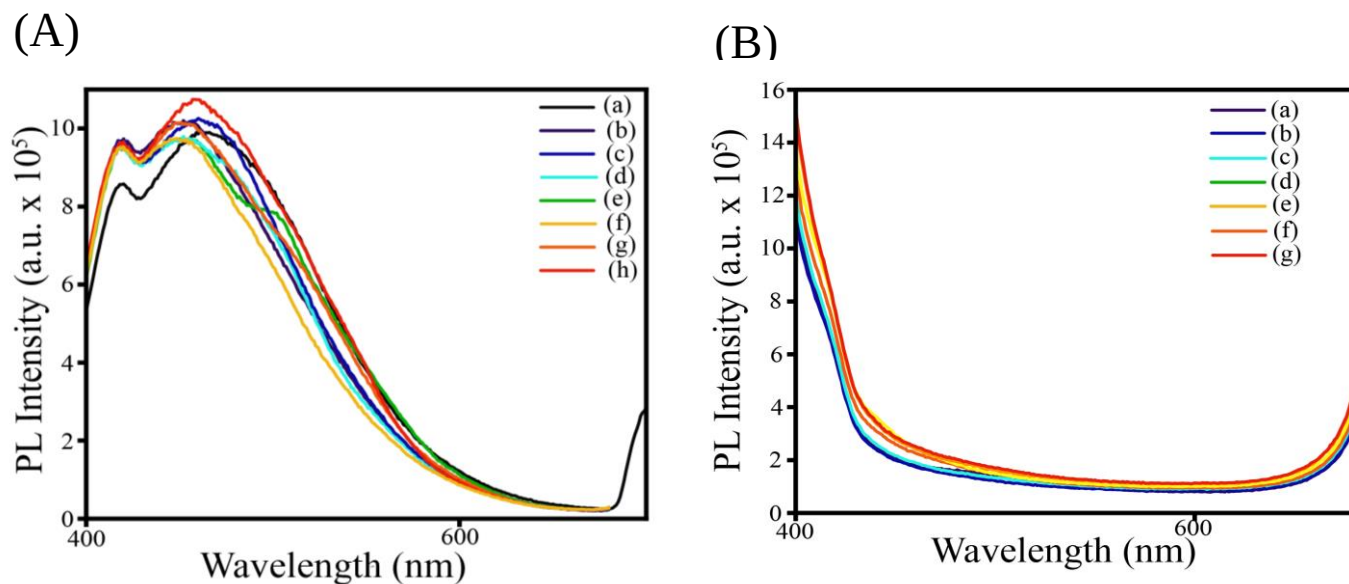


Fig. S4 (A) Photoluminescence spectra of ascorbic acid acquired at (a) 0 min, (b) 14 min, (c) 22 min, (d) 30 min, (e) 40 min, (f) 50 min, (g) 60 min and (h) 120 min. **(B)** Photoluminescence spectra of zinc acetate dihydrate acquired at (a) 0 min, (b) 10 min, (c) 20 min, (d) 30 min, (e) 40 min, (f) 50 min and (g) 60 min. The excitation wavelength was set at 365 nm. Here 0 min refers to the time when zinc acetate and ascorbic acid were mixed.

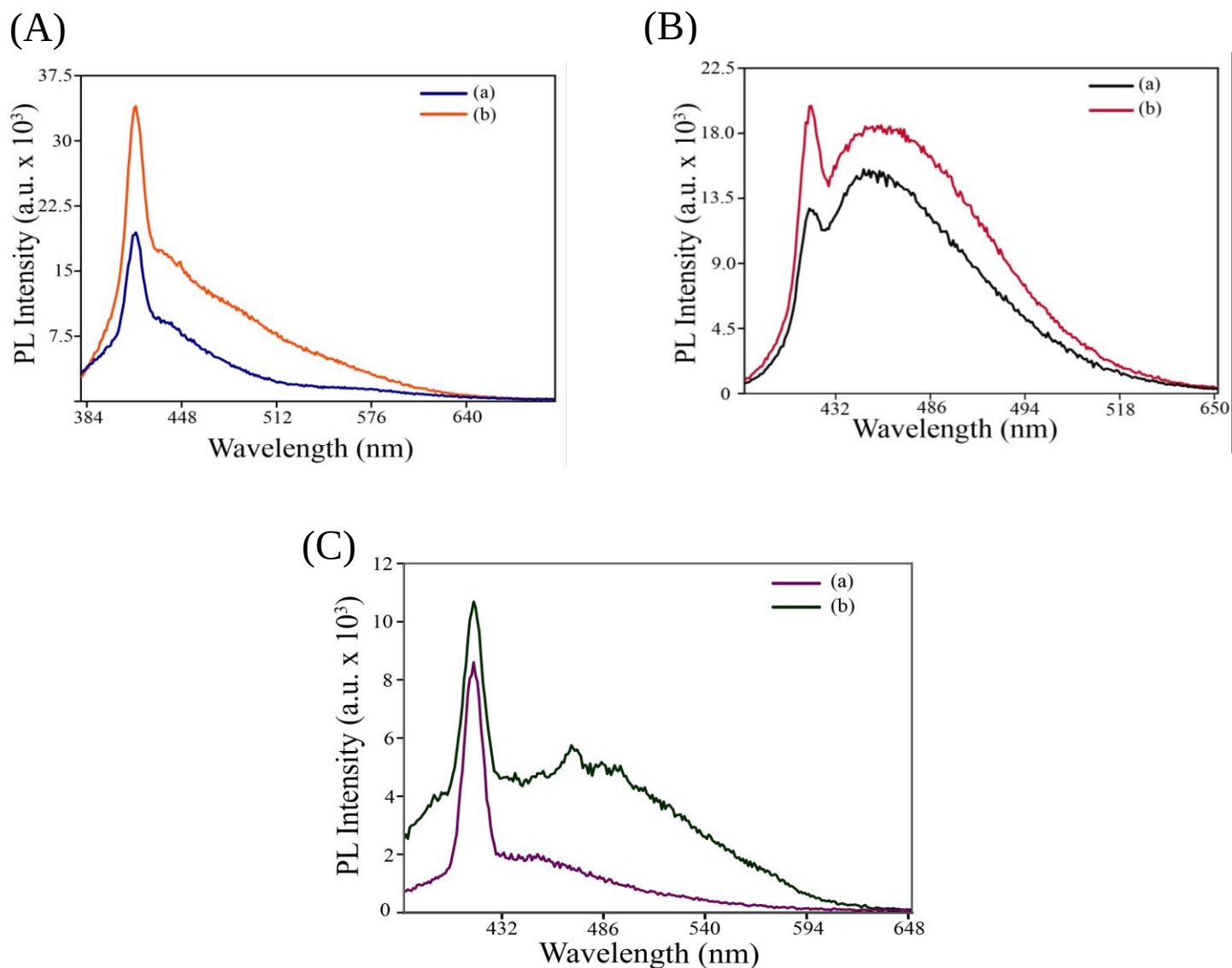


Fig. S5 (A) Photoluminescence spectra of a mixture of ~ 200 mg of cobalt acetate and ~ 18.0 mg of ascorbic acid acquired at (a) 6 h and (b) 11 h. **(B)** Photoluminescence spectra of a mixture of ~ 200 mg of nickel acetate and ~ 18 mg of ascorbic acid acquired at (a) 6 h and (b) 11 h. **(C)** Photoluminescence spectra of a mixture of ~ 200 mg of copper acetate and ~ 18 mg of ascorbic acid acquired at (a) 6 h and (b) 11 h. The excitation wavelength was set at 365 nm.

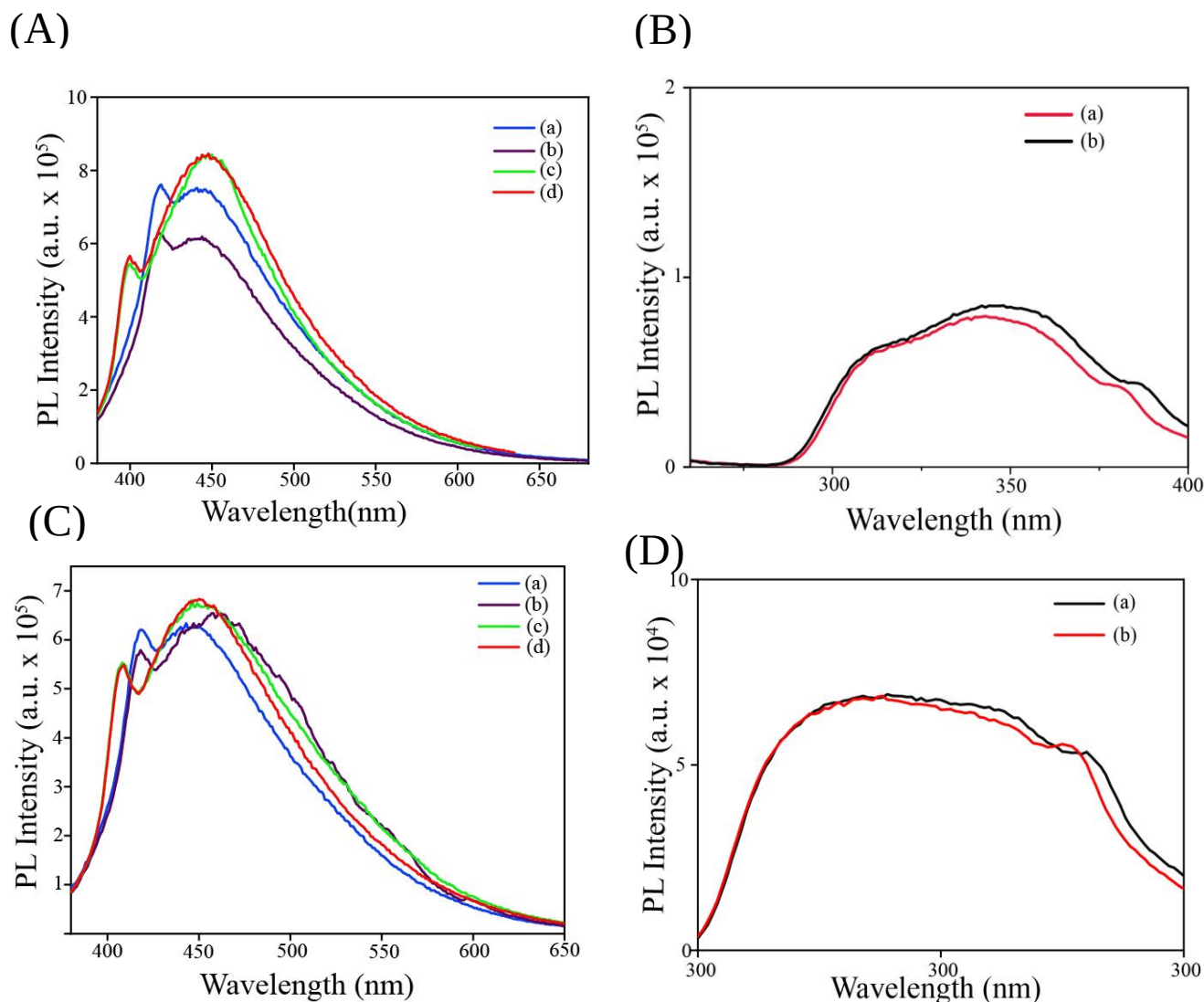


Fig. S6 (A) Emission spectra of the reaction mixture containing ~ 200 mg of zinc perchlorate and ~ 18.0 mg of ascorbic acid acquired at (a) 1 h, (b) 2 h, (c) 3 h and (d) 8 h. The excitation wavelength was set at 365 nm. **(B)** Excitation spectra of the reaction mixture containing ~ 200.0 mg of zinc perchlorate and ~ 18.0 mg ascorbic acid acquired at (a) 3 h and (b) 8 h. Emission wavelength was set at corresponding emission maxima. **(C)** Emission spectra of the reaction mixture containing ~ 200 mg zinc chloride and ascorbic acid acquired at (a) 1 h, (b) 2 h, (c) 3 h and (d) 8 h. Excitation wavelength was set at 365 nm. **(D)** Excitation spectra of the reaction mixture containing ~ 200 mg zinc chloride and ascorbic acid acquired at (a) 3 h and (b) 8 h. Emission wavelength was set at corresponding emission maxima.

