

Supplementary Information

Self-assembled Superstructures Derived from suitably substituted Phenanthro[9,10-d] imidazole-Based Zn(II)/Cd(II) Complexes for selective detection of Acetone

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Experimental section

Synthesis of L1: A mixture of 2-hydroxy benzaldehyde (293 mg, 2.40 mmol), Phenanthrene-9,10-dione (500 mg, 2.40 mmol), and ammonium acetate (2.4 gm, 31.13 mmol) in glacial acetic acid (15 mL) was heated at 100°C for 12 h with continuous stirring. The hot reaction mixture was cooled to room temperature, whereupon a white solid was precipitated. This white solid was collected by filtration and washed with dilute aqueous NaHCO₃ solution followed by distilled water. This white residue was dried and purified by column chromatography on silica gel eluting with Hexane/CHCl₃ (95:5, v/v). Yield = 561 mg, (1.8 mmol, 75.4%) (Scheme S1). (¹H NMR, CDCl₃, 500 MHz, δppm): 11.47 (s, 1H), 8.65 (t, *J* = 8.7Hz, 2H), 8.41 (d, *J* = 7.9Hz, 1H), 8.24 (d, *J* = 7.1Hz, 1H), 8.10 (q, *J* = 1.35Hz, *J* = 6.45Hz, 1H), 7.72-7.63 (m, 4H), 7.45-7.42 (m, 1H), 7.16 (d,

$J=8.25\text{Hz}$, 1H), 7.04 (t, $J=7.5\text{Hz}$, 1H) ESI-MS (m/z): $[\text{M}+\text{H}]^+ = 309.3407$ (calculated); 309.6000 (observed).

Synthesis of L2: A mixture of 2-hydroxy4-methoxy benzaldehyde (365 mg, 2.40 mmol), Phenanthrene-9,10-dione (500 mg, 2.40 mmol), and ammonium acetate (2.4 gm, 31.13 mmol) in glacial acetic acid (15 mL) was heated at 100°C for 12 h with continuous stirring. The hot reaction mixture was cooled to room temperature, where upon a white solid was precipitated. This white solid was collected by filtration and washed with dilute aqueous NaHCO_3 solution followed by distilled water. This white residue was dried and purified by column chromatography on silica gel eluting with Hexane/ CHCl_3 (95:5, v/v). Yield = 450 mg, (1.32 mmol, 55.07%) (Scheme S1) (^1H NMR, CDCl_3 , 500 MHz, δppm): 11.67 (s, 1H), 8.72(t, $J= 8.15\text{Hz}$, 2H), 8.48 (d, $J= 7.7\text{Hz}$, 1H), 8.29 (d, $J= 7.7\text{Hz}$, 1H), 8.03 (d, $J= 8.7\text{Hz}$, 1H), 7.75-7.67 (m, 4H), 6.67-6.62 (m, 2H), 3.89 (s, 3H), $[\text{M}+2\text{H}]^+ = 342.3905$ (calculated); 342.1000 (observed).

Synthesis of L3: A mixture of 2-hydroxy 5-nitro benzaldehyde (401 mg, 2.40 mmol), Phenanthrene-9,10-dione (500 mg, 2.40 mmol), and ammonium acetate (2.4 gm, 31.13 mmol) in glacial acetic acid (15 mL) was heated at 100°C for 12 h with continuous stirring. The hot reaction mixture was cooled to room temperature, where upon a yellow solid was precipitated. This yellow solid was collected by filtration and washed with dilute aqueous NaHCO_3 solution followed by distilled water. This yellow residue was dried and purified by column chromatography on silica gel eluting with $\text{CH}_3\text{OH}/\text{CHCl}_3$ (7:93, v/v). Yield = 682 mg, (1.91 mmol, 80.04%) (Scheme S1). (^1H NMR, $\text{d}_6\text{-DMSO}$, 500 MHz, δppm): 14.17 (S, 1H), 9.09-9.08 (m, 1H), 8.79 (t, $J=7.65\text{Hz}$, $J=6.85\text{Hz}$, 2H), 8.39 (t, $J= 7.10\text{Hz}$, $J=6.85\text{Hz}$, 2H), 8.13-8.10 (m, 1H), 7.71 (q, $J=7.05\text{Hz}$, $J=7.3\text{Hz}$, 2H), 7.63 (q, $J=7.05\text{Hz}$, $J=7.15\text{Hz}$, 2H), 7.10 (t, $J=7.9\text{Hz}$, 1H) $[\text{M}-\text{H}]^+ = 354.3383$ (calculated); 354.0000 (observed).

Synthesis of (L1)₂Zn: (L1)₂Zn was prepared by a mixture of L1 (200 mg, 0.65 mmol) and zinc chloride (44.4 mg, 0.32 mmol) in dry methanol (30 mL) stirred at room temperature for 24 hours. On completion of reaction, the precipitate was separated as white-colored solid which was filtered, dried, and recrystallized from cold methanol. Yield: 198 mg (0.28 mmol, 89.2%) (Scheme S1). $[\text{M}+\text{H}]^+ = 687.0853$ (calculated); 687.6500 (observed).

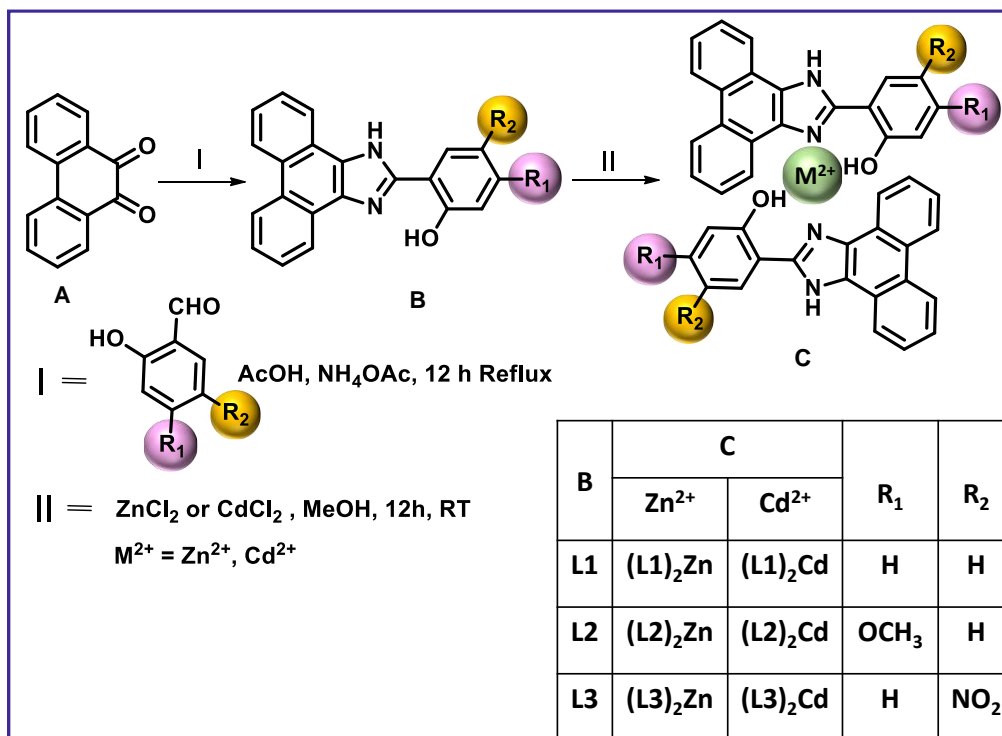
Synthesis of (L1)₂Cd: (L1)₂Cd was prepared by a mixture of L1 (200 mg, 0.65 mmol) and Cadmium chloride (59.57 mg, 0.32 mmol) in dry methanol (30 mL) stirred at room temperature for 24 hours. On completion of reaction, the precipitate was separated as white-colored solid which was filtered, dried, and recrystallized from cold methanol. Yield: 155 mg (0.21 mmol, 65.2%) (Scheme S1). [M]⁺ = 733.1083 (calculated); 732.5500 (observed).

Synthesis of (L2)₂Zn: (L2)₂Zn was prepared by a mixture of L2 (200 mg, 0.58 mmol) and zinc chloride (40.1 mg, 0.29 mmol) in dry methanol (30 mL) stirred at room temperature for 24 hours. On completion of reaction, the precipitate was separated as white-colored solid which was filtered, dried, and recrystallized from cold methanol. Yield: 142 mg (0.19 mmol, 65.6%) (Scheme S1). [M-2H]⁺ = 744.1293 (calculated); 744.1500 (observed).

Synthesis of (L2)₂Cd: (L2)₂Cd was prepared by a mixture of L2 (200 mg, 0.58 mmol) and Cadmium chloride (53.7 mg, 0.29 mmol) in dry methanol (30 mL) stirred at room temperature for 24 hours. On completion of reaction, the precipitate was separated as white-colored solid which was filtered, dried, and recrystallized from cold methanol. Yield: 173 mg (0.21 mmol, 74.4%) (Scheme S1). [M+H]⁺ = 794.1603 (calculated); 794.1000 (observed).

Synthesis of (L3)₂Zn: (L3)₂Zn was prepared by a mixture of L3 (200 mg, 0.56 mmol) and zinc chloride (38.4 mg, 0.28 mmol) in dry methanol (30 mL) stirred at room temperature for 24 hours. On completion of reaction, the precipitate was separated as yellow-colored solid which was filtered, dried, and recrystallized from cold methanol. Yield: 186 mg (0.24 mmol, 85.16%) (Scheme S1). [M]⁺ = 776.0883 (calculated); 776.5500 (observed).

Synthesis of (L3)₂Cd: (L3)₂Cd was prepared by a mixture of L3 (200 mg, 0.56 mmol) and Cadmium chloride (51.3 mg, 0.28 mmol) in dry methanol (30 mL) stirred at room temperature for 24 hours. On completion of reaction, the precipitate was separated as red-colored solid which was filtered, dried, and recrystallized from cold methanol. Yield: 201 mg (0.24 mmol, 87.2%) (Scheme S1). [M+H]⁺ = 824.1114 (calculated); 824.3000 (observed).



