Supporting information

Copper (II), Zinc (II) and Cadmium (II) Formylbenzoate Complexes: Reactivity and Emission Properties

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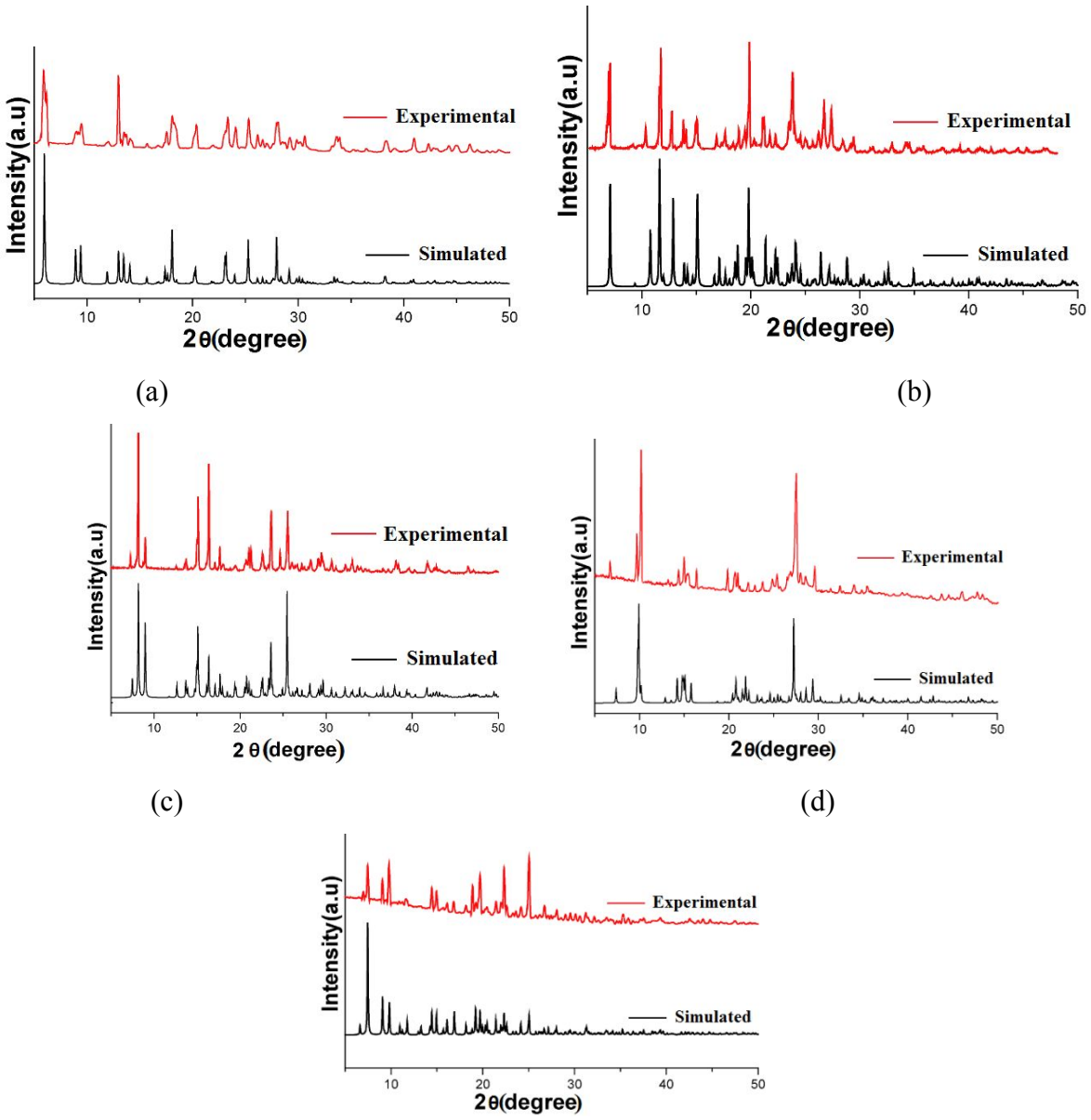


Figure S1: PXRD of (a) Complex **1**; (b) Complex **2;** (c) Complex **3**; (d) Complex **4**; (e) Complex **5**