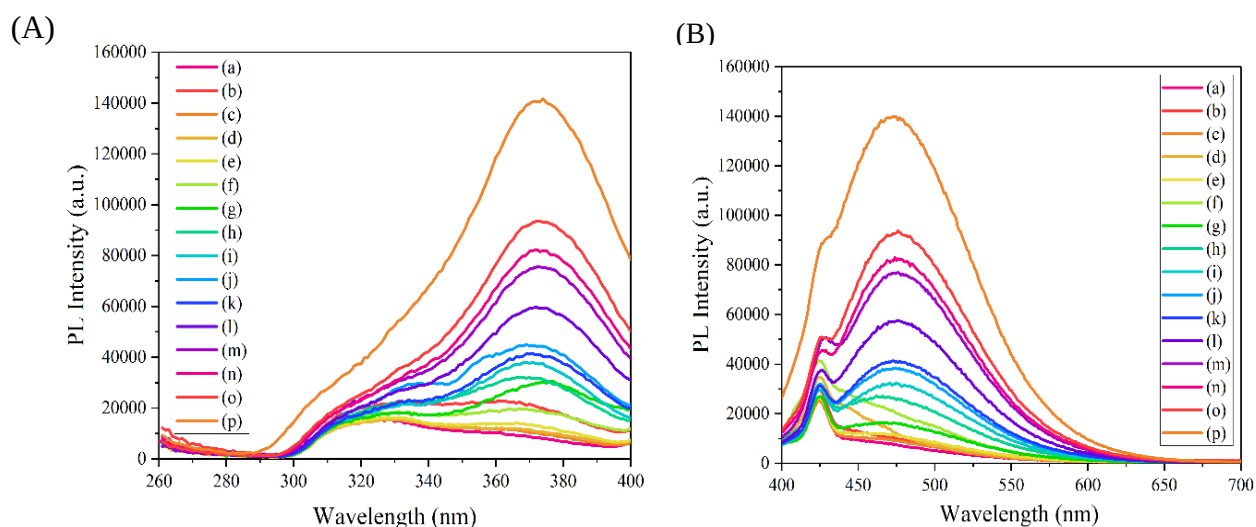


Fig. S7 (A) Excitation spectra of the product of reaction between zinc formate and ascorbic acid recorded at (a) 0 min, (b) 10 min, (c) 20 min, (d) 30 min, (e) 40 min, (f) 50 min, (g) 60 min, (h) 90 min, (i) 120 min, (j) 150 min, (k) 180 min, (l) 240 min, (m) 360 min, (n) 420 min, (o) 480 min, and (p) 1440 min. The emission wavelength was fixed at 471 nm. **(B)** Emission spectra of the product of reaction between zinc formate and ascorbic acid recorded at (a) 0 min, (b) 10 min, (c) 20 min, (d) 30 min, (e) 40 min, (f) 50 min, (g) 60 min, (h) 90 min, (i) 120 min, (j) 150 min, (k) 180 min, (l) 240 min, (m) 360 min, (n) 420 min, (o) 480 min, and (p) 1440 min. The excitation wavelength was fixed at 371 nm.

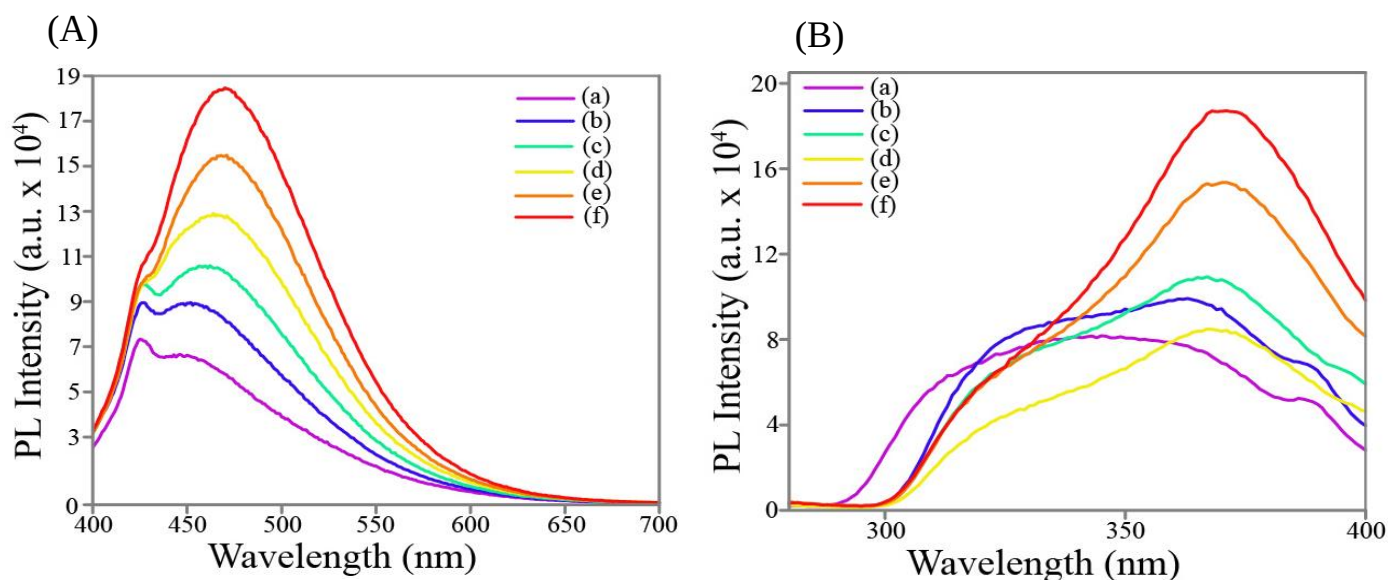


Fig. S8 (A) Emission spectrum of a mixture of (a) ~ 127 mg of zinc chloride and ~ 18.0 mg of ascorbic acid and that following addition of ~ 200 mg sodium acetate and recorded after (b) 24 min, (c) 60 min, (d) 90 min, (e) 142 min and (f) 180 min; excitation wavelength was set at 371 nm. **(B)** Excitation spectrum of a mixture of (a) ~ 127 mg of zinc chloride and ~ 18.0 mg of ascorbic acid and that following addition of ~ 200 mg sodium acetate and recorded after (b) 24 min, (c) 60 min, (d) 90 min, (e) 142 min and (f) 180 min. Emission wavelength was set at corresponding emission maxima.

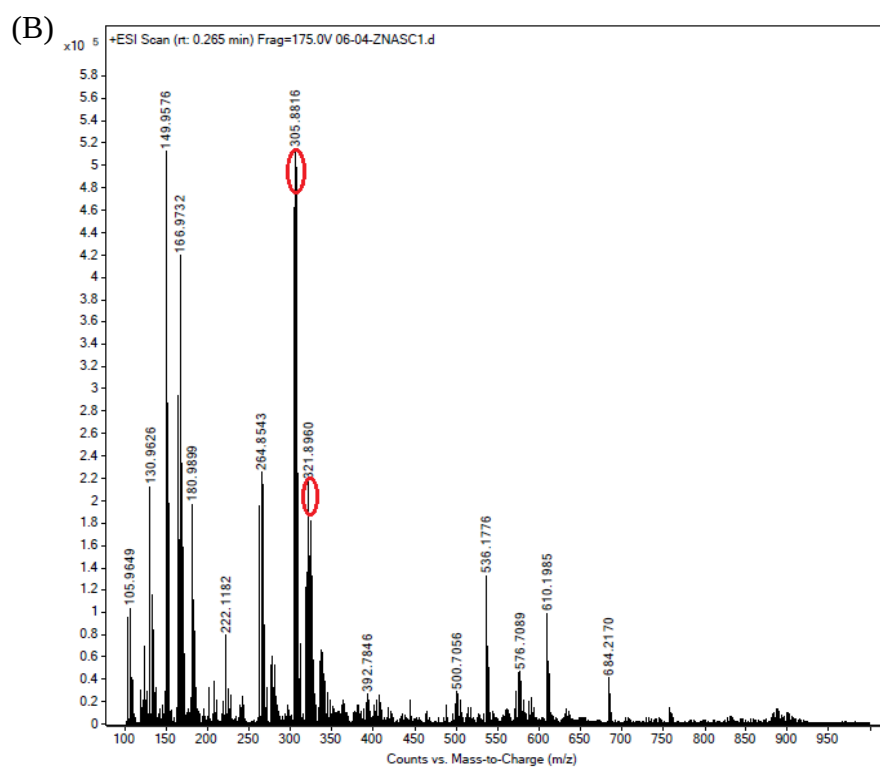
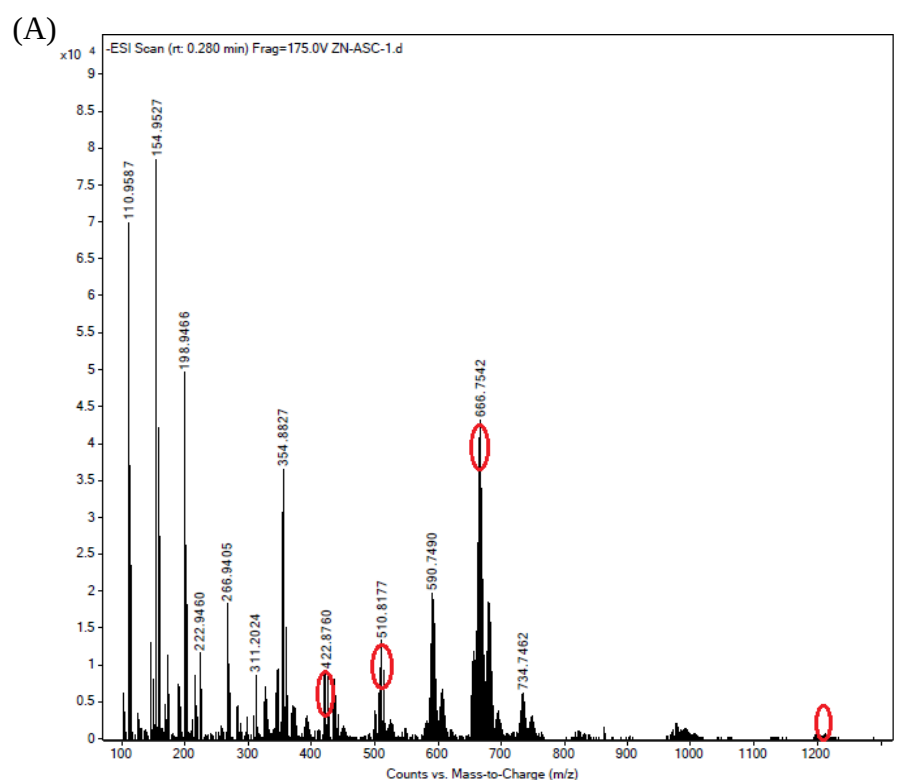
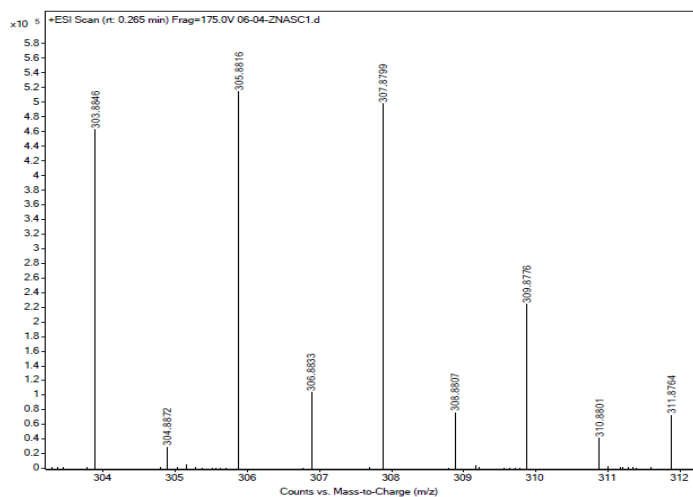


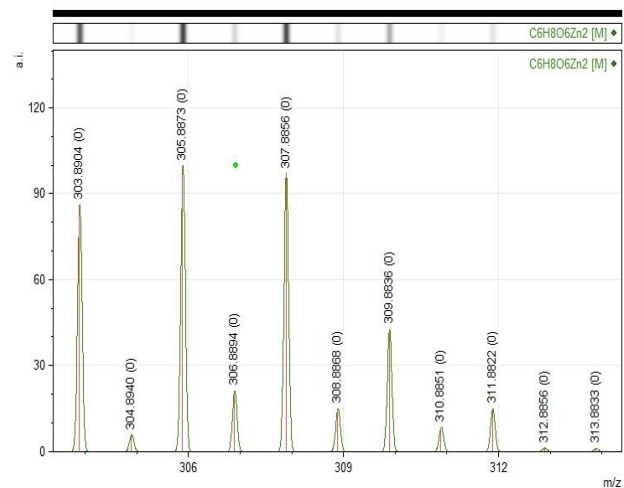
Fig. S9 (A) Mass spectrum of the reaction medium recorded in ESI -ve mode at 0.280 min and (B) Mass spectrum of the reaction medium recorded in ESI +ve mode at 0.265 min. Mass peaks

highlighted in red circles have been reported separately in the manuscript and supporting information, along with simulated spectra.