Scheme 1. Methodology adopted for the synthesis of **L1**, **L2**, **L3** and their corresponding metal complexes **(L1)₂Zn**, **(L1)₂Cd**, **(L2)₂Zn**, **(L2)₂Cd**, **(L3)₂Zn**, and **(L3)₂Cd**.

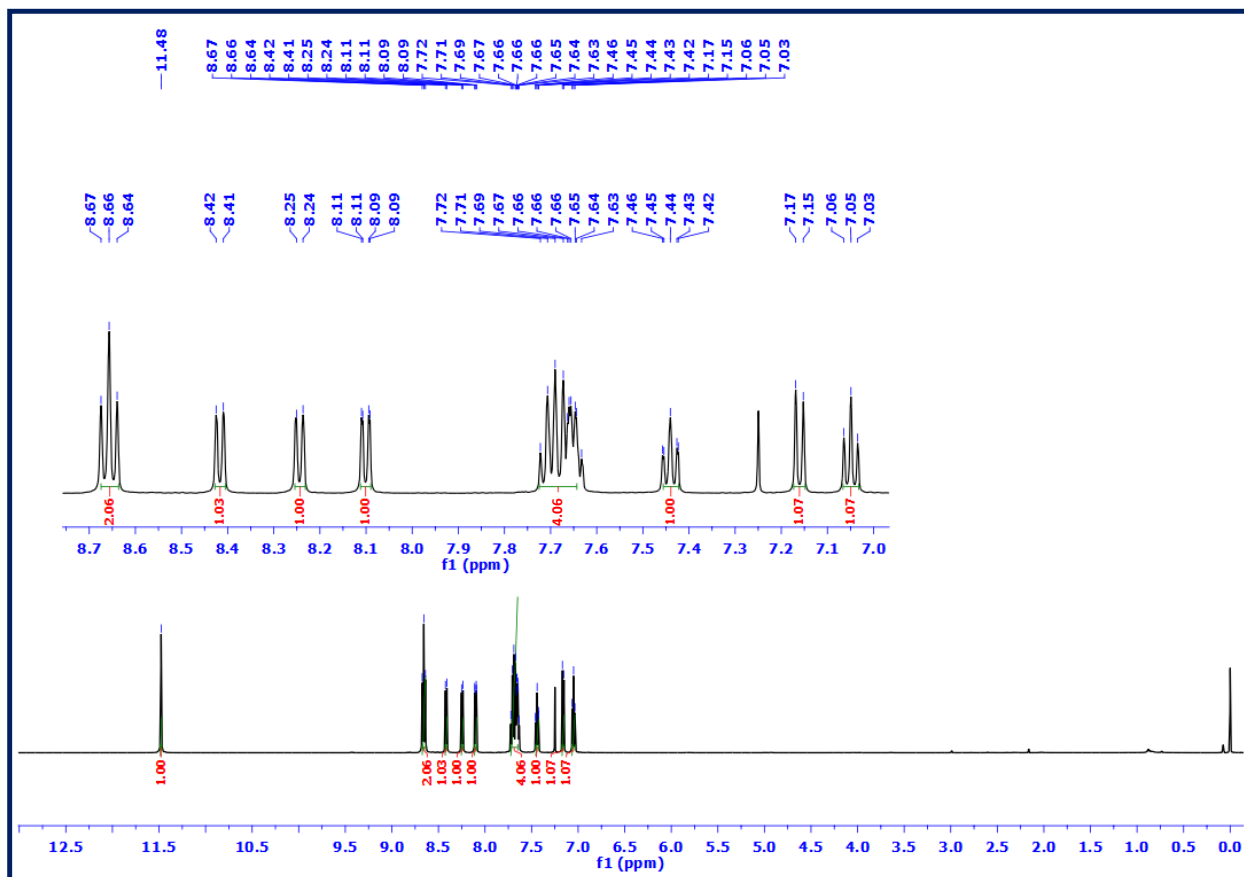


Figure S1. ¹H-NMR spectra of L1 in CDCl₃.

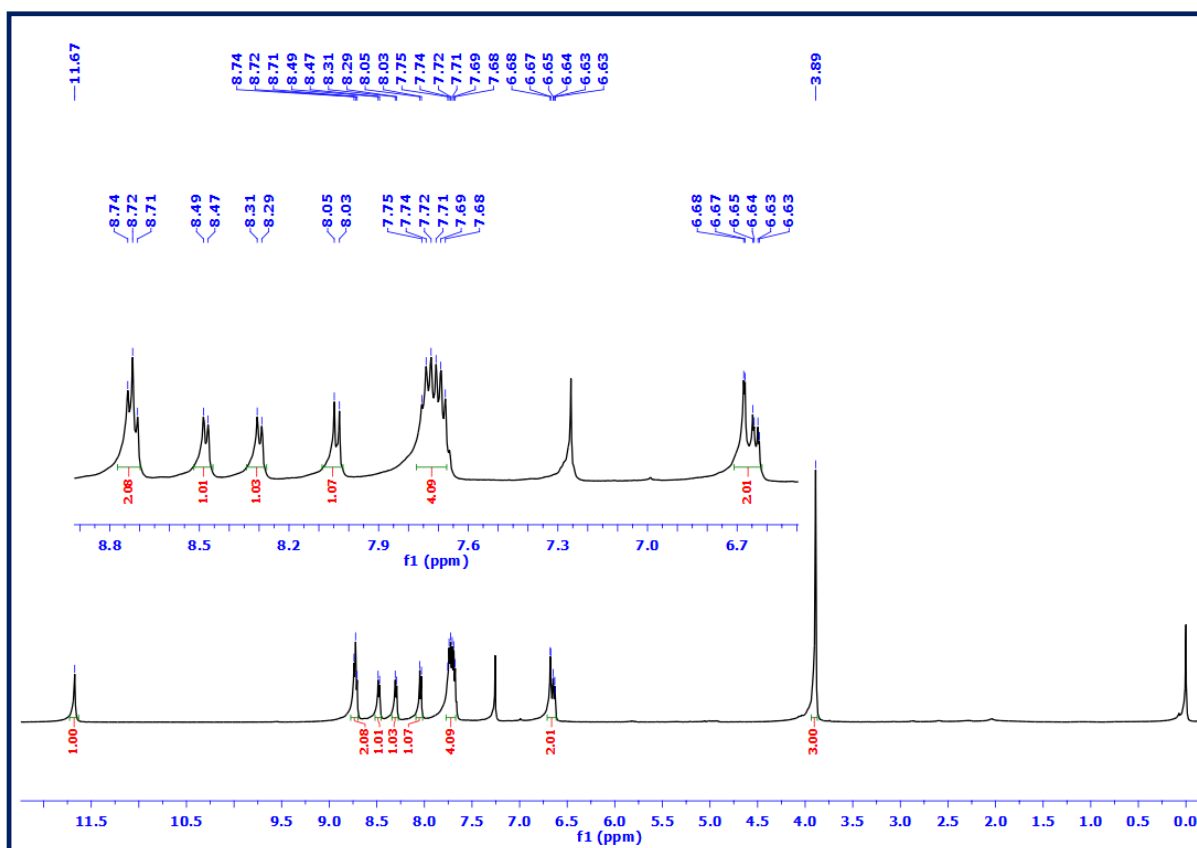


Figure S2. ¹H-NMR spectra of L2 in CDCl₃.

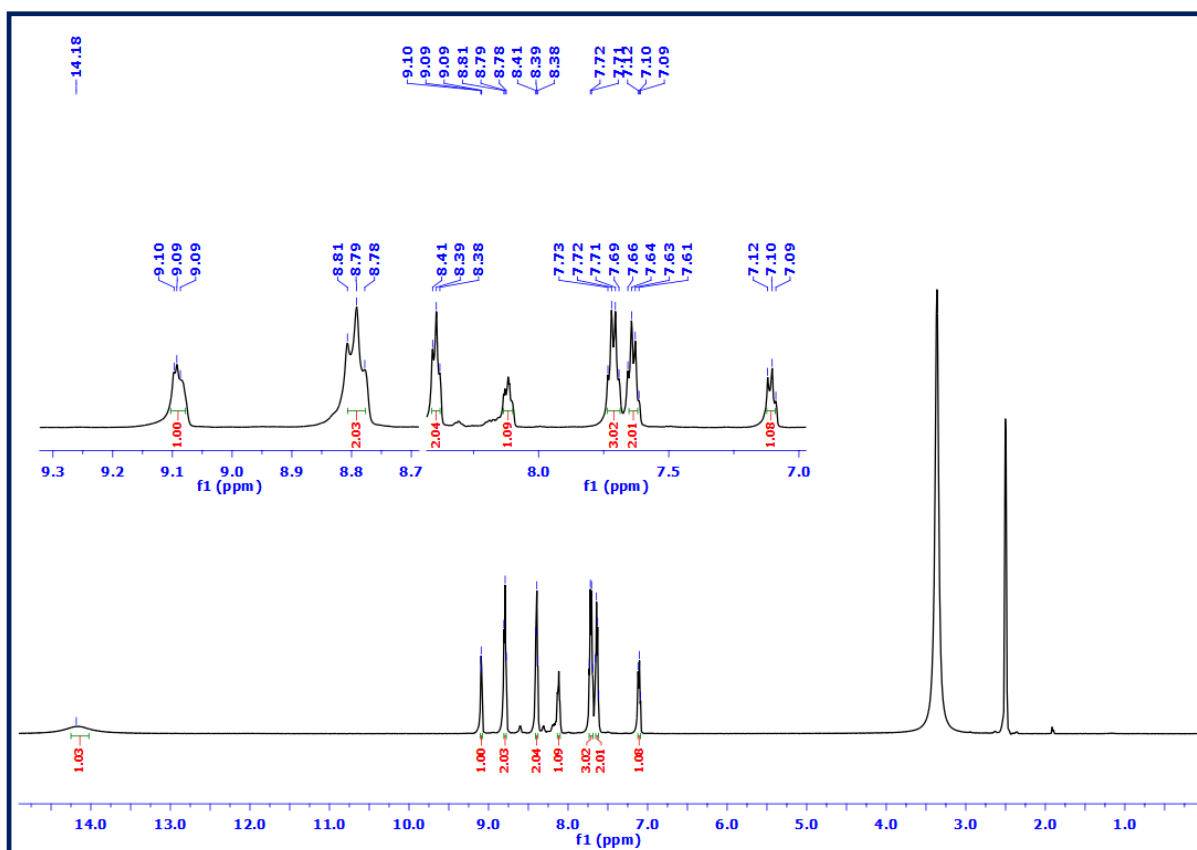


Figure S3. ¹H-NMR spectra of L3 in d₆-DMSO.