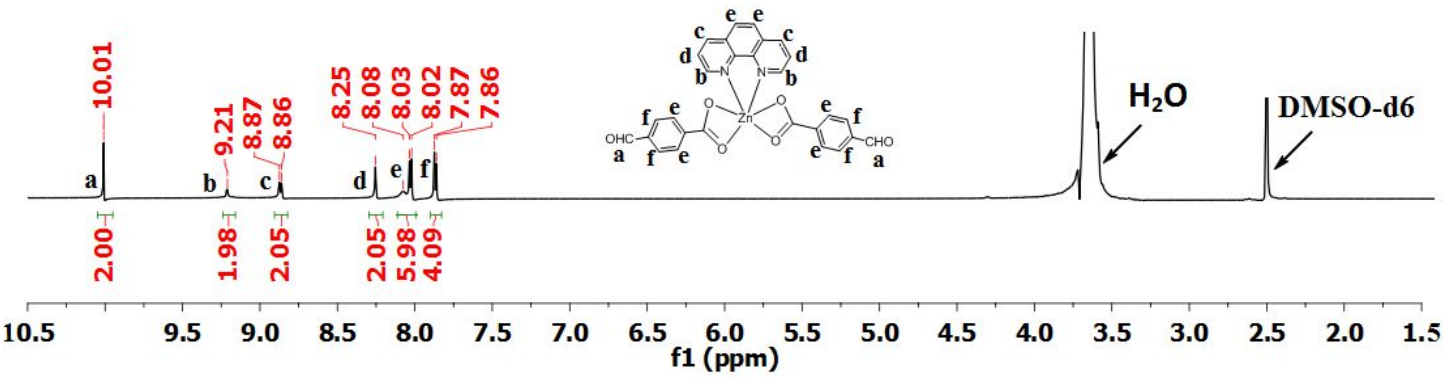


Figure S2: ^{1}H-NMR (DMSO-d^{6}) spectra of Complex **2** (the assignments of protons are as per numbers a-f in the structure).

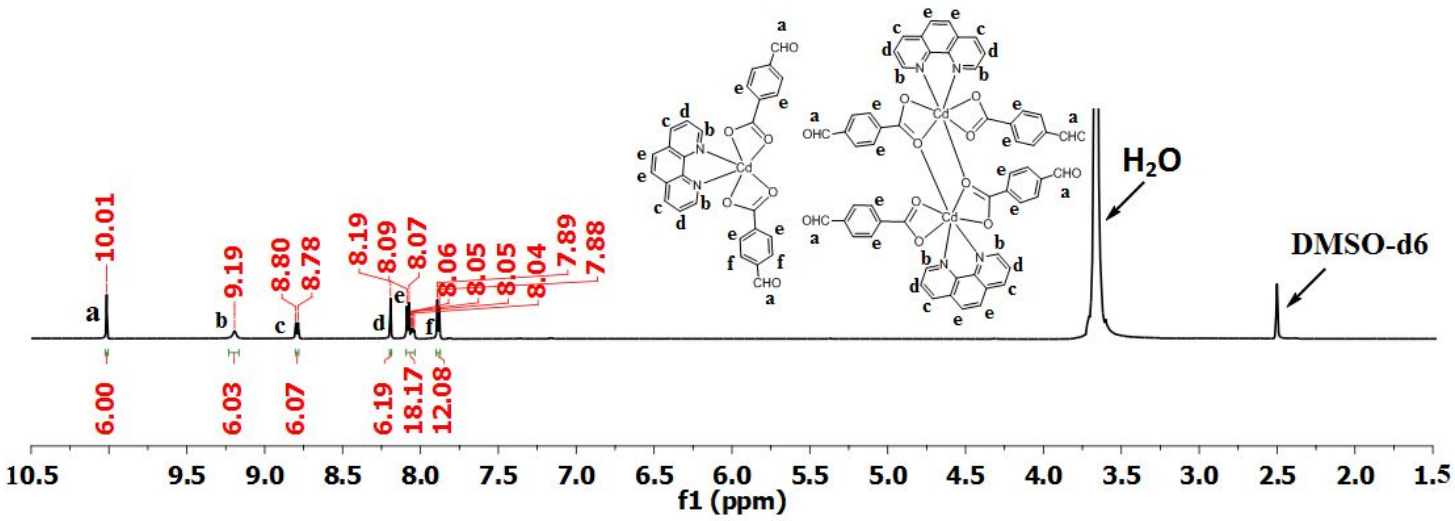
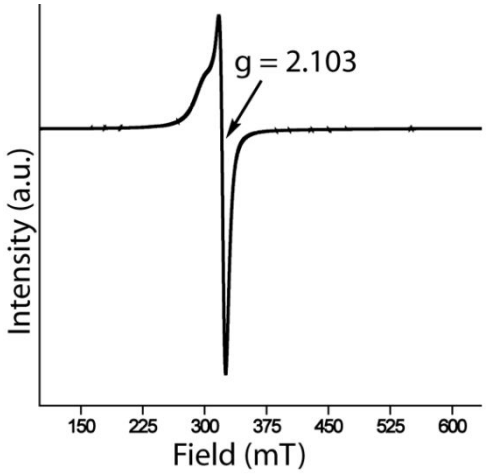
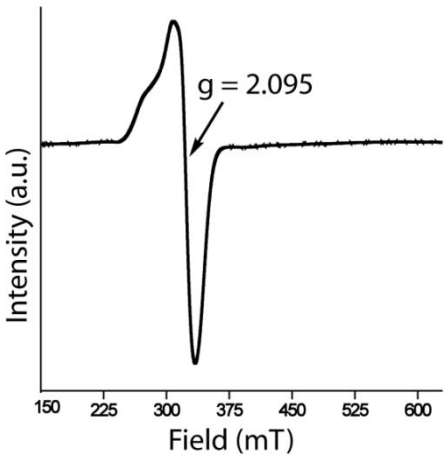