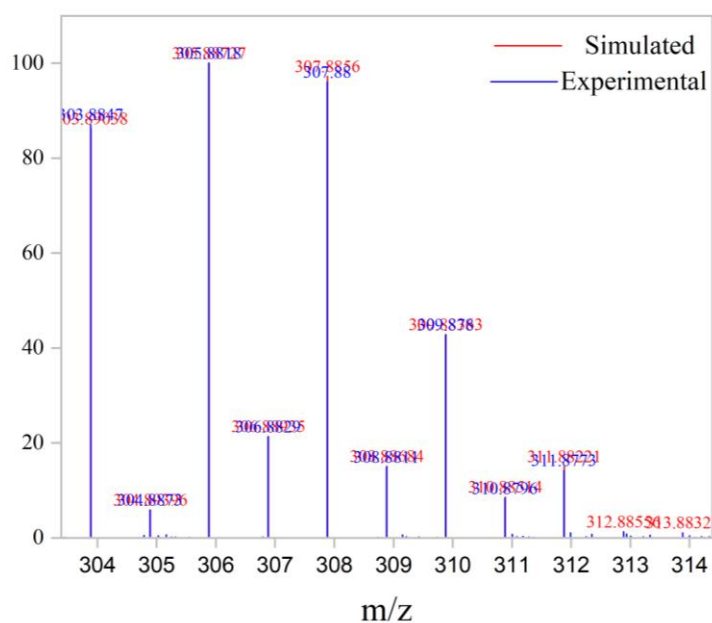
(A)



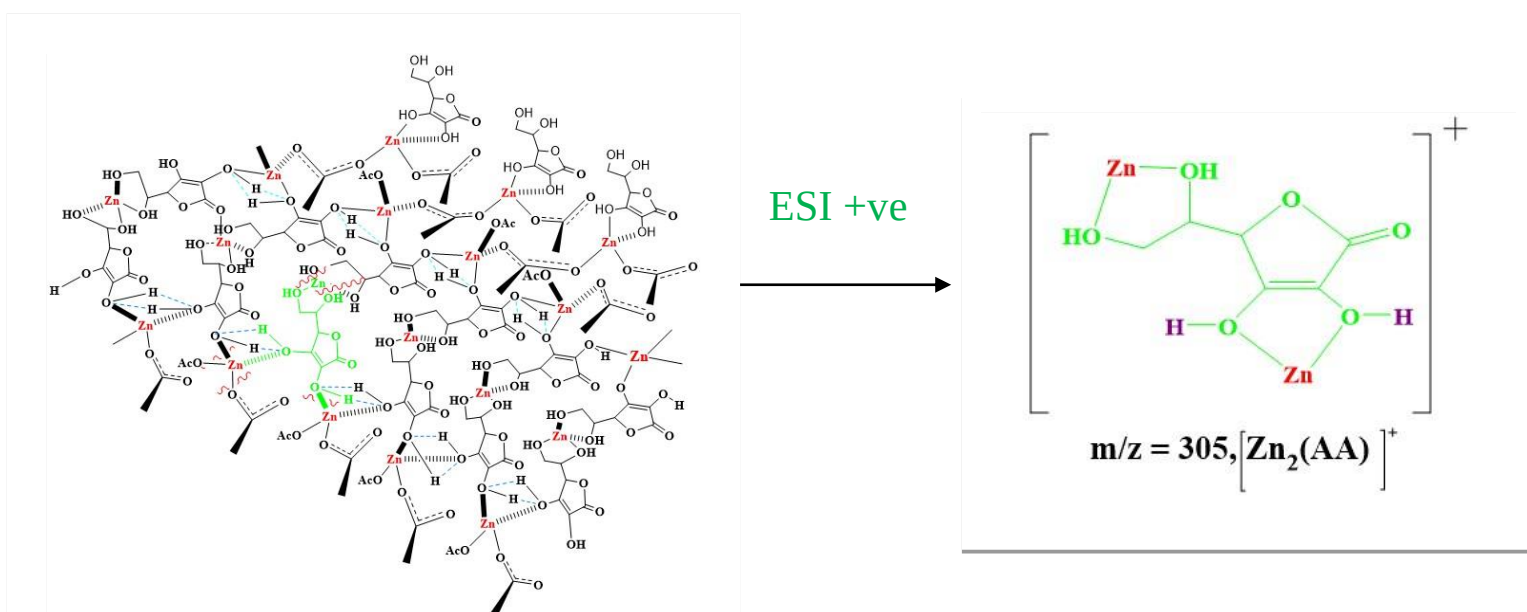
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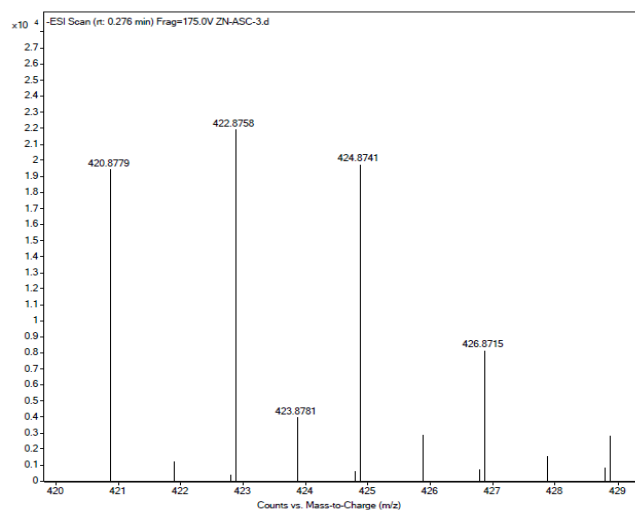
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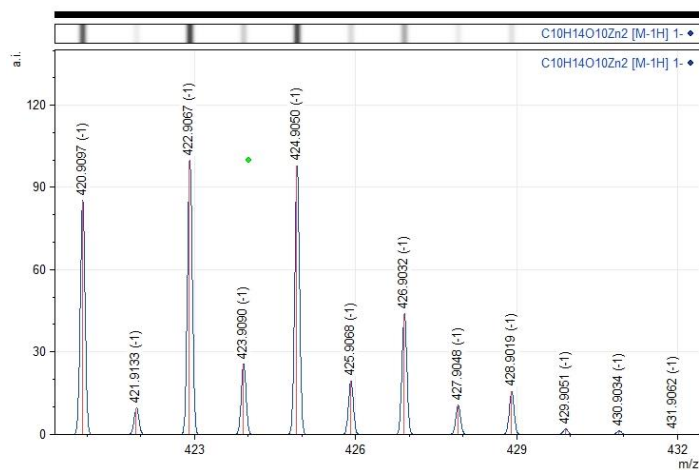
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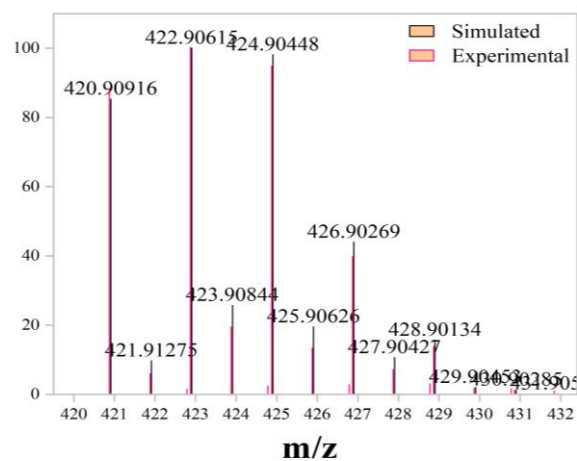
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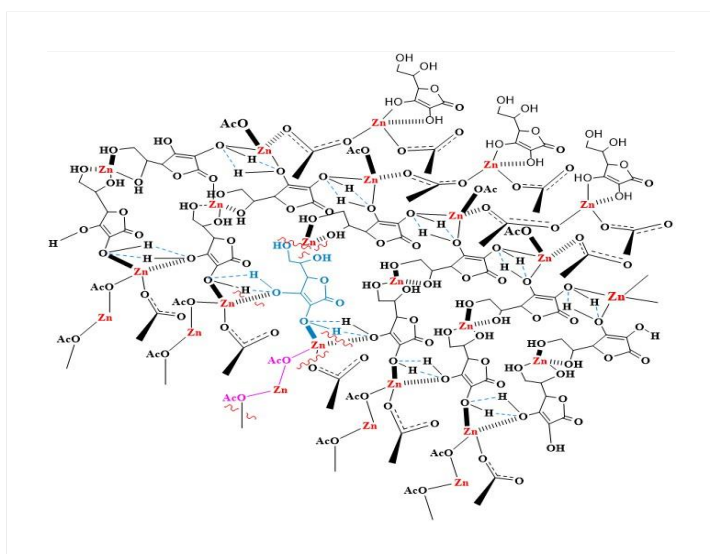
(F)



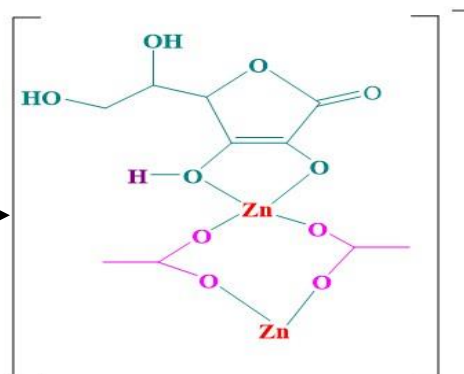
(G)



(H)

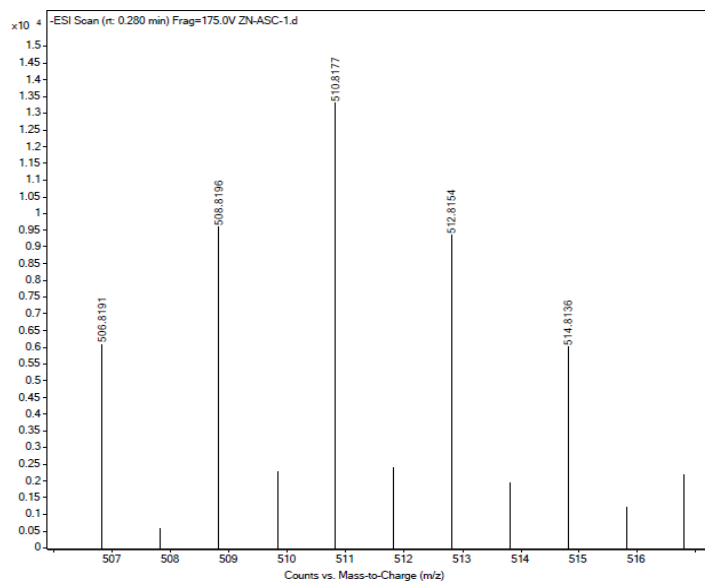


ESI-ve

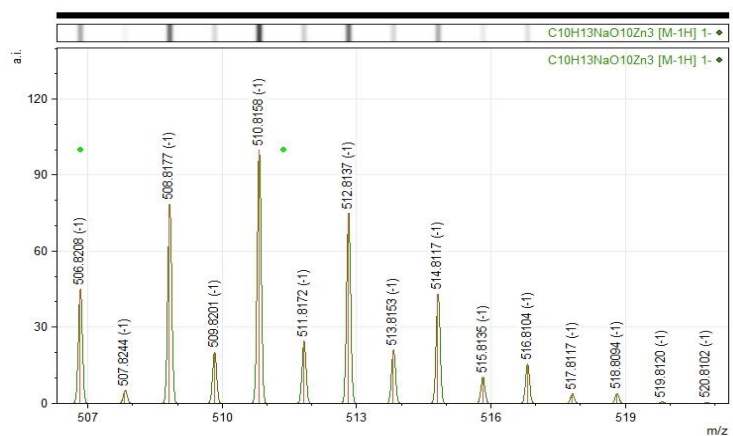


$$m/z = 424, [Zn_2(AA)(OAc)_2]^-$$

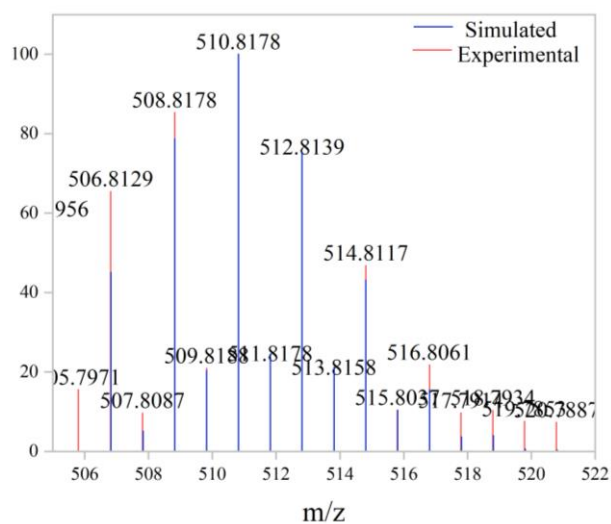
(I)