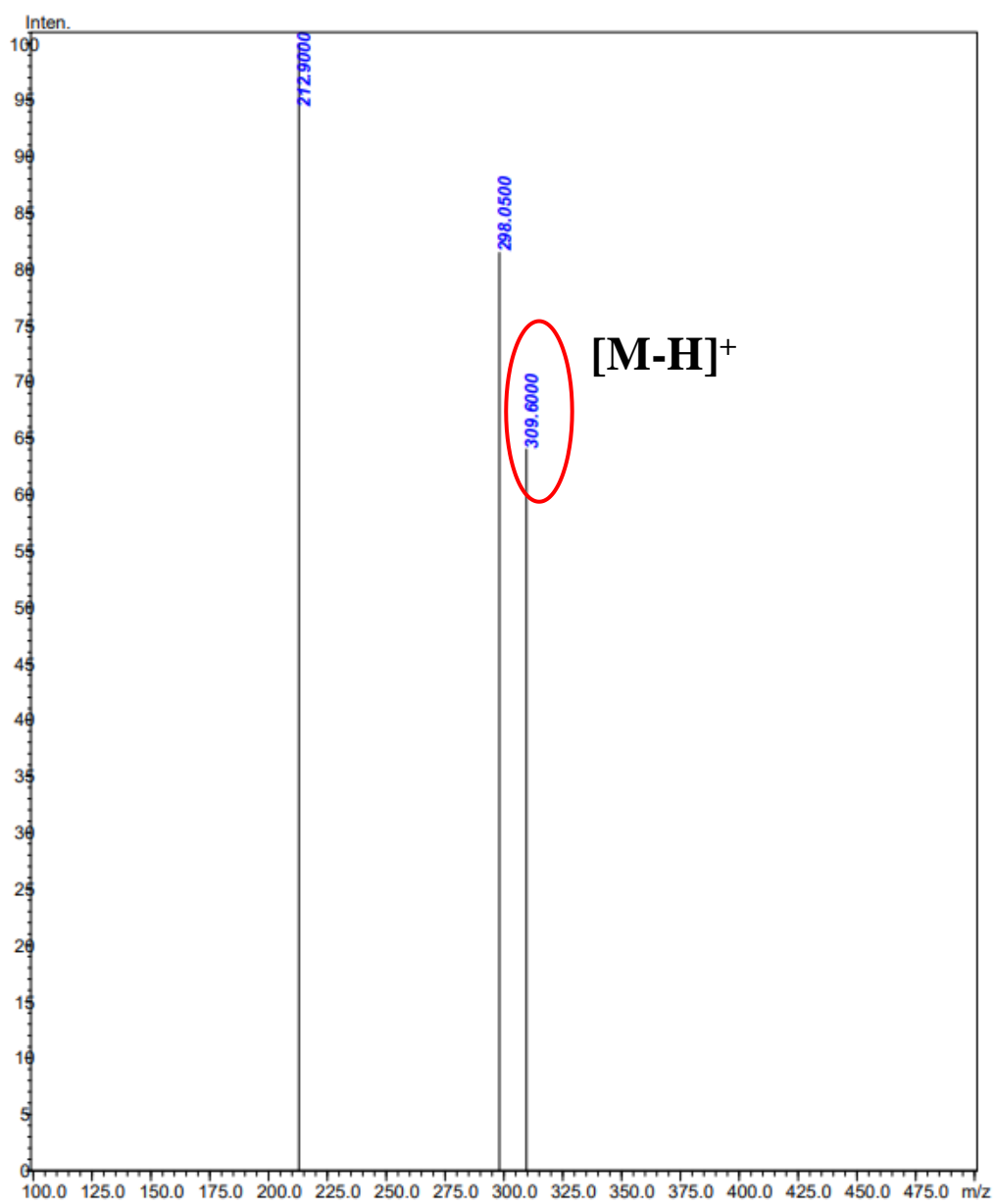


Figure S4. ESI Mass spectra of **L1**.

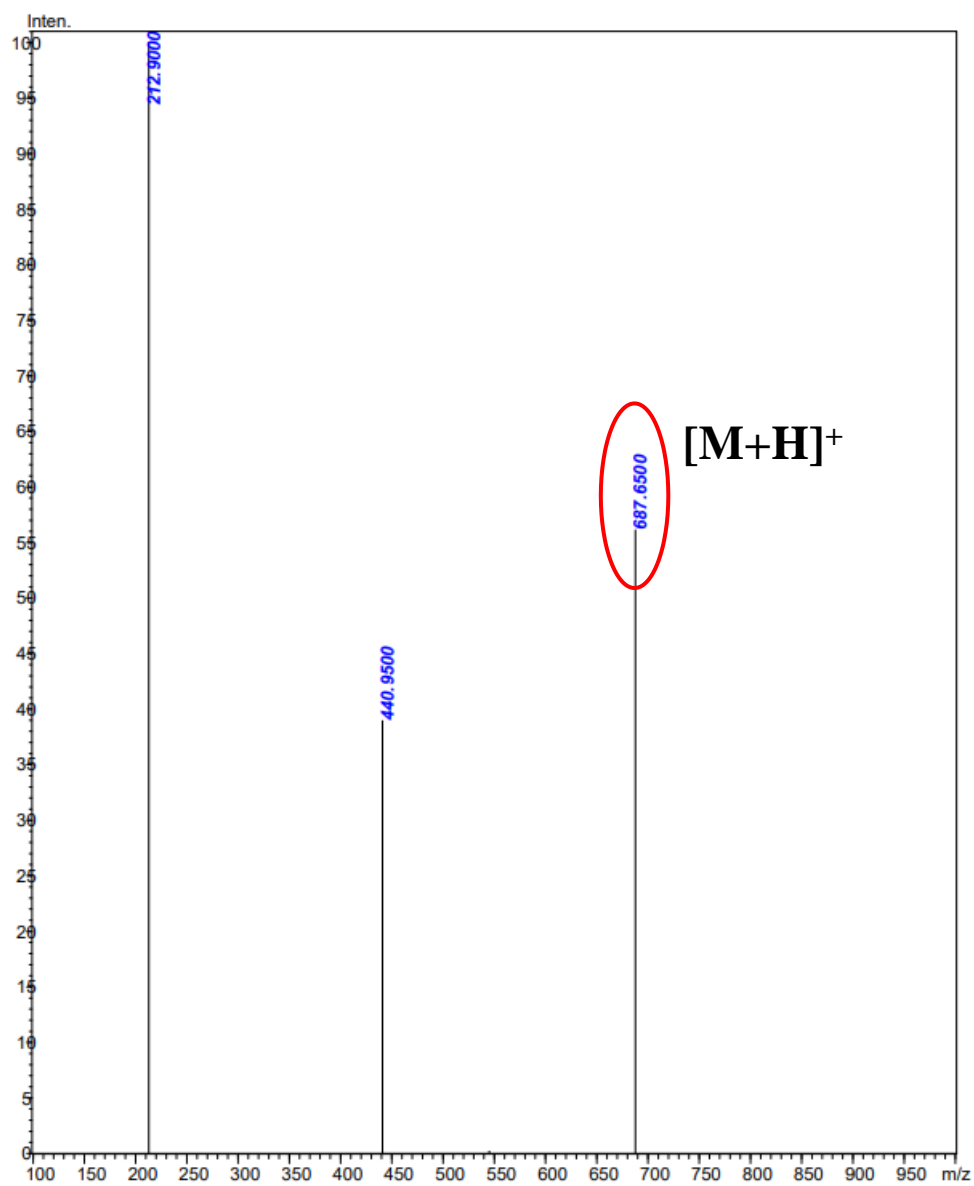


Figure S5. ESI Mass spectra of (L1)₂Zn.