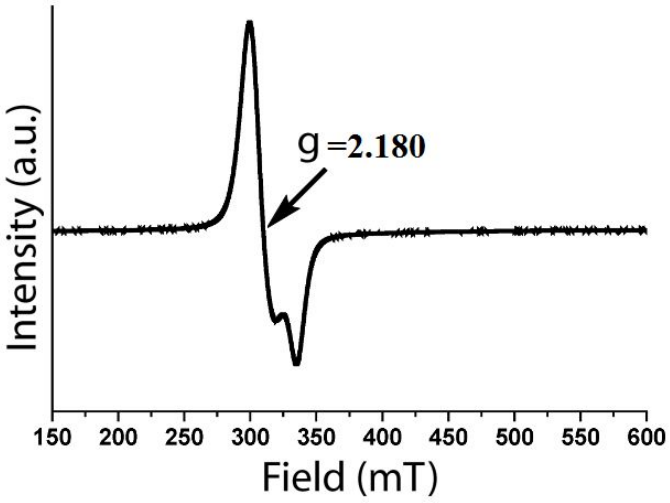
Figure S3: ^{1}H-NMR (DMSO-d^{6}) spectra of Complex **5** (the assignments of protons are as per numbers a-f in structure).



(a)



(b)



(c)

Figure S4: ESR spectra of (a) Complex **1**, (b) Complex **3**, (c) Complex **4**.

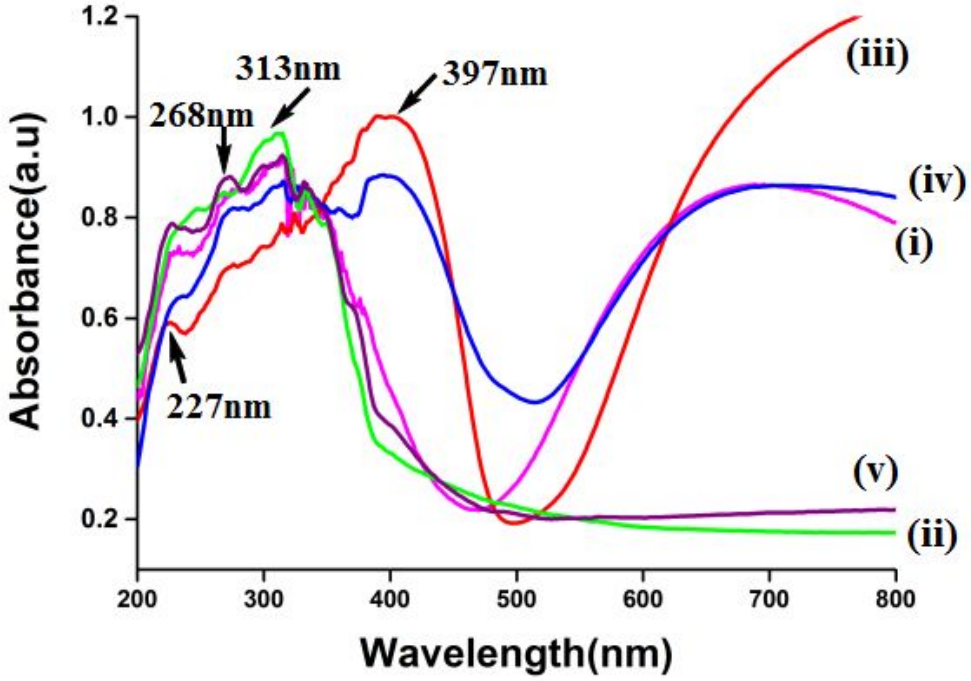


Figure S5: Solid state UV-Visible spectra of complexes (i) complex **1** (ii) complex **2** (iii) complex **3** (iv) complex **4** and (v) complex **5**