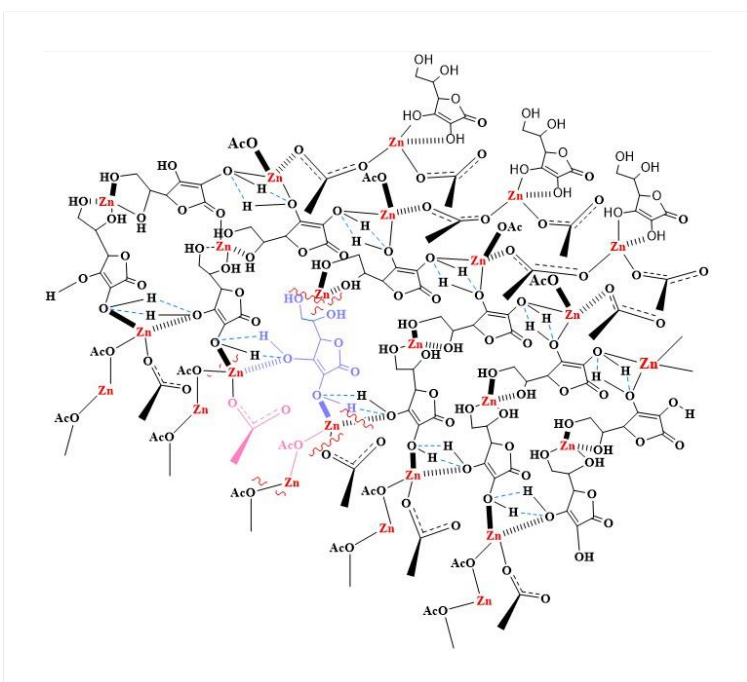
(J)



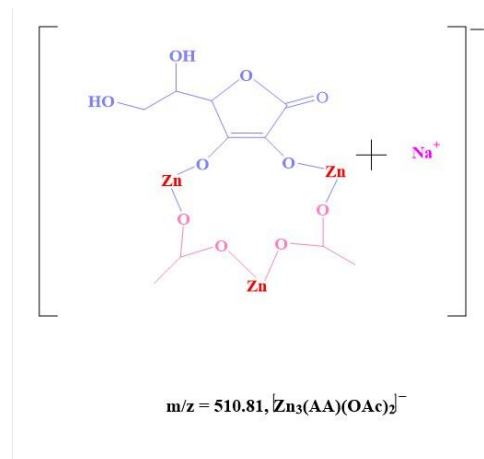
(K)



(L)

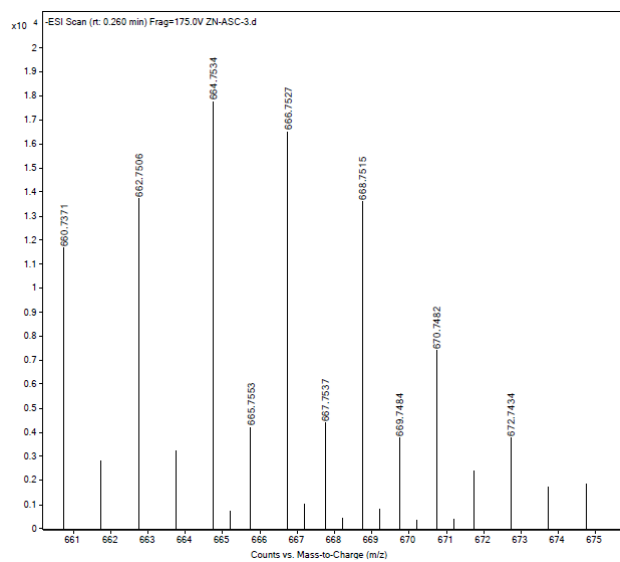


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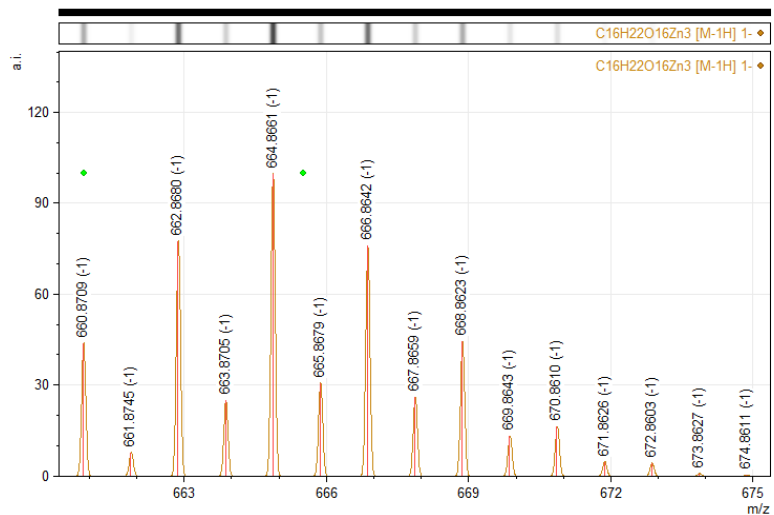


S13

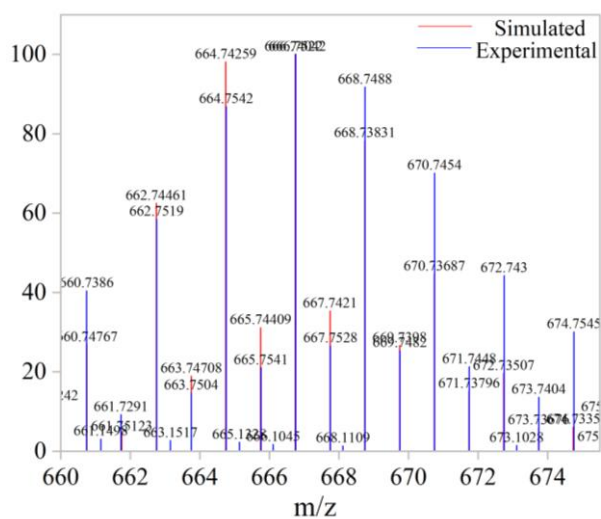
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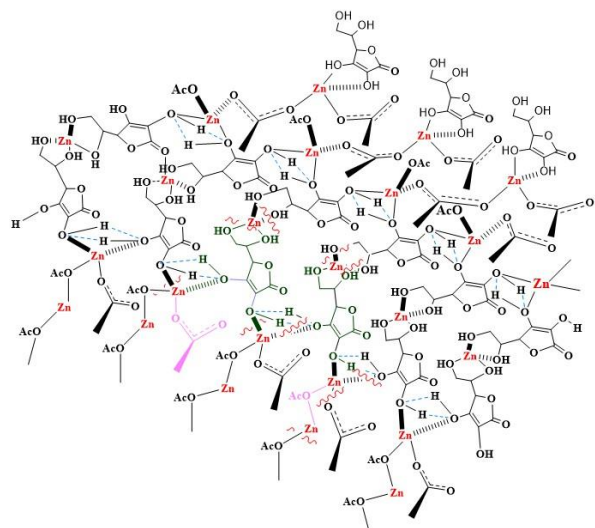
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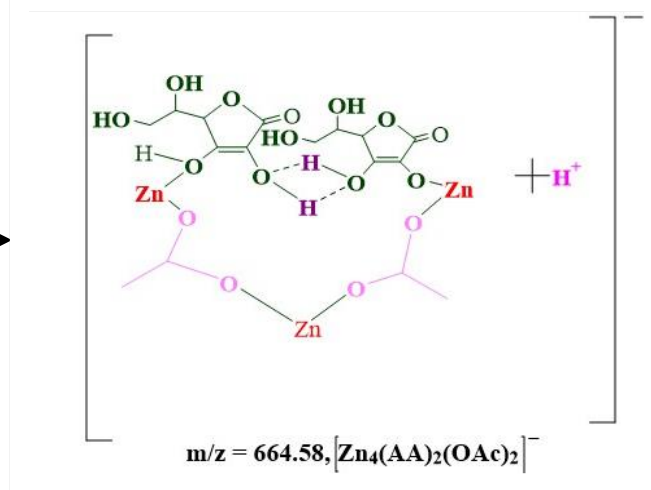
(O)



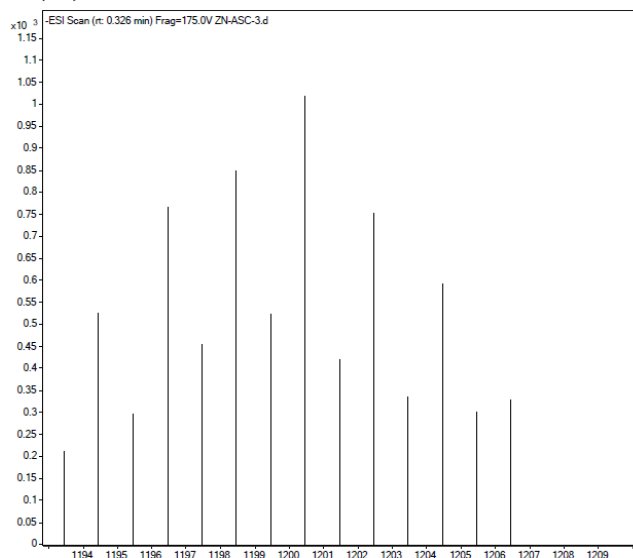
(P)



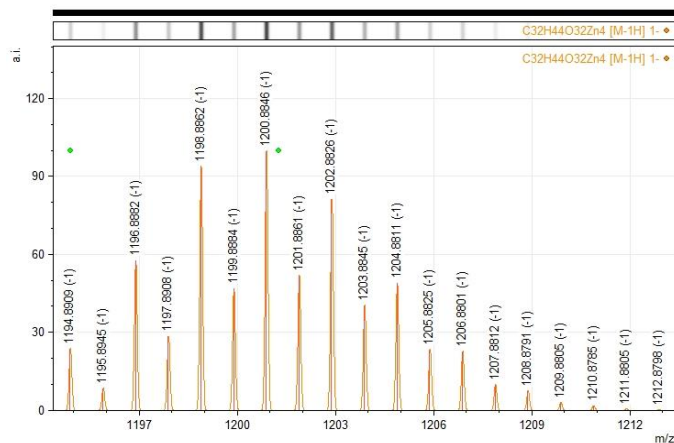
ESI -ve



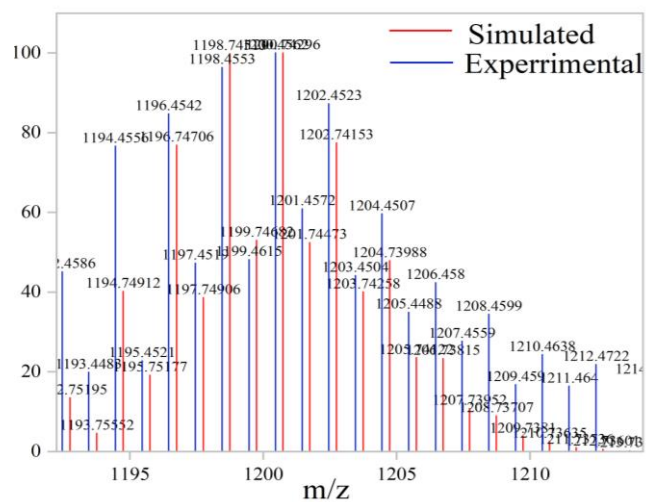
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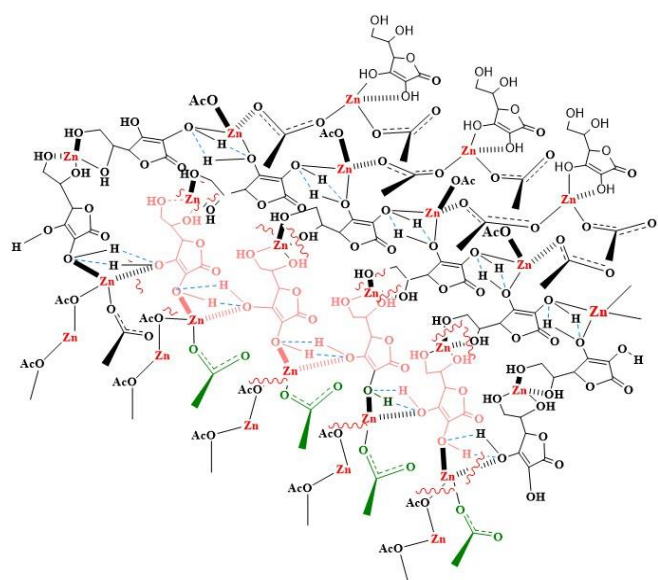
(R)



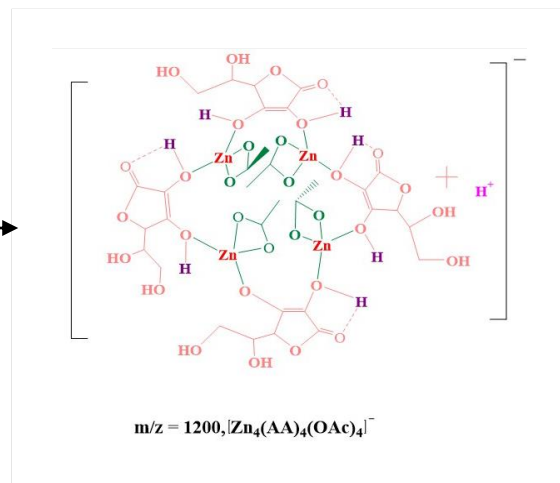
(S)



(T)



ESI -ve



(U)