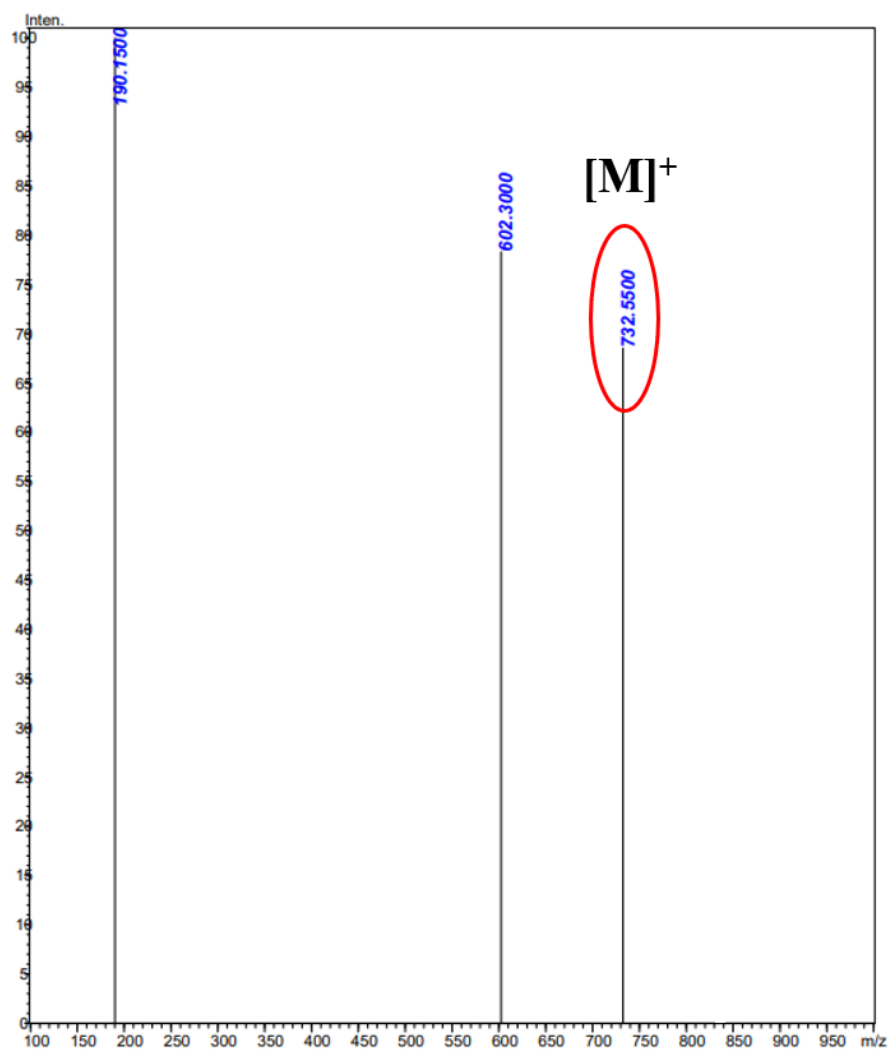


Figure S6. ESI Mass spectra of $(L1)_2Cd$

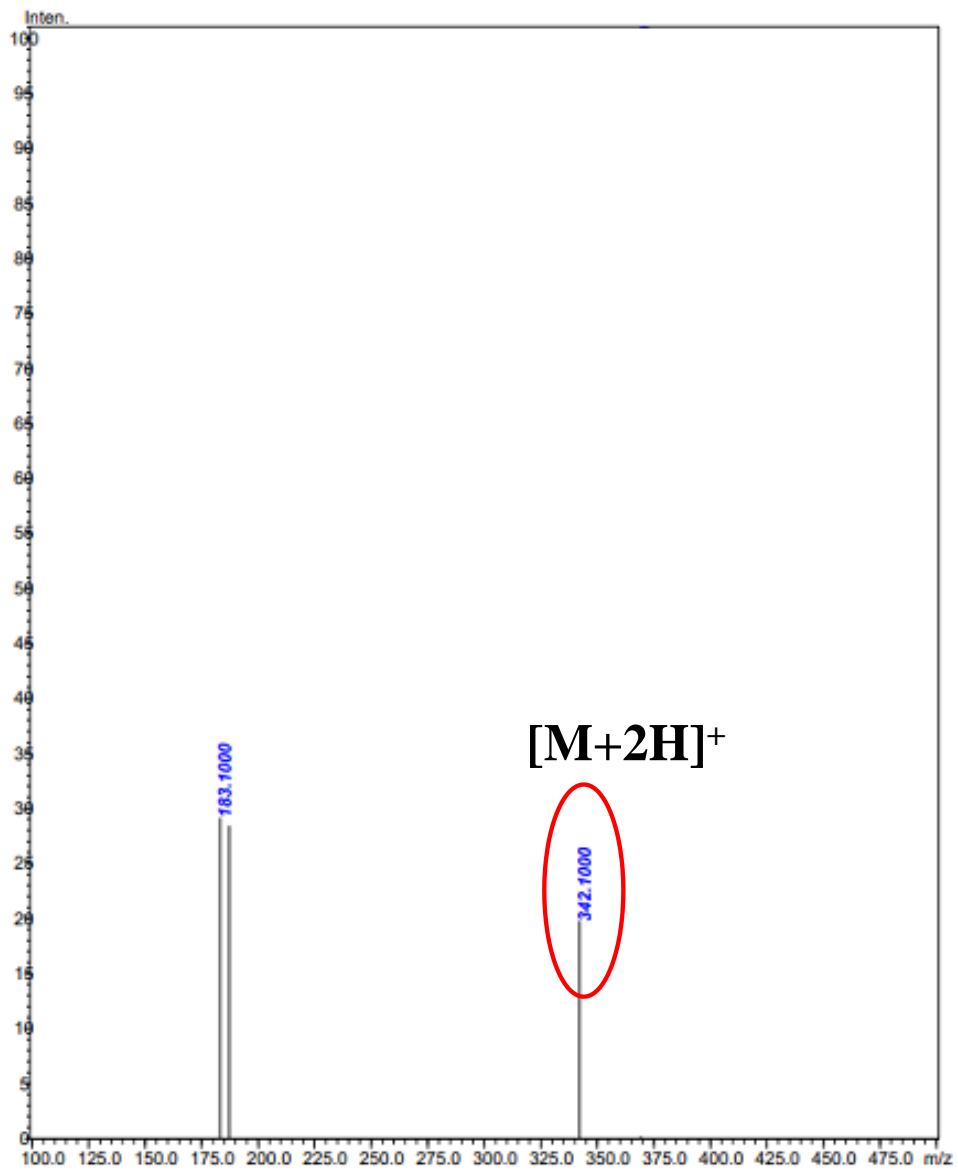


Figure S7. ESI Mass spectra of **L2**

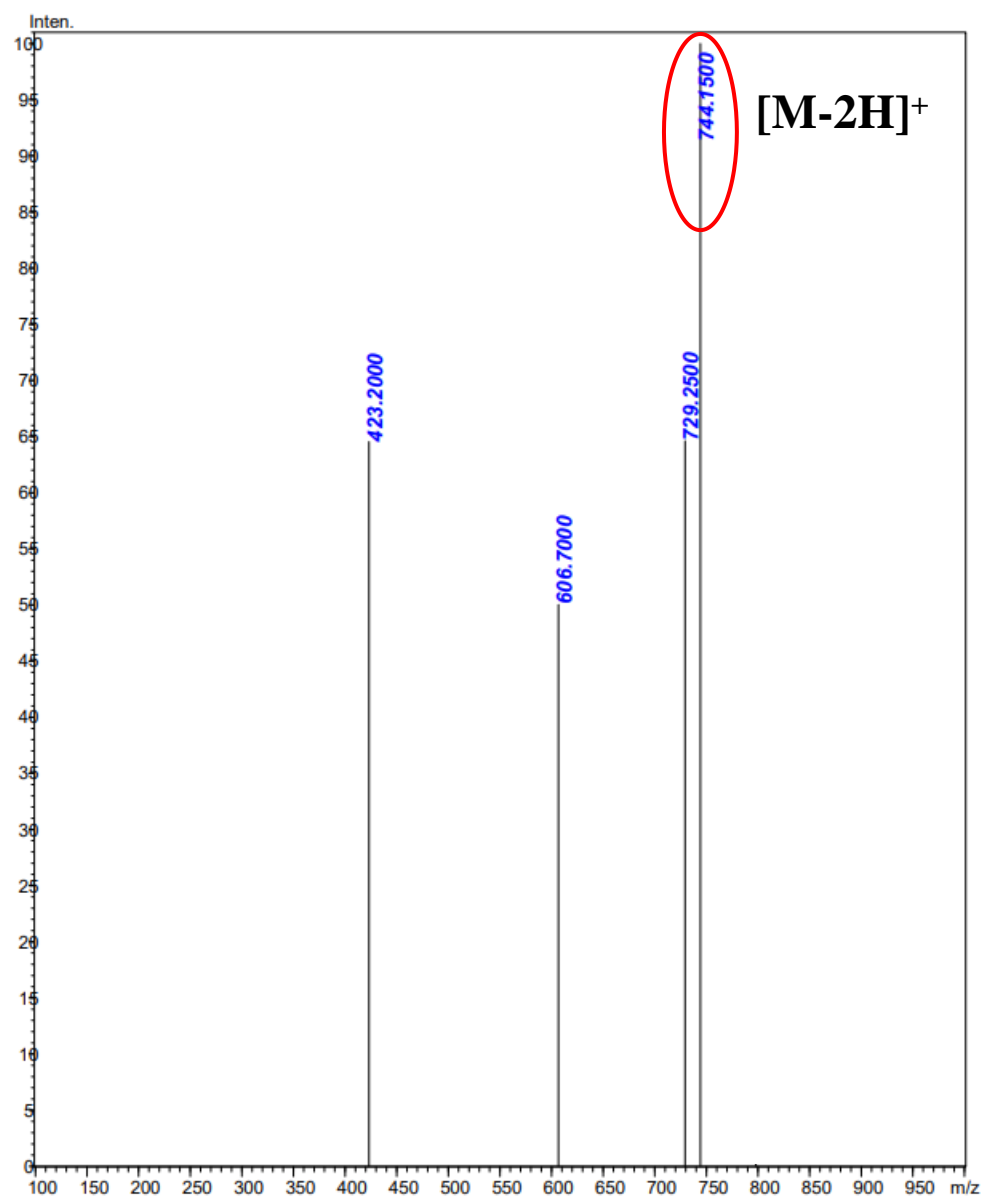


Figure S8. ESI Mass spectra of $(L2)_2Zn$

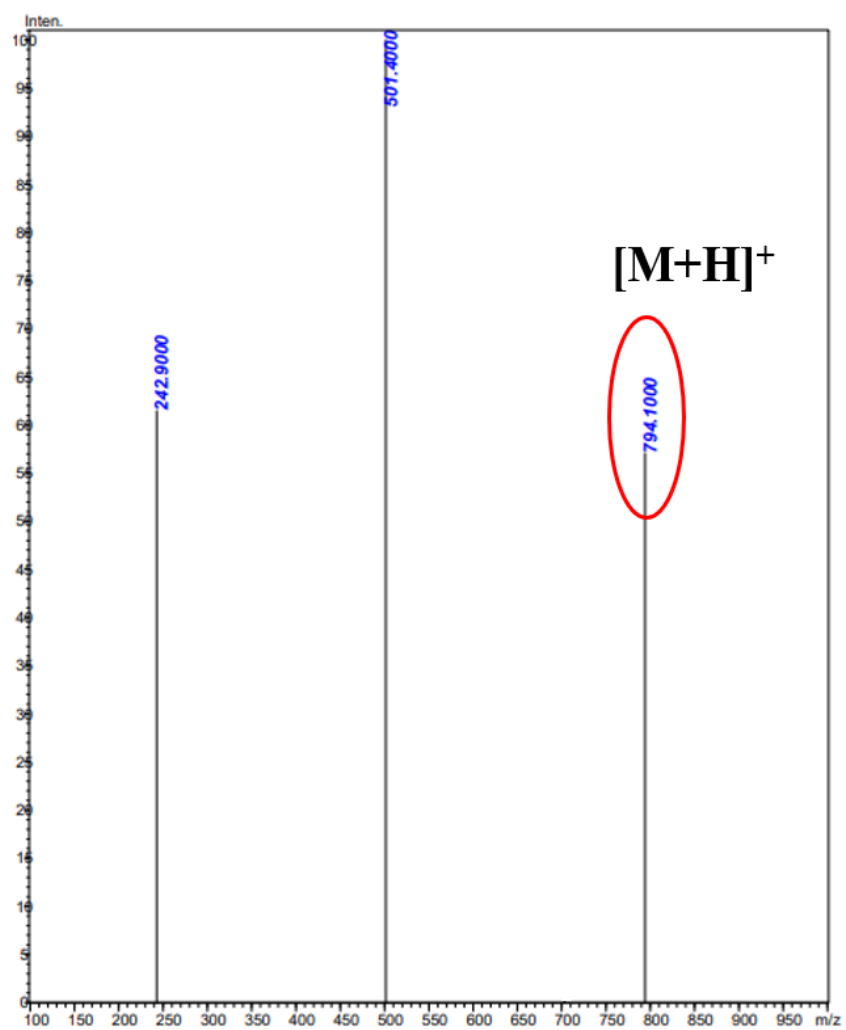


Figure S9. ESI Mass spectra of $(L2)_2Cd$