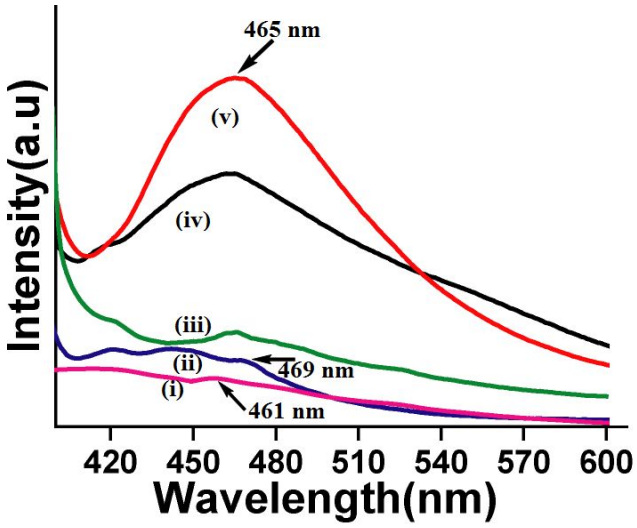


Figure S6: The fluorescence emission spectra of solid sample of complexes **(i) 4**; **(ii) 1**; (iii) **3**; (iv) **2** and (v) **5** (λ_{ex} =385 nm).