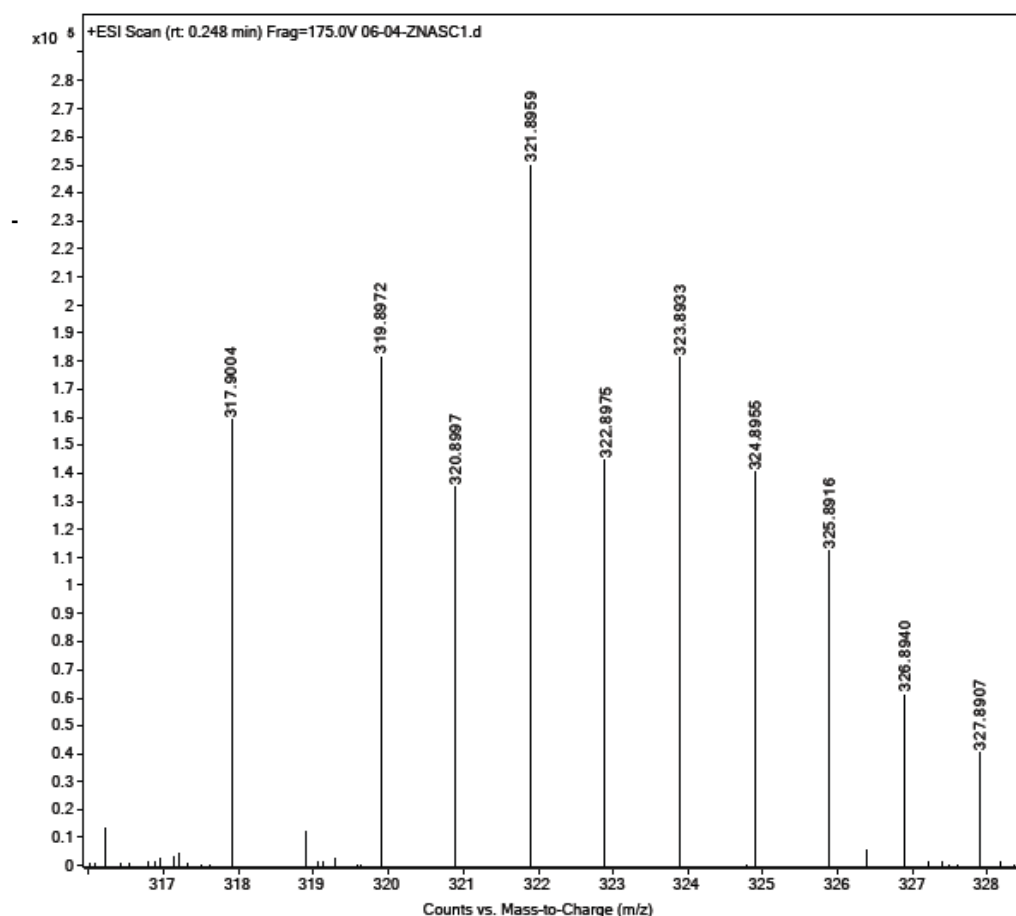


Fig. S10 (A) Experimental mass spectrum of the luminescent dispersion indicating presence of $[Zn_2AA]^+$. (B) Simulated mass spectrum of $[Zn_2AA]^+$. (C) Overlay of experimental and simulated spectrum. (D) Possible fragmentation pattern for the mass fragment. (E) Experimental mass spectrum of the luminescent dispersion indicating presence of $[Zn_2AA(OAc)_2]^-$. (F) Simulated mass spectrum of $[Zn_2AA(OAc)_2]^-$. (G) Overlay of experimental and simulated spectrum. (H) Possible fragmentation pattern for the mass fragment. (I) Experimental mass spectrum of the luminescent dispersion indicating presence of $[Zn_3AA(OAc)_2 + Na^+]^-$. (J) Simulated mass spectrum of $[Zn_3AA(OAc)_2 + Na^+]^-$. (K) Overlay of experimental and simulated spectrum. (L) Possible fragmentation pattern for the mass fragment. (M) Experimental mass spectrum of the luminescent dispersion indicating presence of $[Zn_3AA_2(OAc)_2 + H^+]^-$. (N) Simulated mass spectrum of $[Zn_3AA_2(OAc)_2 + H^+]^-$. (O) Overlay of experimental and simulated spectrum. (P) Possible fragmentation pattern for the mass fragment. (Q) Experimental mass spectrum of the luminescent dispersion

indicating presence of $[\text{Zn}_5\text{AA}_4(\text{OAc})_3]^-$. (R) Simulated mass spectrum of $[\text{Zn}_5\text{AA}_4(\text{OAc})_3]^-$. (S) Overlay of experimental and simulated spectrum. (T) Possible fragmentation pattern for the mass fragment. (U) +ESI mass spectrum corresponding to m/z value 321.89 (that could not be assigned).

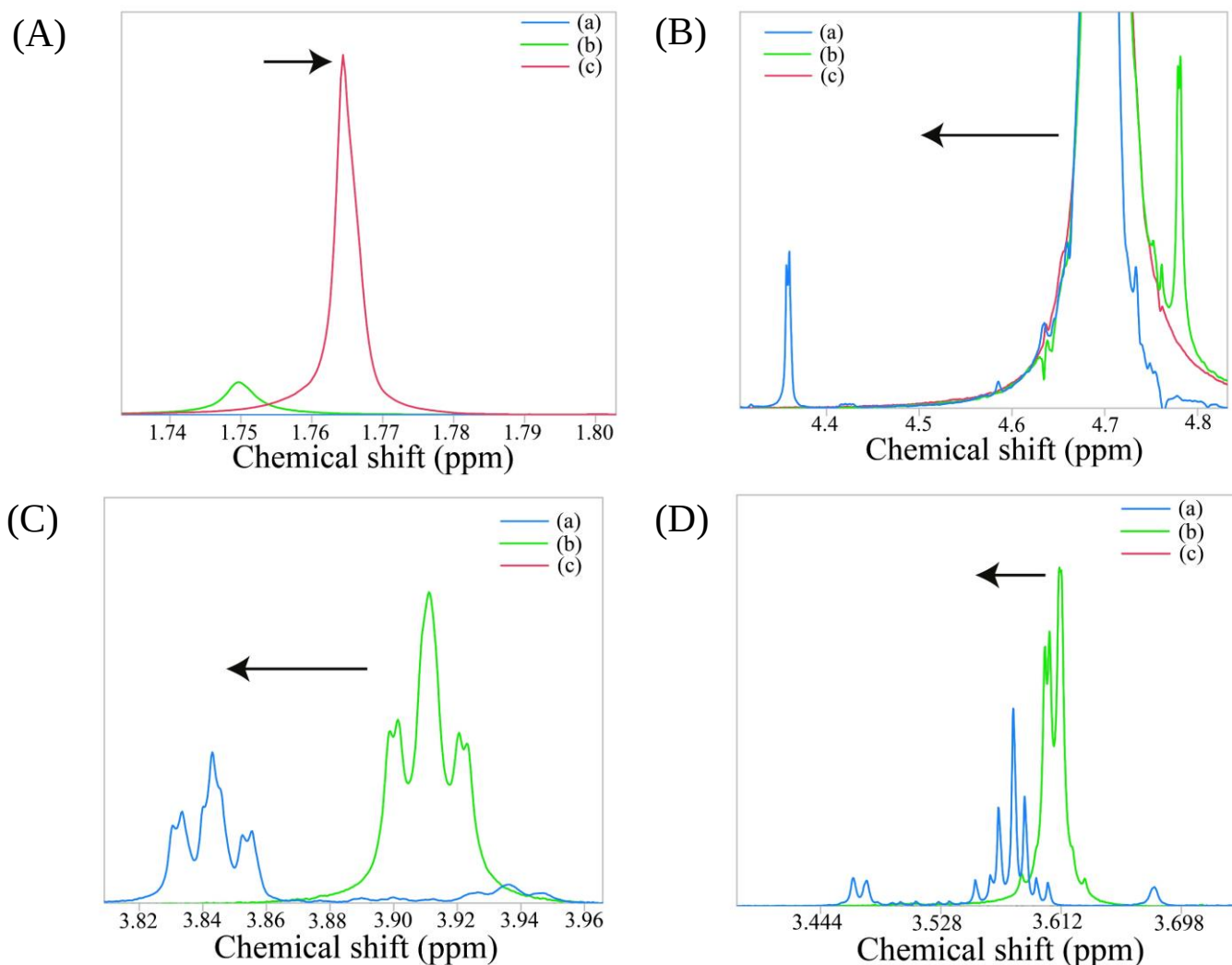
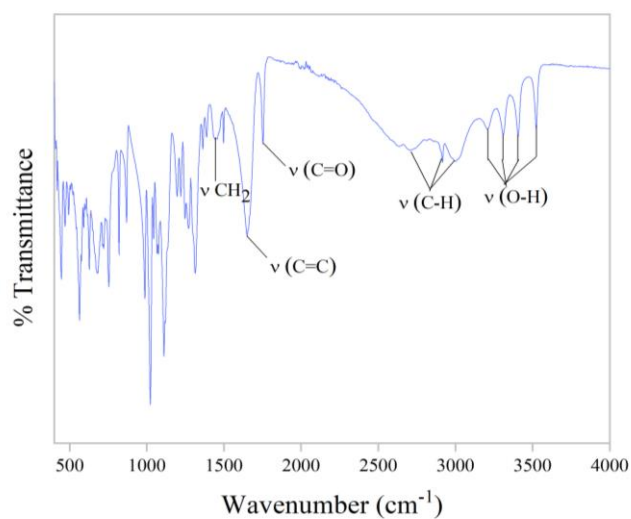
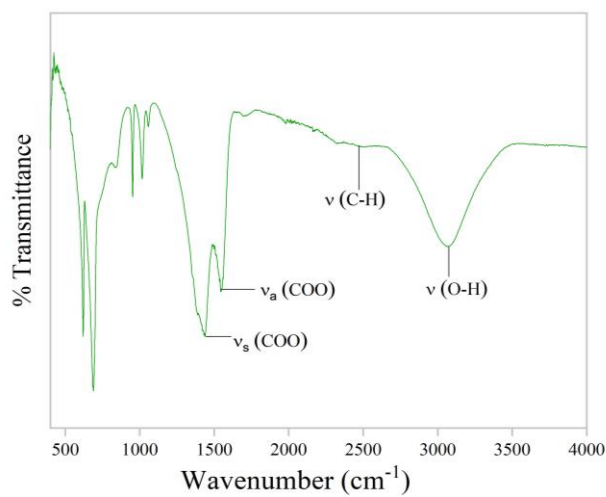


Fig. S11 (A-D) Expanded NMR spectra of dispersion of (a) $\text{Zn}_x(\text{AA})_y(\text{OAc})_z$ NPs., (b) ascorbic acid and (c) zinc acetate, highlighting the chemical shifts of $\text{Zn}_x(\text{AA})_y(\text{OAc})_z$ NPs. as compared to ascorbic acid and zinc acetate. The spectra refer to the those in Fig. 5 in the manuscript.

(A)



(B)



(C)

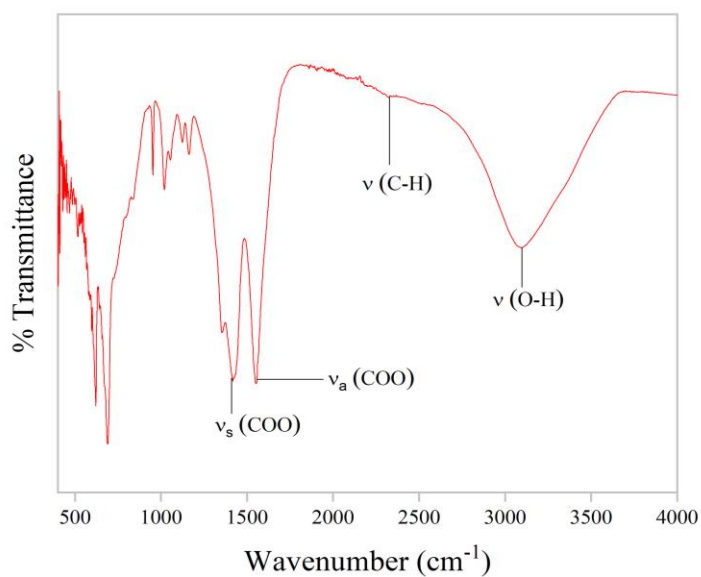


Fig. S12 FTIR spectra of (A) ascorbic acid, (B) zinc acetate and (C) $\text{Zn}_x(\text{AA})_y(\text{OAc})_z$ nanoparticles.