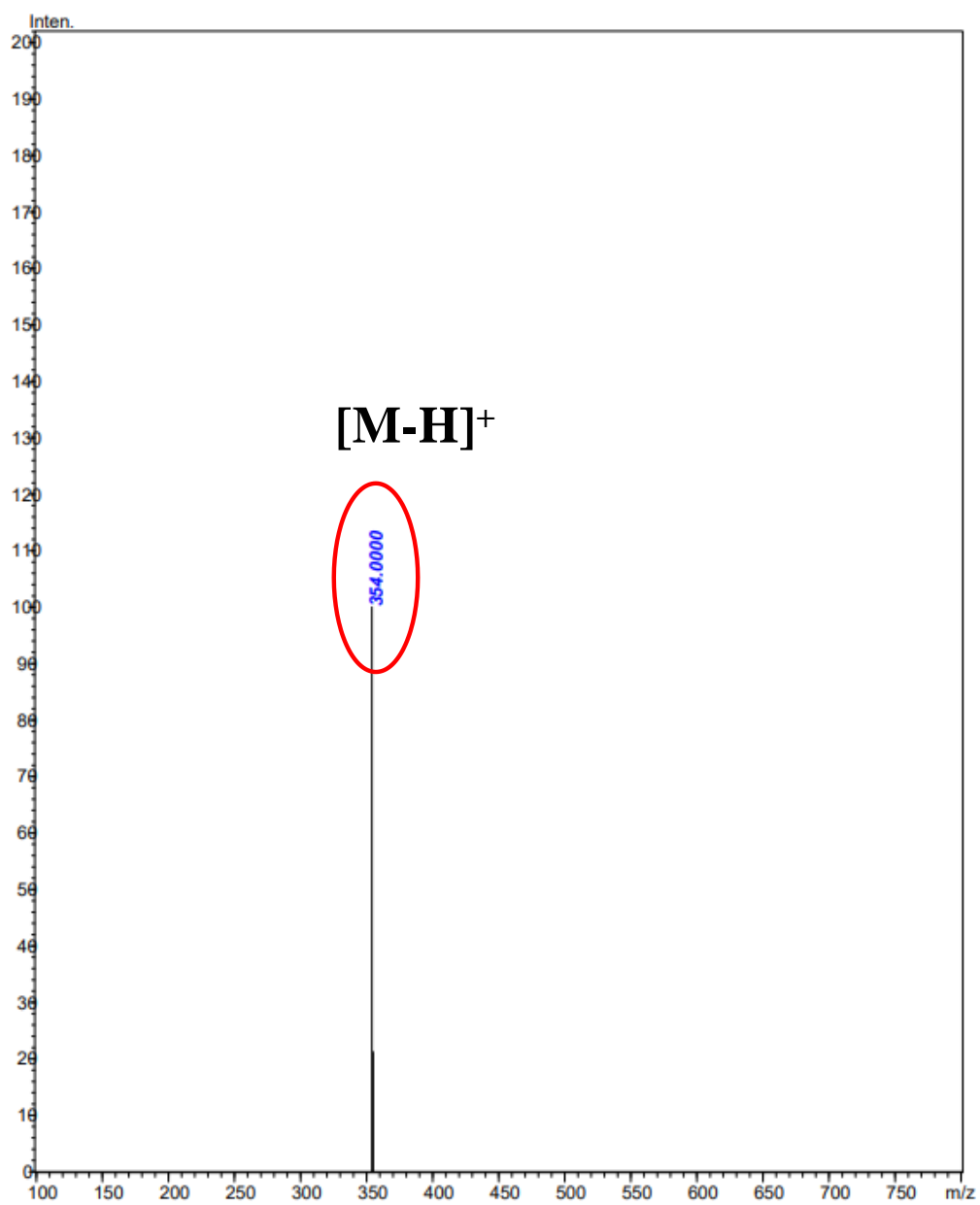


Figure S10. ESI Mass spectra of **L3**

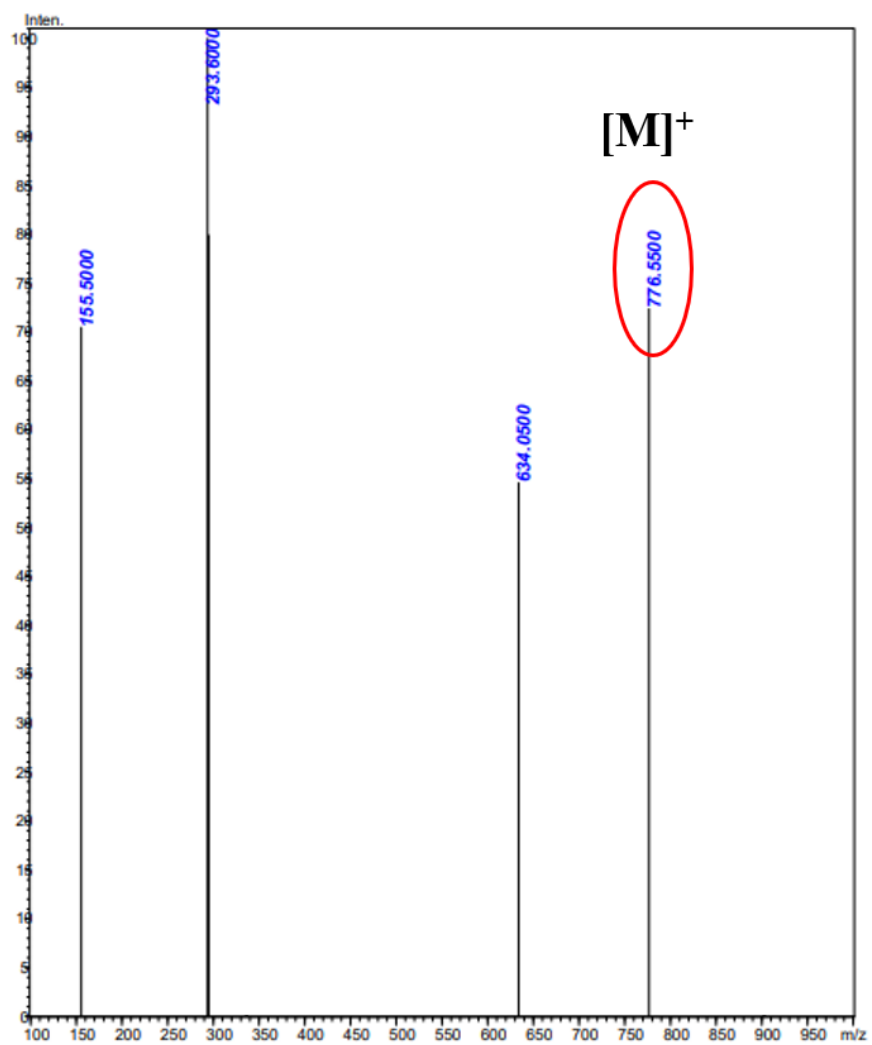


Figure S11. ESI Mass spectra of $(L3)_2Zn$

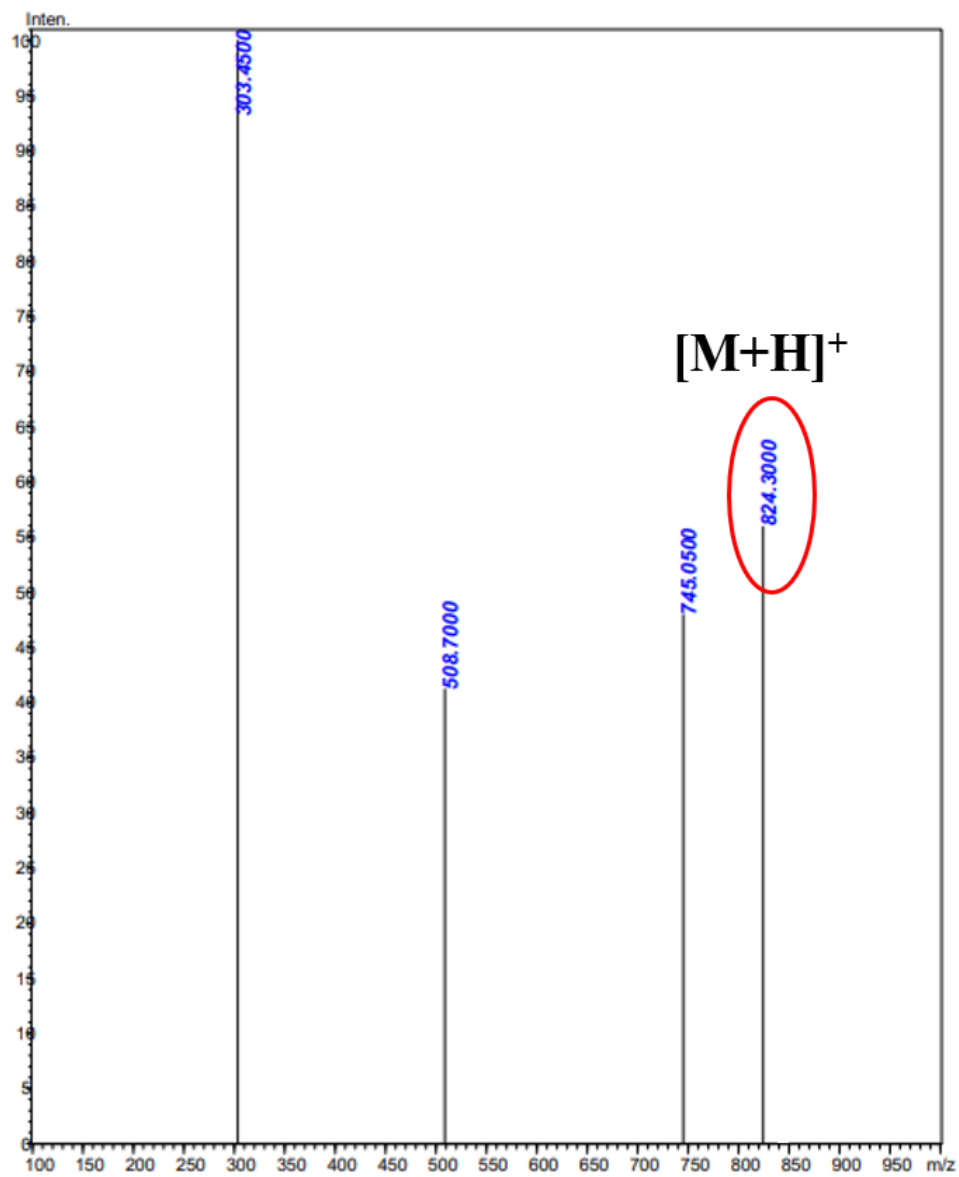


Figure S12. ESI Mass spectra of (L3)₂Cd

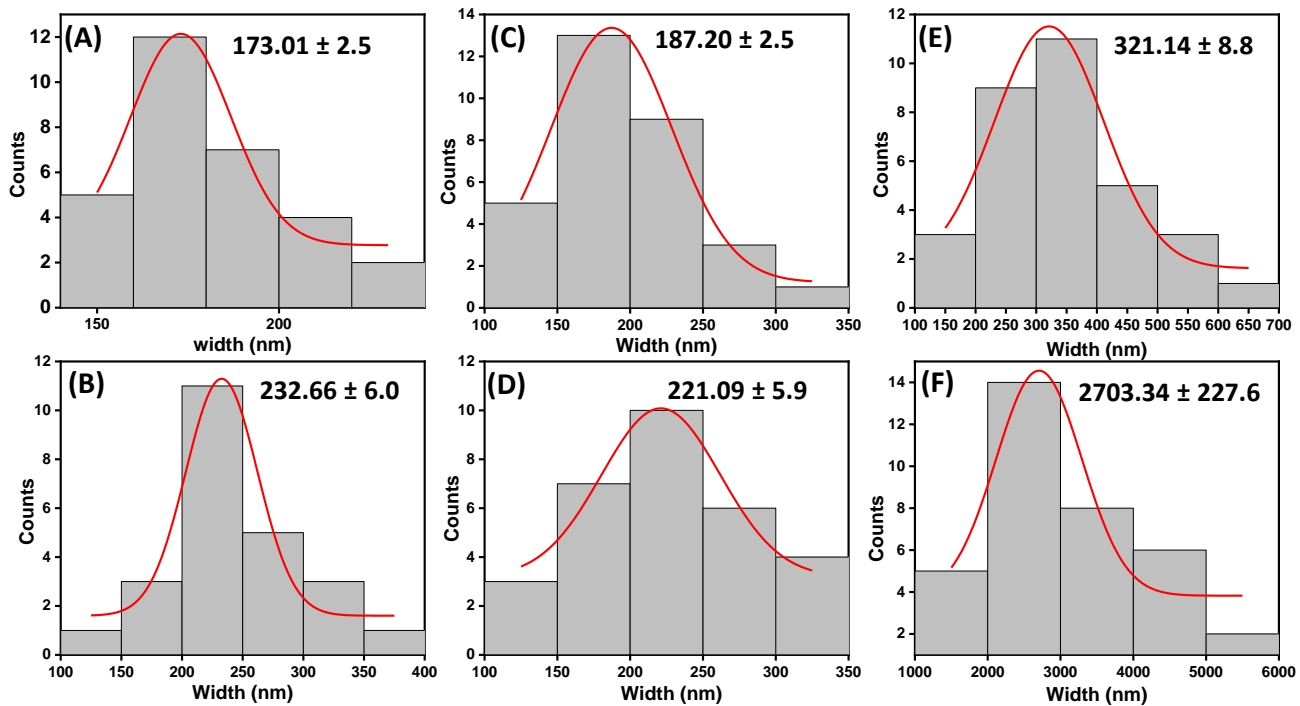