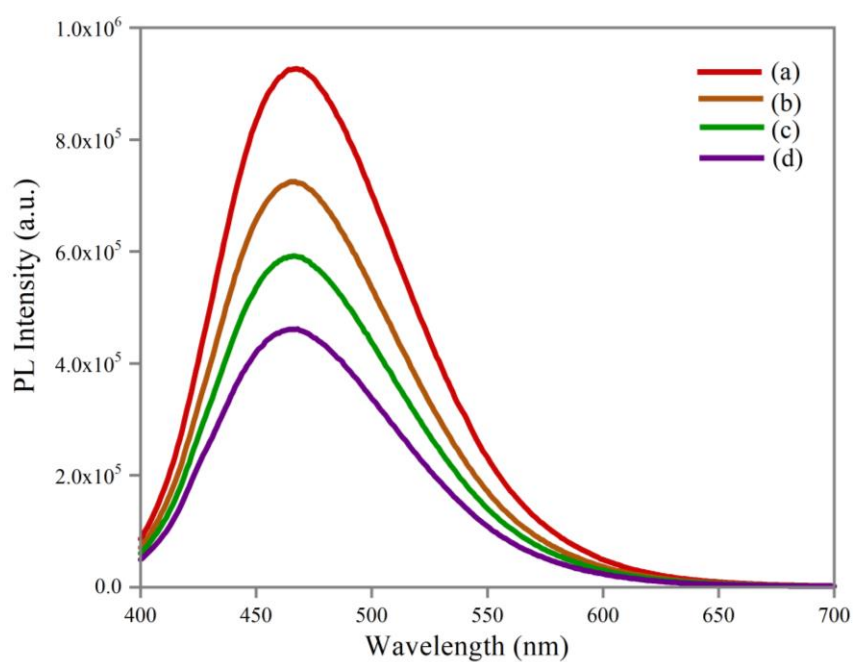


Fig. S13 Photoluminescence spectra of (a) 2 mL of $\text{Zn}_x(\text{AA})_y(\text{OAc})_z$ nanoparticle dispersion, 2 mL of dispersion was added with either (b) 500 μL of water, (c) 1000 μL water, or (d) 1500 μL water. The excitation wavelength was set at 371 nm.

Additional Figures:

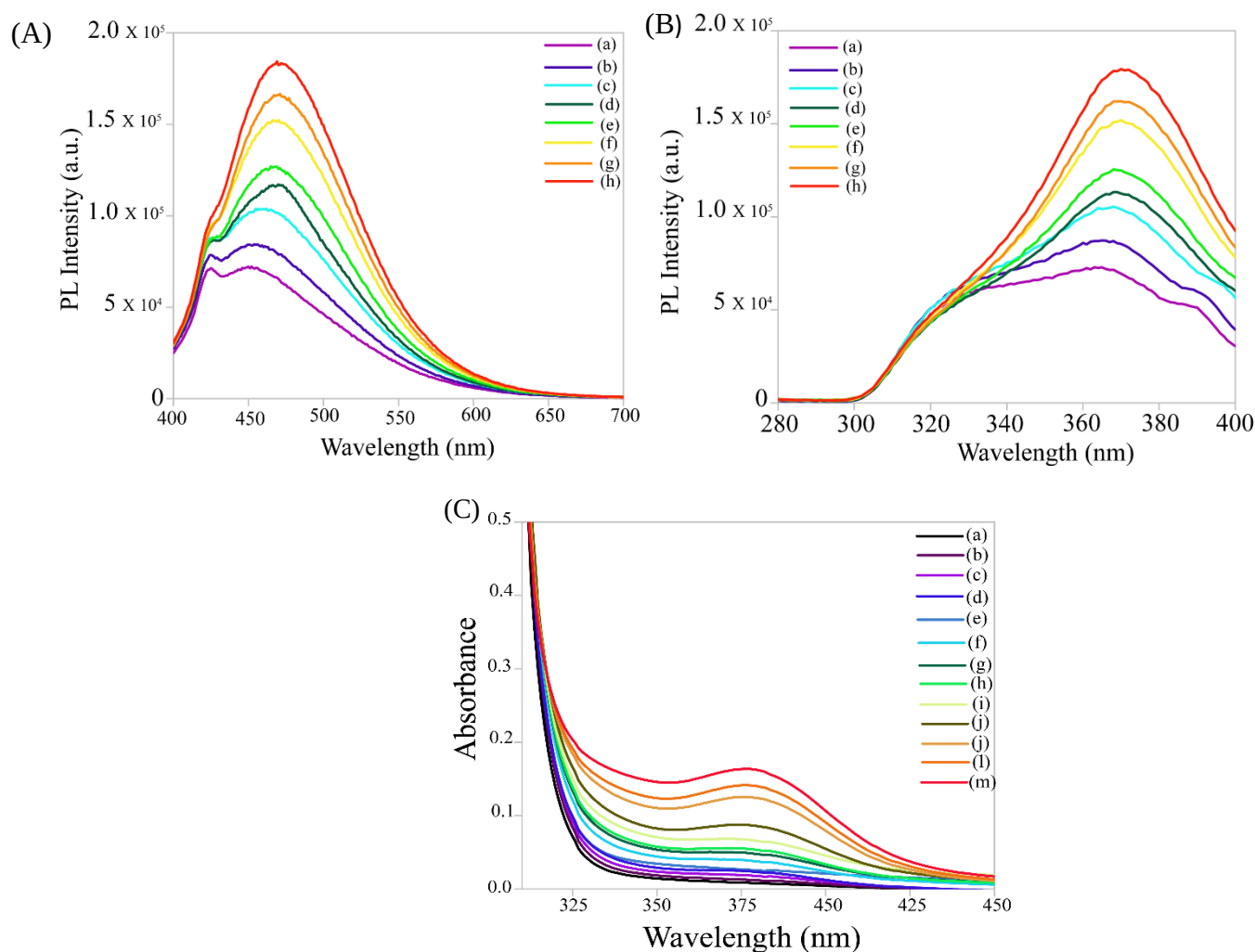


Fig. S14 (A) Photoluminescence emission spectra of a reaction mixture containing zinc acetate dihydrate and ascorbic acid at (a) 0 min, (b) 10 min, (c) 20 min, (d) 30 min, (e) 40 min, (f) 50 min, (g) 60 min, and (h) 70 min; emission maximum was set at 370 nm. (B) Photoluminescence excitation spectra of a reaction mixture containing zinc acetate dihydrate and ascorbic acid at (a) 0 min, (b) 10 min, (c) 20 min, (d) 30 min, (e) 40 min, (f) 50 min, (g) 60 min, and (h) 70 min, emission maximum for every measurement was set at the corresponding emission maximum. (C) Absorbance spectra of the reaction mixture containing zinc acetate dihydrate, ascorbic acid and $\text{Zn}_x(\text{Asc})_y(\text{OAc})_z$ NPs at (a) 0 min, (b) 10 min, (c) 20 min, (d) 30 min, (e) 40 min, (f) 50 min, (g) 64 min, (h) 72 min, (i) 76 min, (j) 117 min, (l) 194 min, and (m) 240 min.

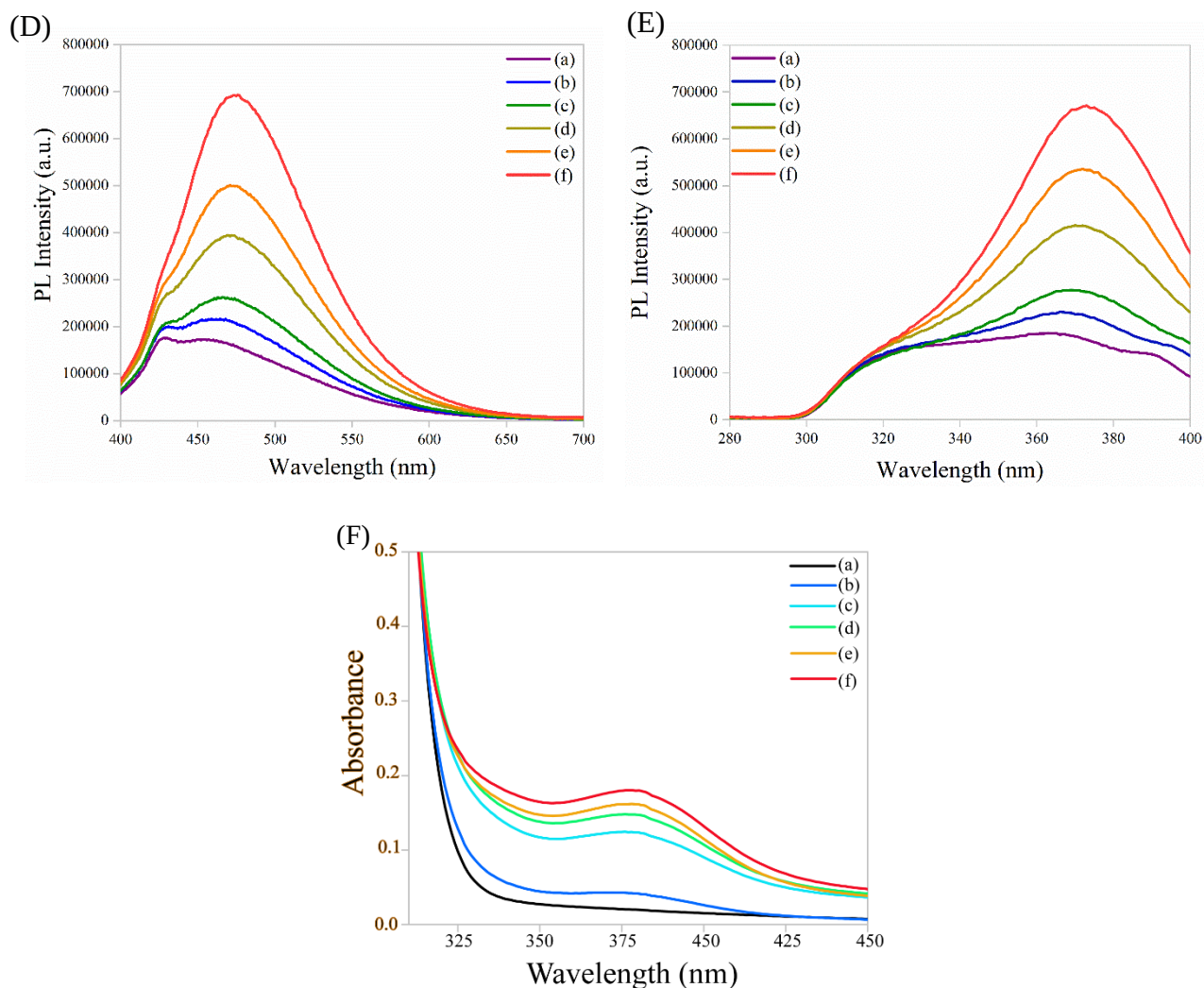


Fig S15 (D) Photoluminescence emission spectra of reaction mixture containing zinc acetate dihydrate and ascorbic acid at (a) 0 min, (b) 20 min, (c) 30 min, (d) 40 min, (e) 50 min, and (f) 75 min; emission maximum was kept fixed at 370 nm. (E) Photoluminescence excitation spectra of reaction mixture containing zinc acetate dihydrate and ascorbic acid at (a) 0 min, (b) 20 min, (c) 30 min, (d) 40 min, (e) 50 min, and (f) 75 min; emission maximum for each recording was fixed at corresponding emission maximum. (F) Absorbance spectra of the reaction mixture containing zinc acetate dihydrate, ascorbic acid and $\text{Zn}_x(\text{Asc})_y(\text{OAc})_z$ NPs at (a) 0 h, (b) 1 h, (c) 3 h, (d) 4 h, (e) 5 h, and (f) 6 h.

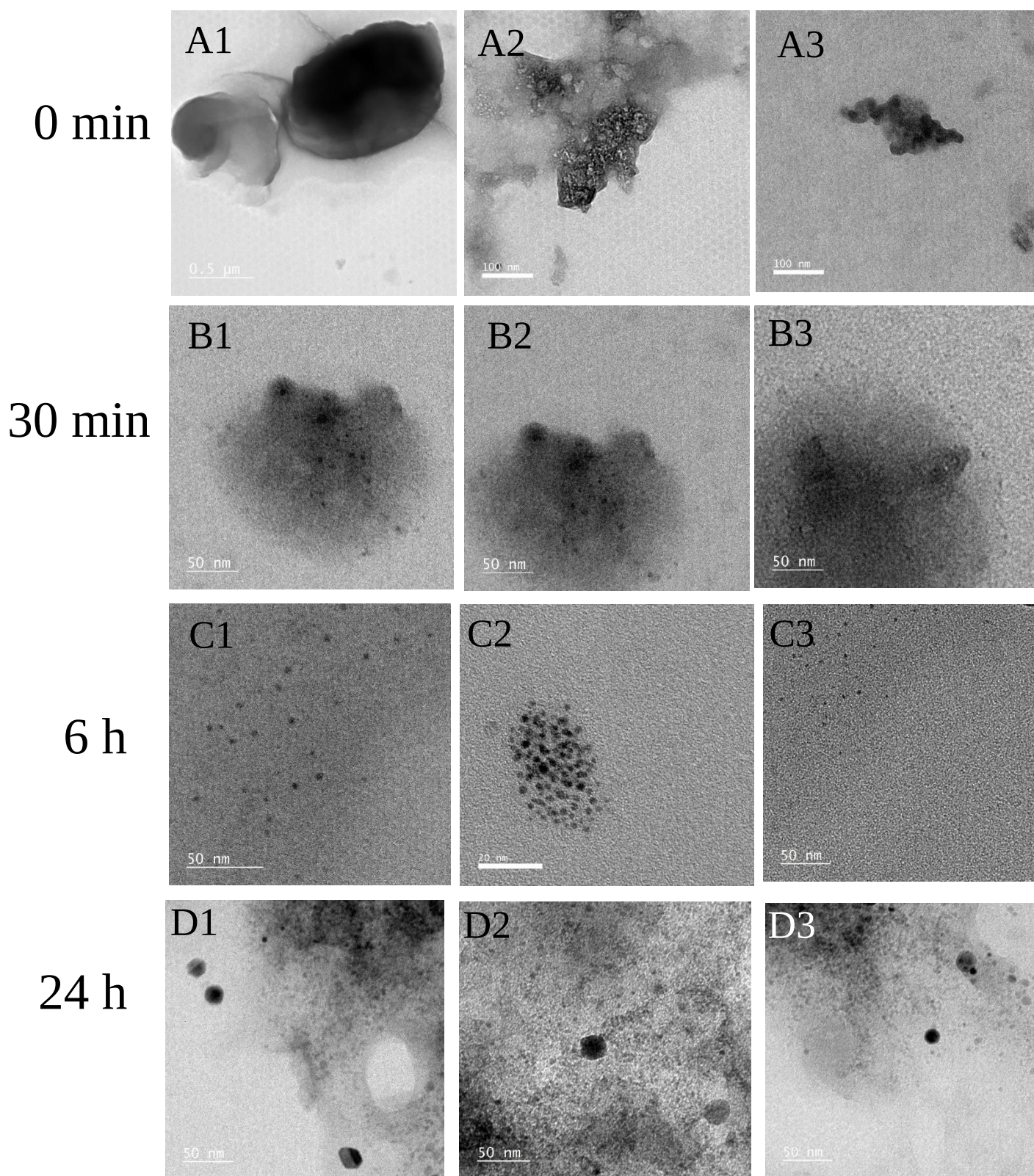


Fig. S16 (A1-A3) Transmission electron microscopic images of the reaction mixture comprising of zinc acetate dihydrate and ascorbic acid drop cast on the TEM grid at 0 h. (B1-B3) Transmission electron microscopic images of the reaction mixture comprising of zinc acetate dihydrate and ascorbic acid drop cast on the TEM grid at 30 min. (C1-C3) Transmission electron microscopic images of the reaction mixture comprising of zinc acetate dihydrate and ascorbic acid drop cast on the TEM grid at 6 h. (D1-D3) Transmission electron microscopic images of the reaction mixture comprising of zinc acetate dihydrate and ascorbic acid drop cast on the TEM grid at 24 h following mixing of zinc acetate dihydrate and ascorbic acid.

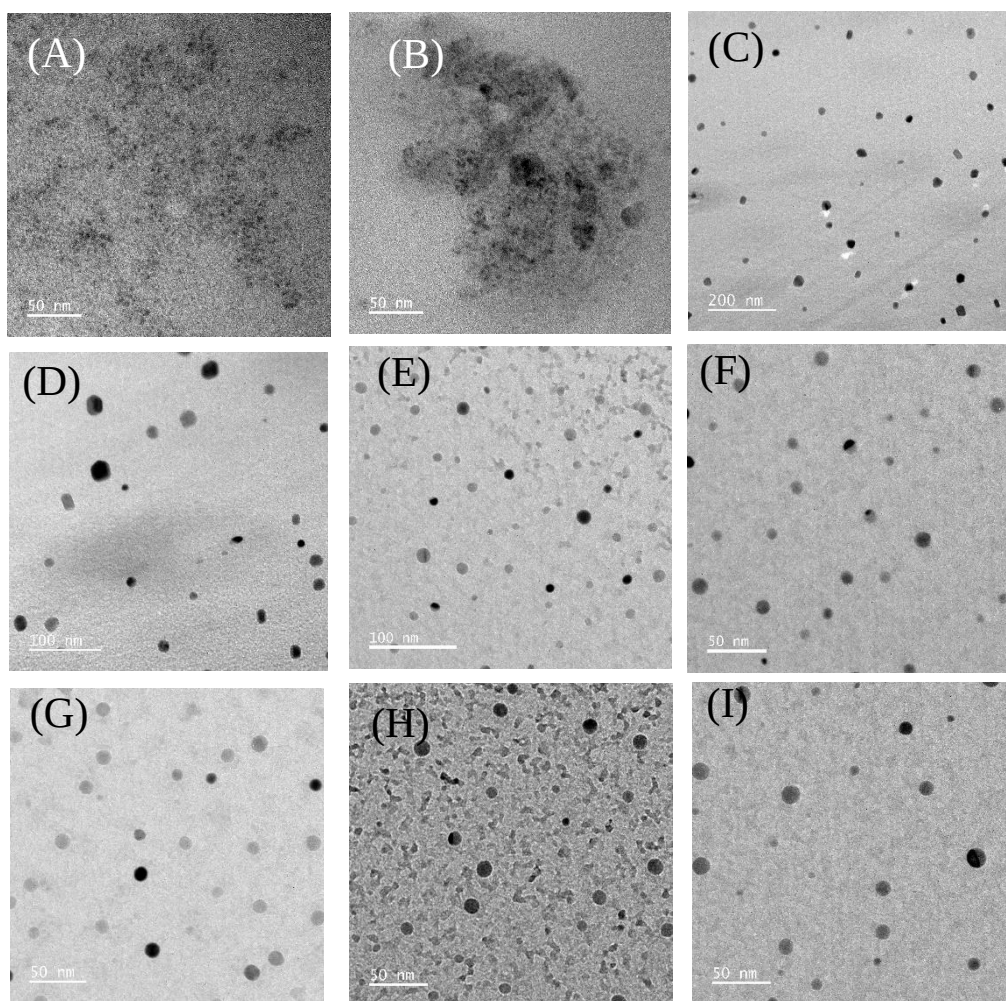


Fig. S17 Transmission electron microscopic images of the product of reaction between zinc acetate dihydrate and ascorbic acid acquired over various regions of the TEM grid acquired for different samples at different times (A-B, sample prepared within 6 h; C-I, sample prepared after 24 h of reaction).

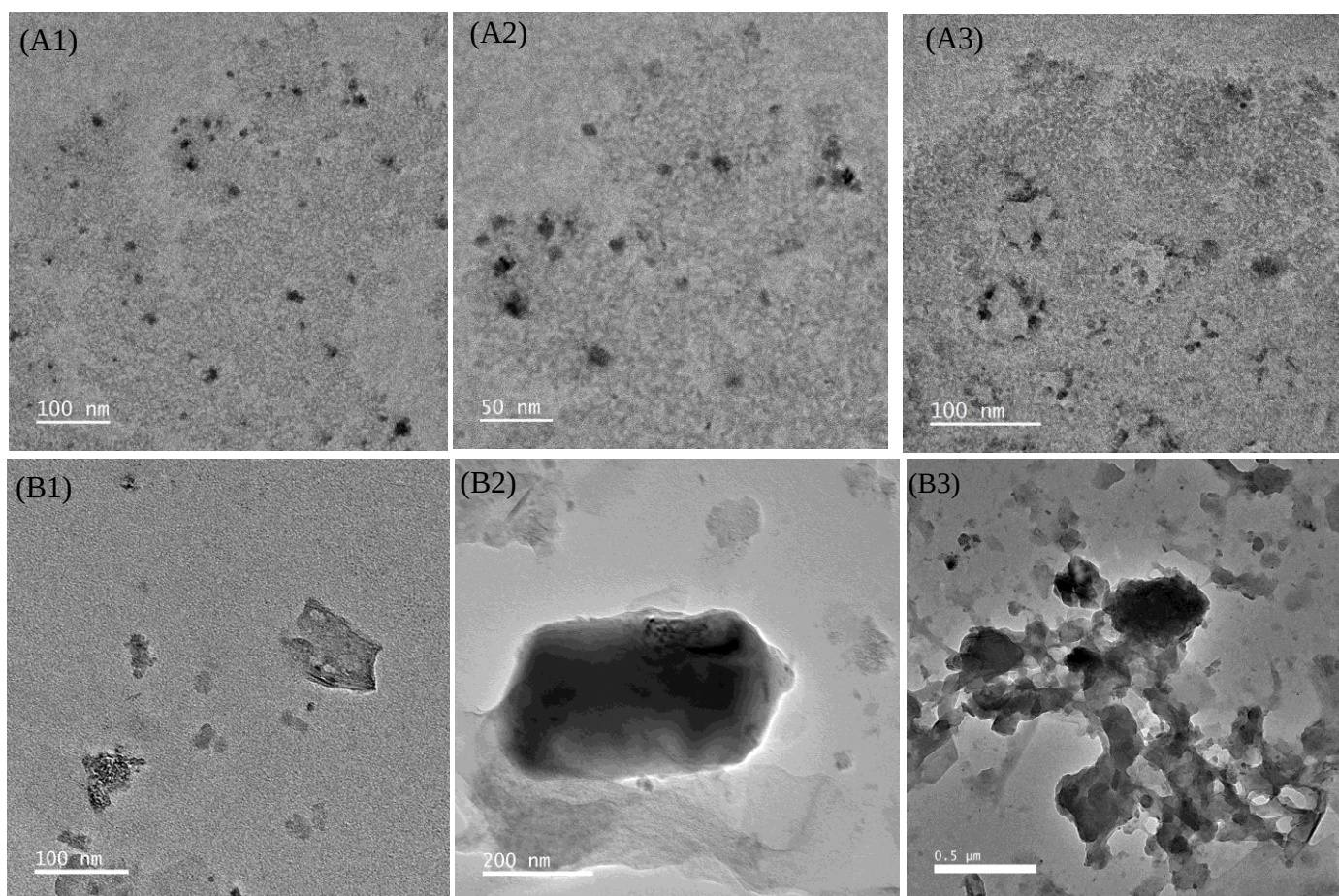


Fig. S18 (A1-A3) Transmission electron microscopic images of the zinc acetate solution stored for 30 days. (B1-B3) Transmission electron microscopic images of the ascorbic acid solution stored for 56 days.

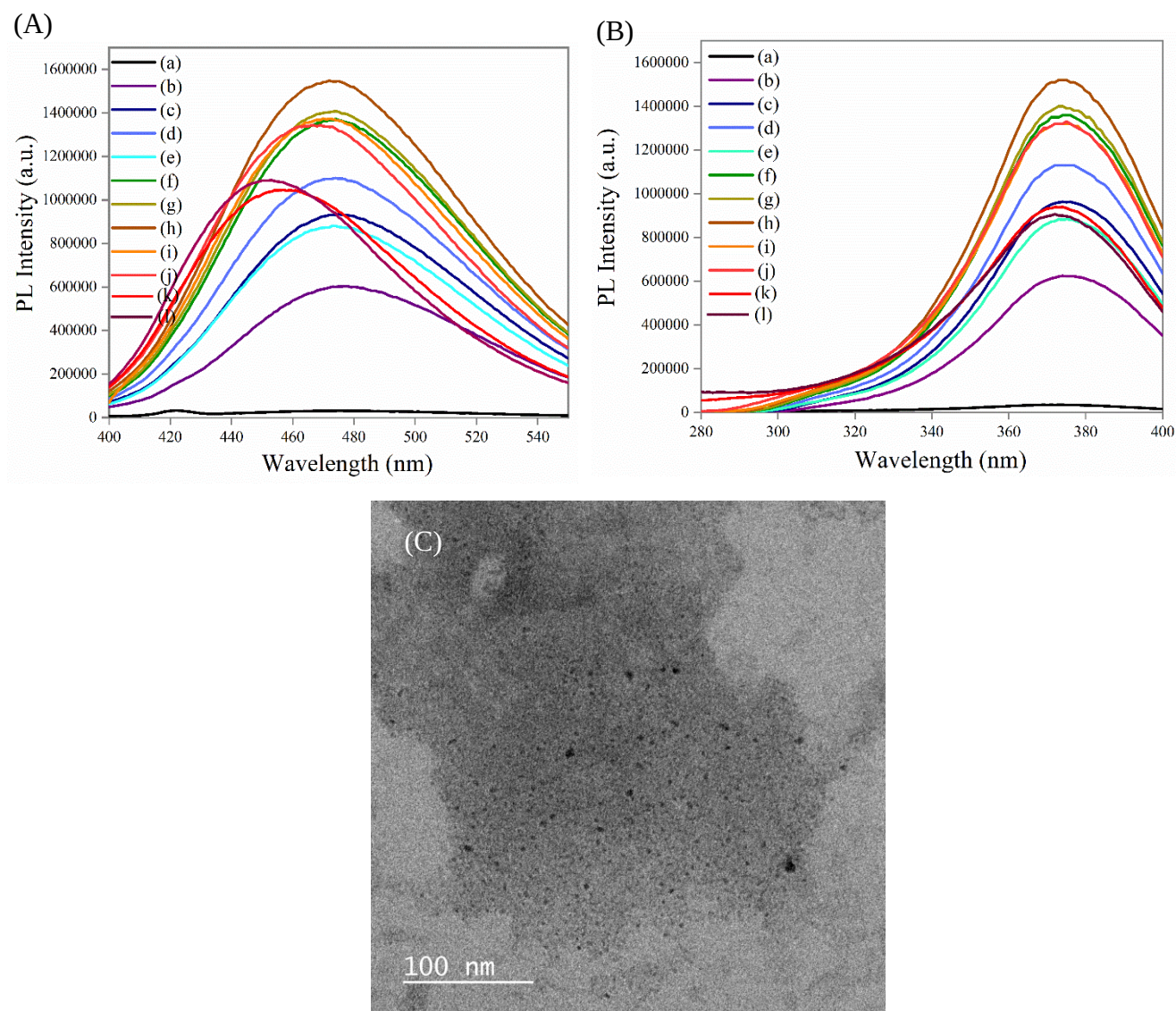


Fig. S19 (A) Photoluminescence emission spectra of a reaction mixture containing zinc acetate dihydrate and ascorbic acid at (a) 1 h, (b) 24 h, (c) 48 h, (d) 72 h, (e) 96 h, (f) 144 h, (g) 168 h, (h) 192 h, (i) 240 h, (j) 288 h, (k) 360 h, and (l) 456; emission maximum was set at 371 nm. (B) Photoluminescence excitation spectra of a reaction mixture containing zinc acetate dihydrate and ascorbic acid (a) 1 h, (b) 24 h, (c) 48 h, (d) 72 h, (e) 96 h, (f) 144 h, (g) 168 h, (h) 192 h, (i) 240 h, (j) 288 h, (k) 360 h, and (l) 456 h, emission maximum for every measurement was set at 476 nm. (C) TEM image acquired for the as synthesized nanoparticle after 16 days of reaction.