Figure S13. Width distribution of (A) $(L1)_2Zn$, (B) $(L1)_2Cd$, (C) $(L2)_2Zn$, (D) $(L2)_2Cd$, (E) $(L3)_2Zn$, and (F) $(L3)_2Cd$ obtained from HR-SEM images

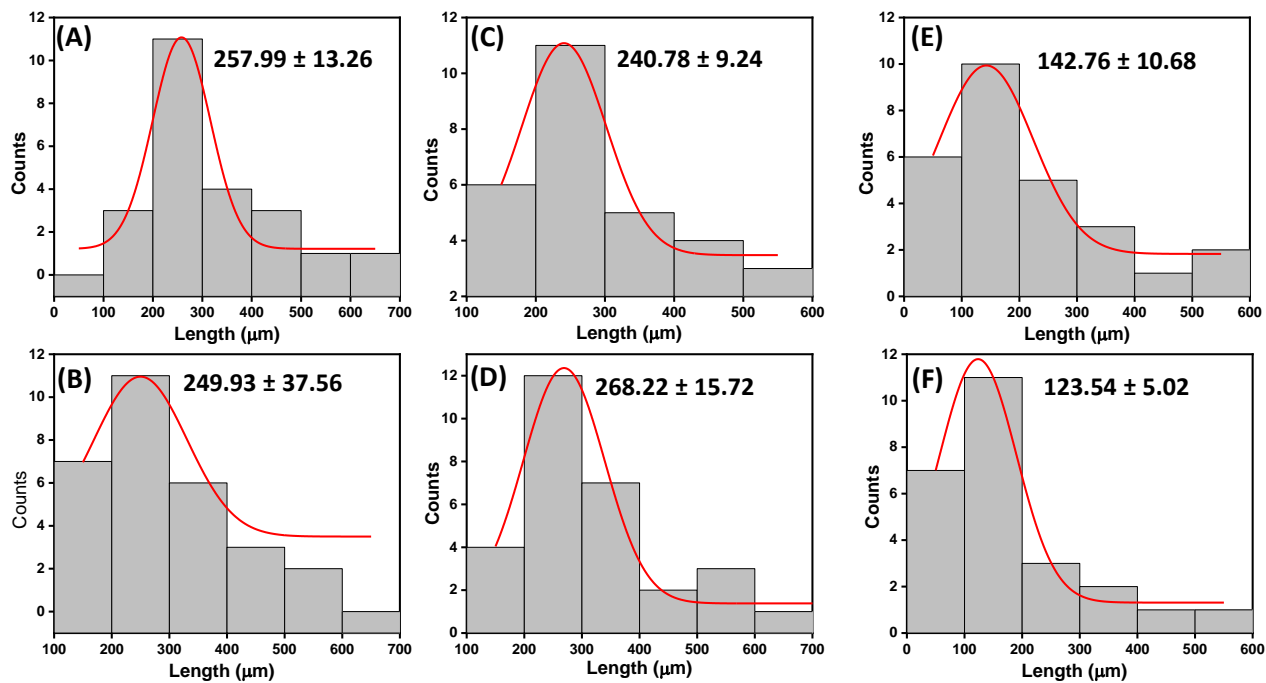


Figure S14. Length distribution of (A) (L1)₂Zn, (B) (L1)₂Cd, (C) (L2)₂Zn, (D) (L2)₂Cd, (E) (L3)₂Zn, and (F) (L3)₂Cd obtained from HR-SEM images

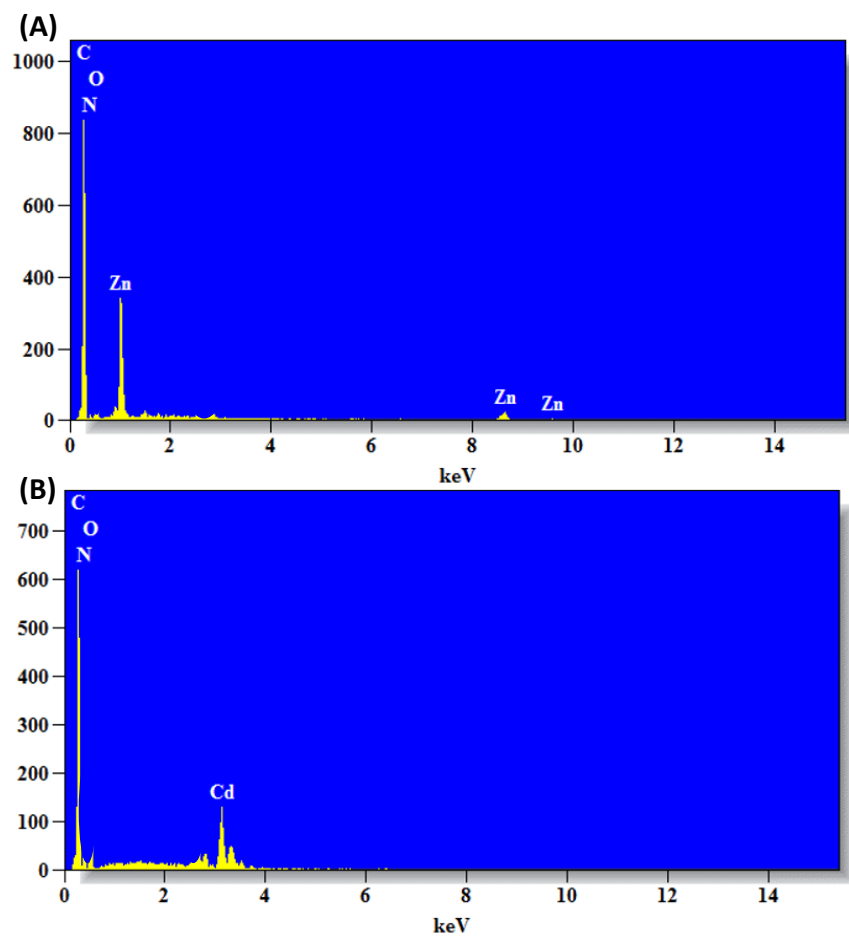


Figure S15. EDX analysis of (A) $(L1)_2Zn$, and (B) $(L1)_2Cd$.

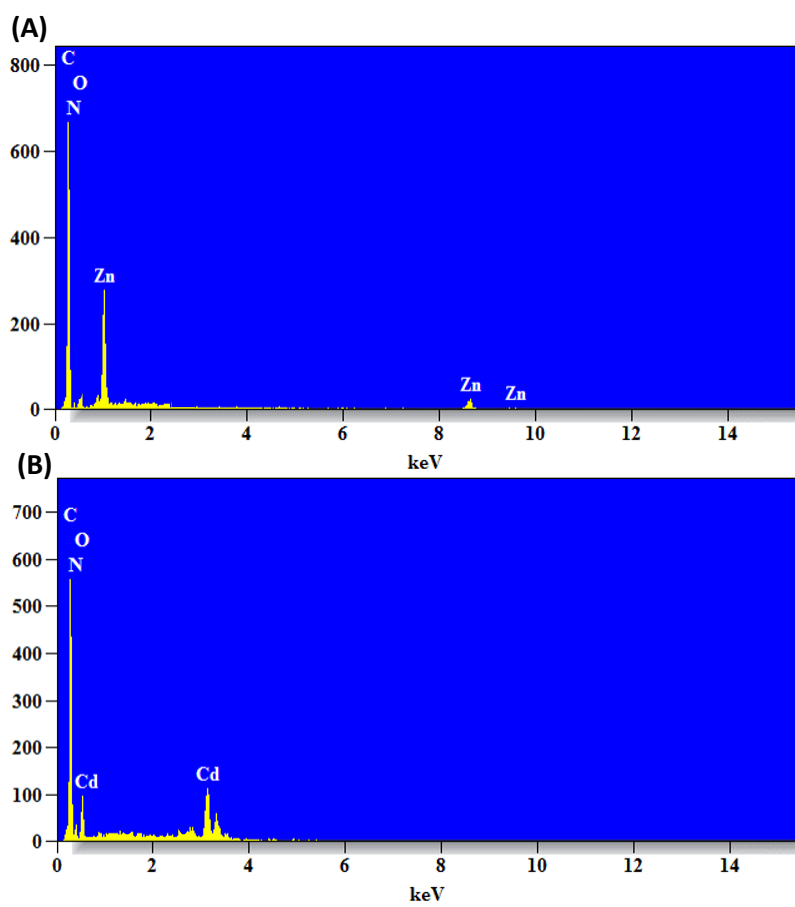


Figure S16. EDX analysis of (A) $(L2)_2Zn$, and (B) $(L2)_2Cd$.

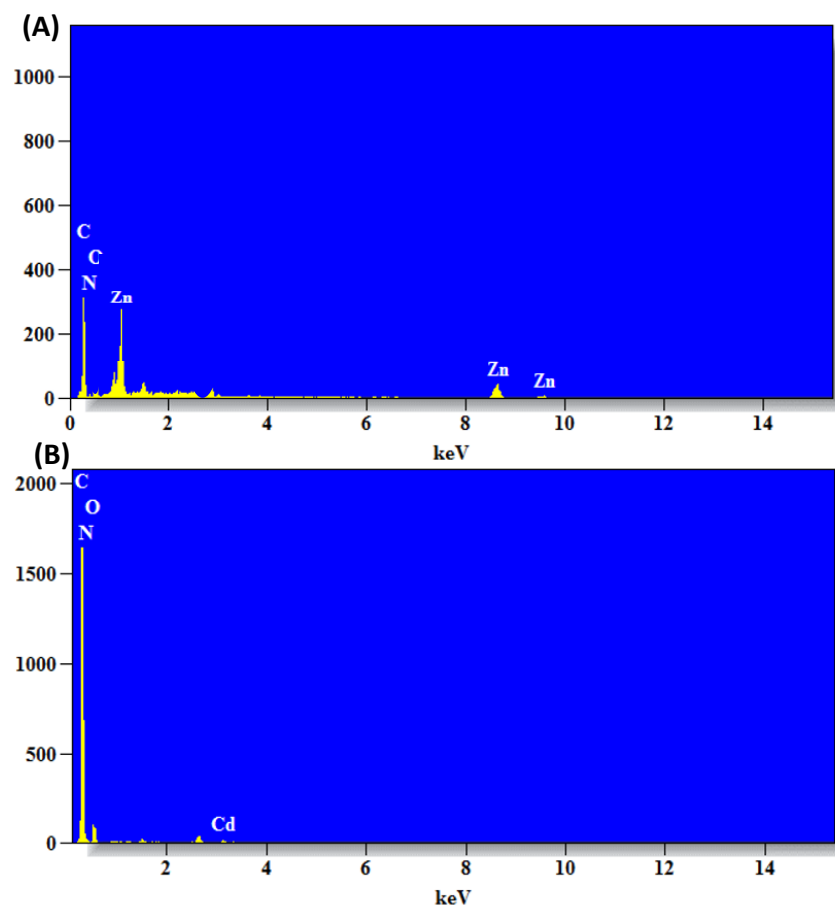


Figure S17. EDX analysis of (A) $(L3)_2Zn$, and (B) $(L3)_2Cd$.

Table S1: Crystallinity (%) data of **(L1)₂Zn**, **(L1)₂Cd**, **(L2)₂Zn**, **(L2)₂Cd**, **(L3)₂Zn**, and **(L3)₂Cd**.

Metal complexes	Crystallinity (%)
(L1)₂Zn	65.29
(L1)₂Cd	51.20
(L2)₂Zn	54.76
(L2)₂Cd	44.18
(L3)₂Zn	59.36
(L3)₂Cd	18.90

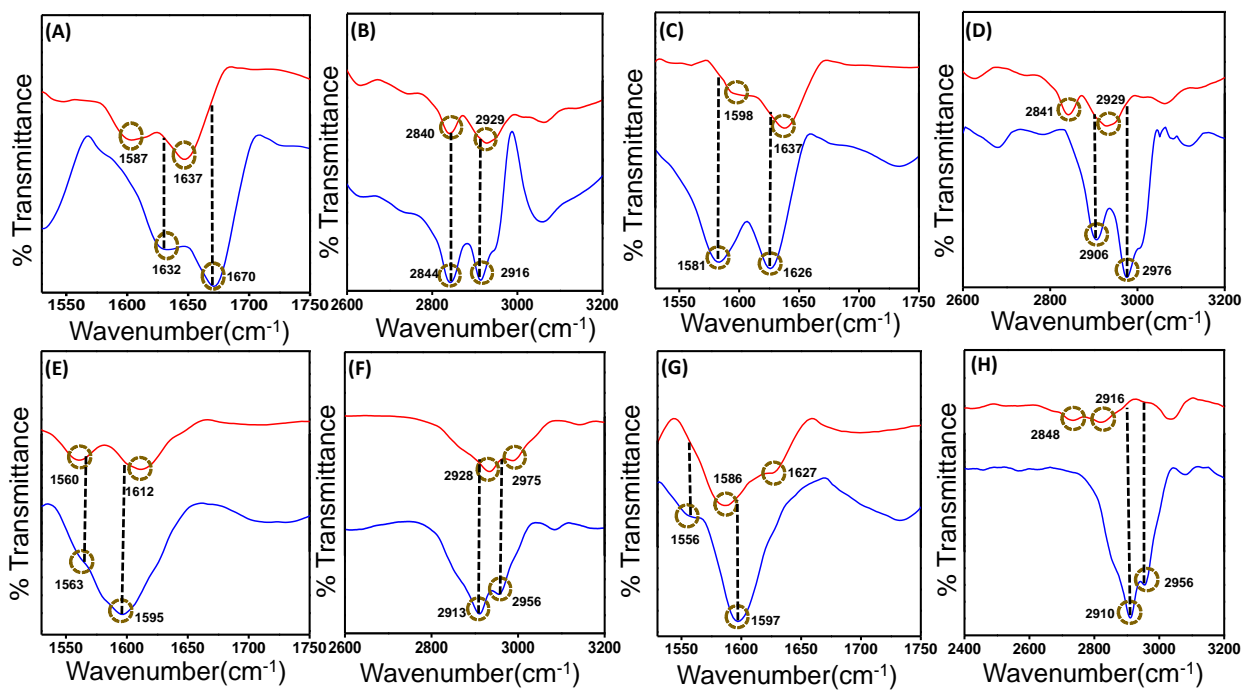


Figure S18. Concentration dependent FT-IR spectra of (A) & (B) $(L_2)_2Zn$, (C) & (D) $(L_2)_2Cd$, (E) & (F) $(L_3)_2Zn$, and (G) & (H) $(L_3)_2Cd$ as concentration varies (red-0.5mg/mL), (blue-2.5mg/mL)

Table S2: Concentration dependent changes in the FT-IR spectral value for ν (C=C str, aromatic), ν (C=N str, aromatic), ν (C-H str, aromatic) and ν (N-H str, imidazole) obtained from dried mass of **(L1)₂M**, **(L2)₂M**, **(L3)₂M** (M=Zn(II) and Cd(II)).