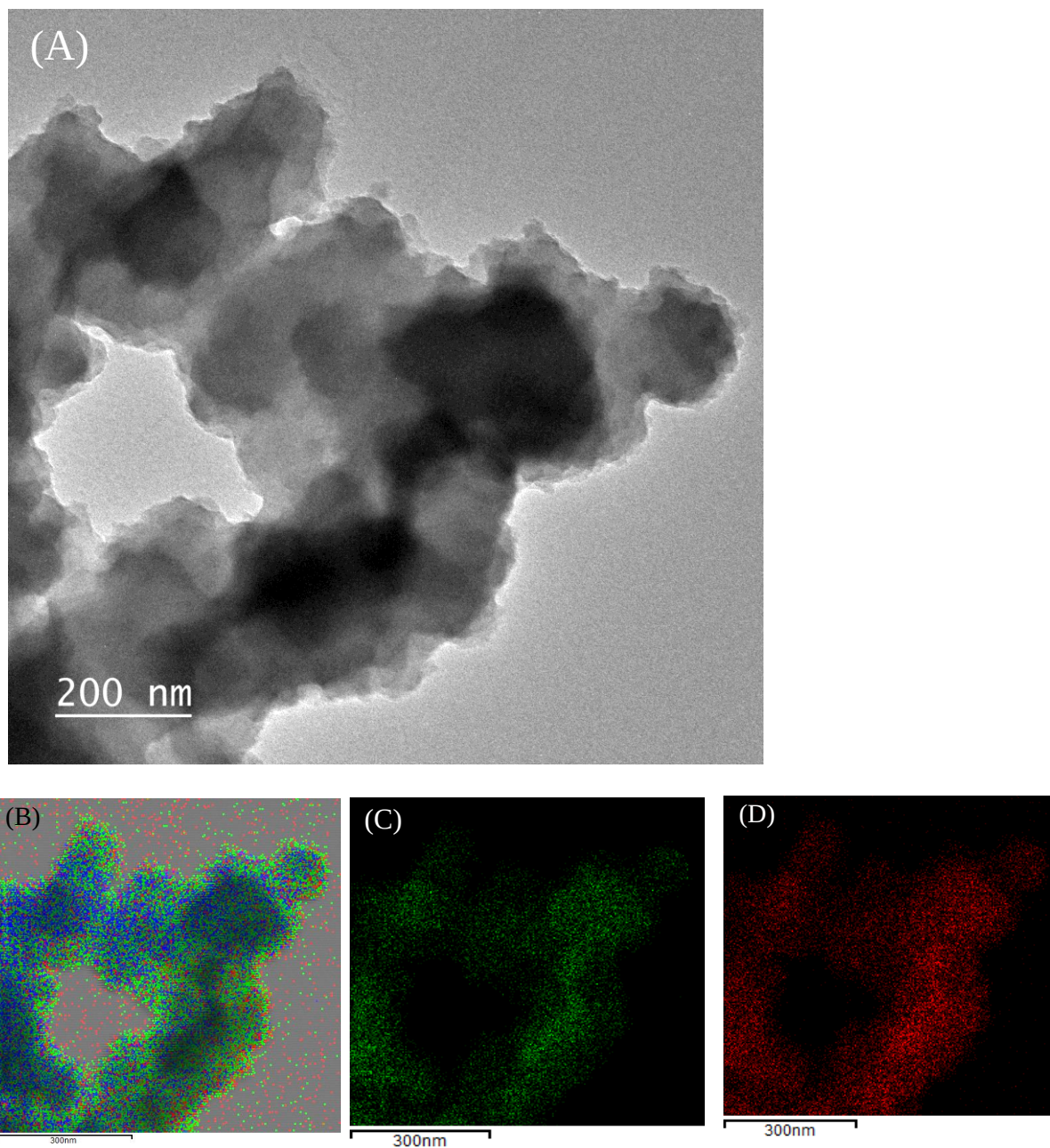


Fig. S20 (A) TEM image, (B) STEM image of $\text{Zn}_x(\text{AA})_y(\text{OAc})_z$ NPs acquired after redispersing the pellet obtained by centrifugation in water after 31 days of reaction. Elemental mapping of (C) Zn, and (D) O $\text{Zn}_x(\text{AA})_y(\text{OAc})_z$ NPs.

Spectrum processing :
Peaks possibly omitted : 1.742, 2.319, 2.628, 3.689, 8.037, 11.420 keV

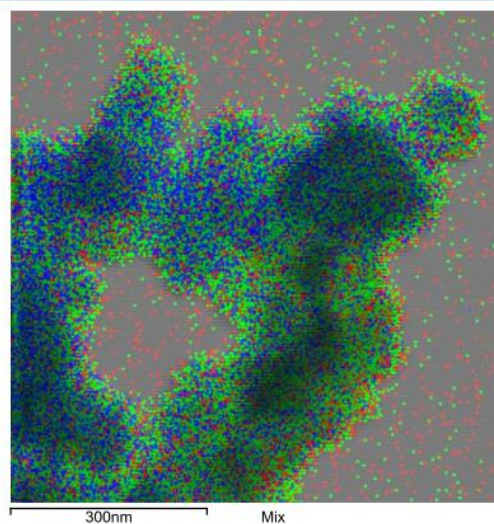
Quantitation method : Cliff Lorimer thin ratio section.
Processing option : All elements analyzed
Number of iterations = 1

Standardless

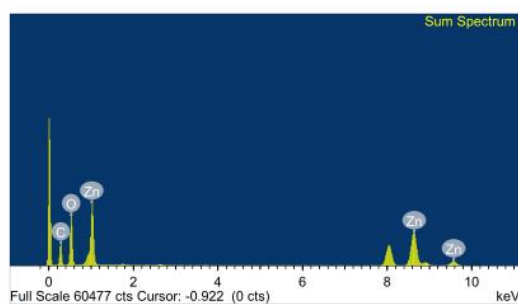
Elem...	Weight%	Atomic%
C K	17.37	33.63
O K	33.69	48.96
Zn K	48.94	17.41

Totals 100.00

(A)



(B)



Comment:

Fig. S21 (A) Elemental Mapping and (B) energy dispersive X-ray analysis for the sample after 16 days of reaction.

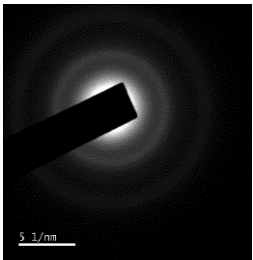
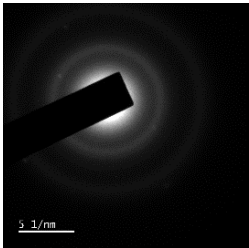
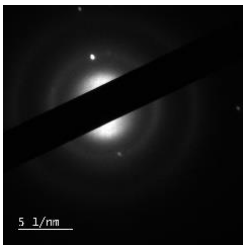
Table S1. Experimentally observed and simulated mass fragments and their corresponding formula assignments.

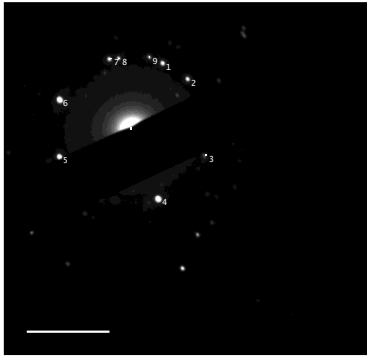
Average mass (observed)	Average mass (simulated)	Component
305.8816	305.8873	$[\text{Zn}_2\text{AA}]^+$
321.8959	-	Could not be assigned
422.87	422.90	$[\text{Zn}_2\text{AA}(\text{OAc})_2]^-$
510.8177	510.8147	$[\text{Zn}_3\text{AA}(\text{OAc})_2 + \text{Na}^+]^+$
664.7542	664.8650	$[\text{Zn}_3\text{AA}_2(\text{OAc})_2 + \text{H}^+]^+$
1200.45	1200.7424	$[\text{Zn}_5\text{AA}_4(\text{OAc})_3]^-$

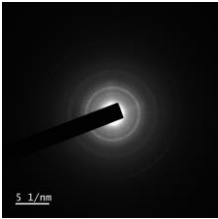
Table S2: Details of chemical shifts of protons of $\text{Zn}_x(\text{AA})_y(\text{OAc})_z$ nanoparticles vis-à-vis zinc ascorbate (as per literature reports).

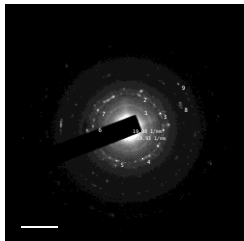
Types of proton	Chemical shift (δ)		Splitting Pattern	
	$\text{Zn}_x(\text{AA})_y(\text{OAc})_z$ NPs	Zinc ascorbate (As per literature reports)	$\text{Zn}_x(\text{AA})_y(\text{OAc})_z$ NPs	Zinc ascorbate (As per literature reports)
H_a	4.35	4.48	doublet	doublet
H_b	3.84	3.97	multiplet	multiplet
H_c, H_d	3.56	3.67-3.70	multiplet	multiplet
$\text{H}_{\text{acetate}}$	1.76	-----	singlet	-----

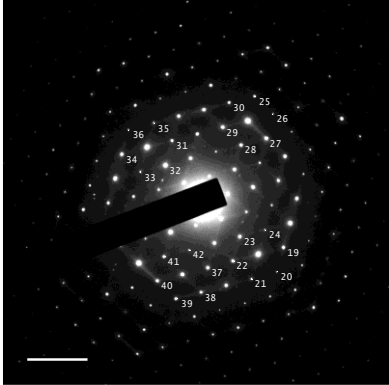
Table S3: Inter-planer distance obtained from SAED pattern acquired for $\text{Zn}_x(\text{Asc})_y(\text{OAc})_z$ NPs

SAED pattern obtained for $\text{Zn}(\text{AA})(\text{OAC})$ nanoparticles	Spot	d-spacing from 000 point
S3A 	1 st ring	0.2149
	2 nd ring	0.1202
S3B 	1 st ring	0.2078
S3C 	1 st ring spot 1	0.2021
	1 st ring spot 2	0.2079
	2 nd ring	0.1281

SAED pattern obtained for Zn(AA)(OAC) nanoparticles	Spot	d-spacing from 000 point
S3D 	1	0.2231
	2	0.2169
	3	0.2074
	4	0.2137
	5	0.2165
	6	0.2160
	7	0.2220
	8	0.2271
	9	0.2192

SAED pattern obtained for zinc acetate	Spot	d-spacing from 000 point
S3E 	1 st ring	0.2659
	2 nd ring	0.1536

SAED pattern obtained for zinc acetate	Spot	d-spacing from 000 point
S3F 	1 2 3 4 5 6 7 8 9	0.3142 0.2159 0.2138 0.2237 0.2177 0.2212 0.2119 0.1298 0.1112

SAED pattern obtained for ascorbic acid	Spot	d-spacing from the center of each distorted hexagonal
S3G 	19	0.4684
	20	0.4569
	21	0.4511
	22	0.4577
	23	0.4902
	24	0.5022
	25	0.4509
	26	0.4641
	27	0.5015
	28	0.5068
	29	0.4634
	30	0.4402
	31	0.4964
	32	0.4725
	33	0.4552
	34	0.4381
	35	0.4953
	36	0.4632
	37	0.4663
	38	0.4631
	39	0.4768
	40	0.4654
	41	0.4794
	42	0.4851