	(L1)₂Zn		(L1)₂Cd		(L2)₂Zn		(L2)₂Cd		(L3)₂Zn		(L3)₂Cd	
	0.5	2.5	0.5	2.5	0.5	2.5	0.5	2.5	0.5	2.5	0.5	2.5
Concentration (mg mL⁻¹)												
ν (C=C, aromatic) cm ⁻¹	1591	1587	1582	1587	1587	1632	1598	1581	1560	1563	1586	1556
ν (C=N, aromatic) cm ⁻¹	1625	1614	1622	1618	1637	1670	1637	1626	1612	1595	1627	1597
ν (C-H, aromatic) cm ⁻¹	2888	2855	2875	2857	2840	2844	2841	2906	2928	2913	2848	2910
ν (N-H, imidazole)cm ⁻¹	2949	2914	2928	2913	2929	2916	2929	2976	2975	2956	2916	2956

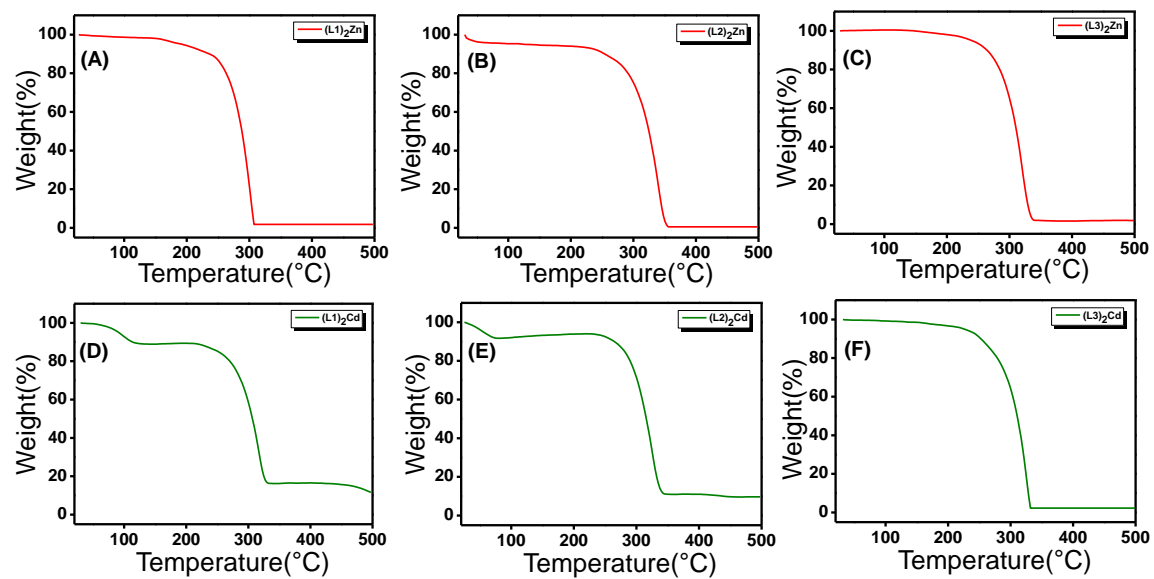


Figure S19. TGA spectra of (A) (L1)₂Zn, (B) (L2)₂Zn, (C) (L3)₂Zn, (D) (L1)₂Cd, (E) (L2)₂Cd, and (F) (L3)₂Cd.

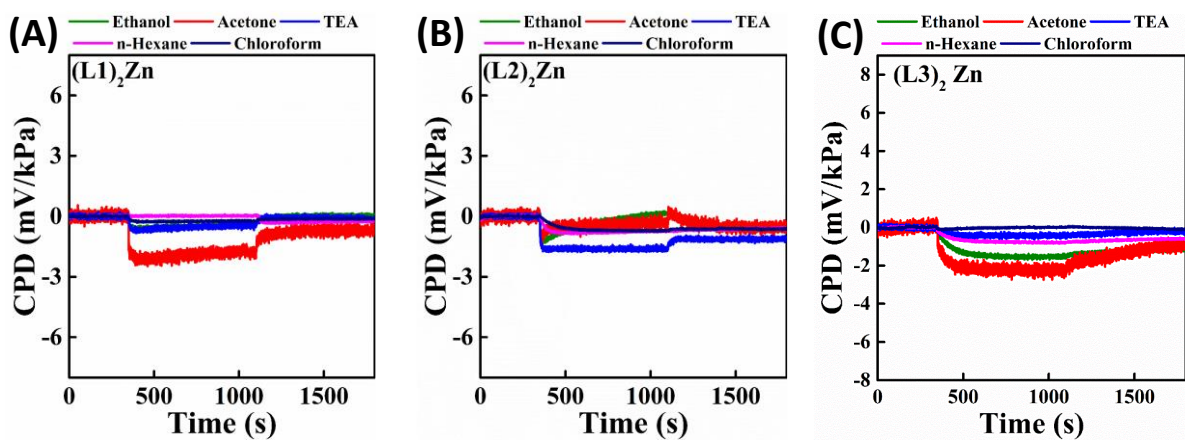


Figure S20. The single point CPD changes in dark and UV light conditions under VOC atmosphere for (A) $(L1)_2Zn$, (B) $(L2)_2Zn$ and (C) $(L3)_2Zn$.

Table S3: The changes in CPD values of metal complexes from dark to UV light

Sample	$(L1)_2Zn$	$(L1)_2Cd$	$(L2)_2Zn$	$(L2)_2Cd$	$(L3)_2Zn$	$(L3)_2Cd$
$ \Delta CPD $ (mV)	39	144.5	211	208.9	152	259.8

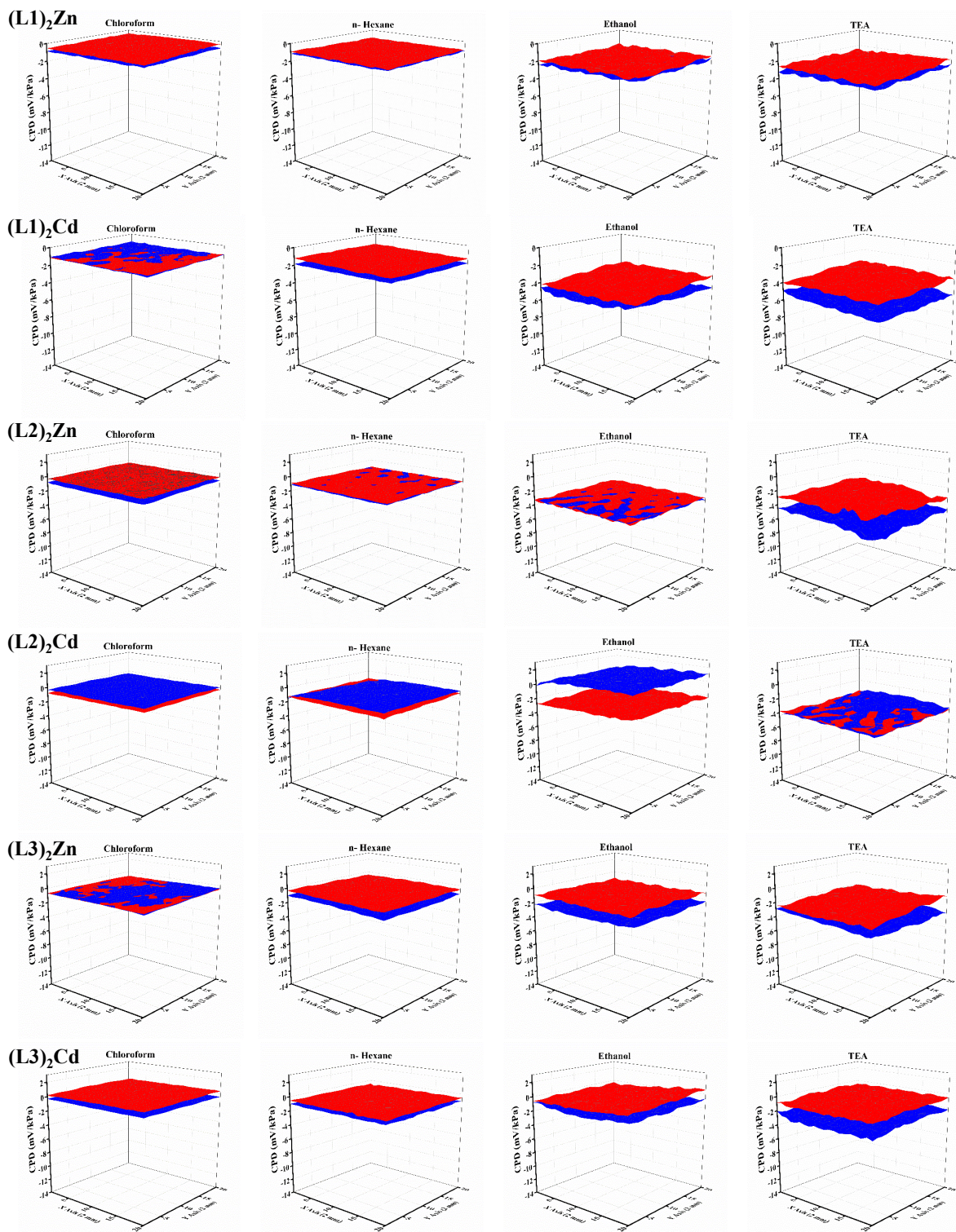


Figure S21. 3D raster scan images under dark (red) and UV light (blue) conditions in VOCs medium for the Zn(II) and Cd(II) complexes of L1, L2, and L3 ligands.