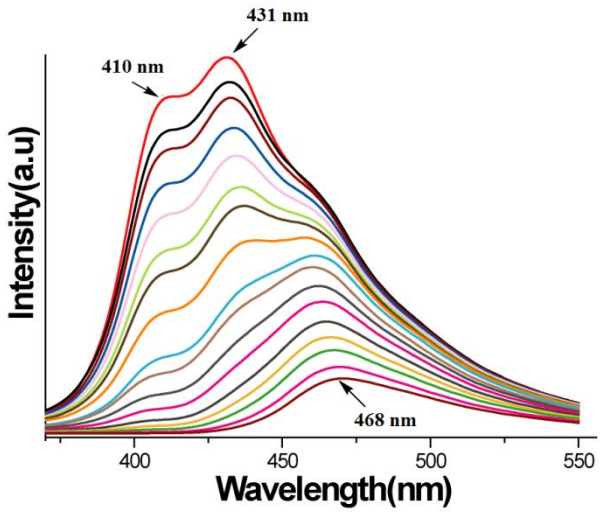
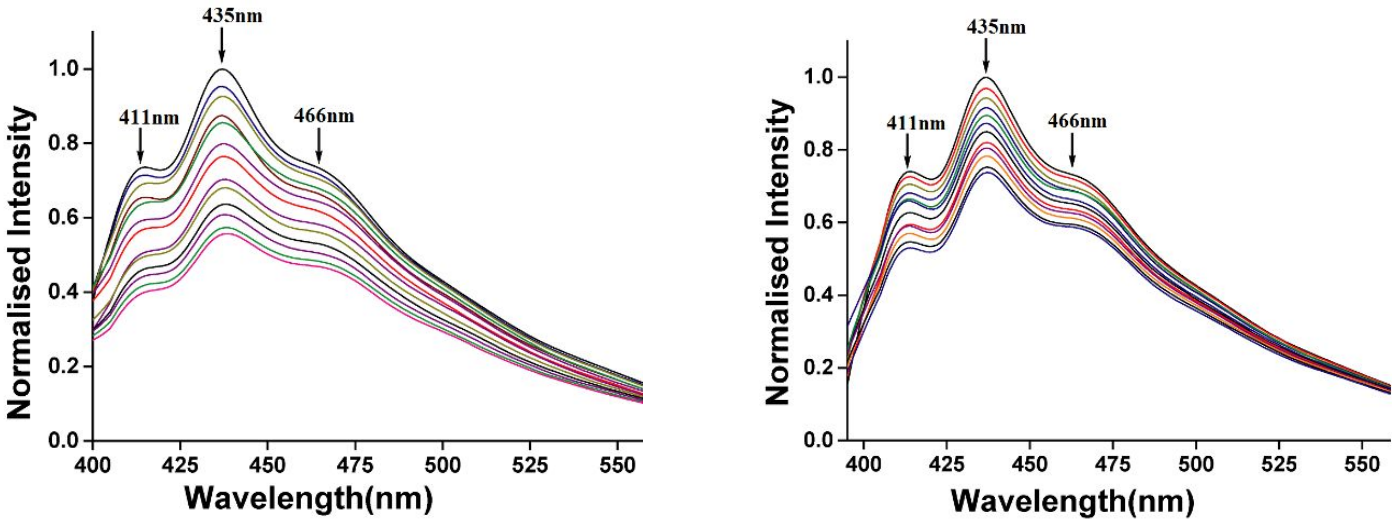
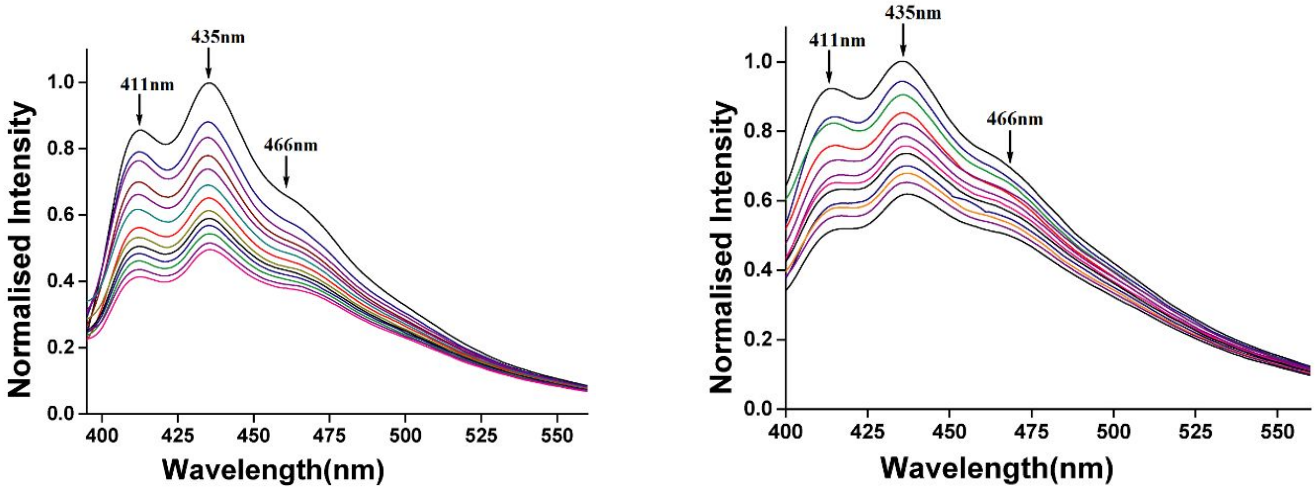


Figure S7: Fluorescence titration (λ_{ex} =350 nm) of complex **2** (10^{-4} M in DMSO) upon addition of 2-amino-5-nitrophenol.



(a) (b)

Figure S8: Fluorescence titration (excitation at 385 nm) of ligand complex **2** (10^{-3} M in DMSO) with (a) 2-nitroaniline, (b) 3-nitroaniline (20 µl aliquot of 10^{-3} M in DMSO).showing quenching of emission .



(a) (b)

Figure S9: Fluorescence titration (excitation at 385 nm) of ligand complex **5** (10^{-4} M in DMSO) with (a) 2-nitroaniline, (b) 3-nitroaniline (20 µl aliquot of 10^{-4} M in DMSO).showing quenching of emission

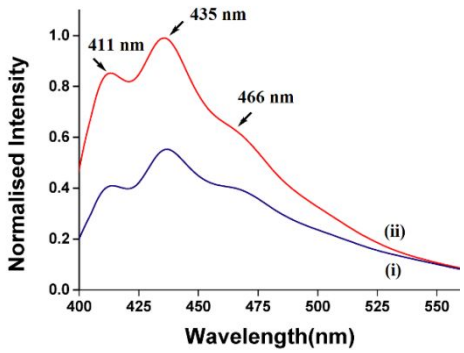
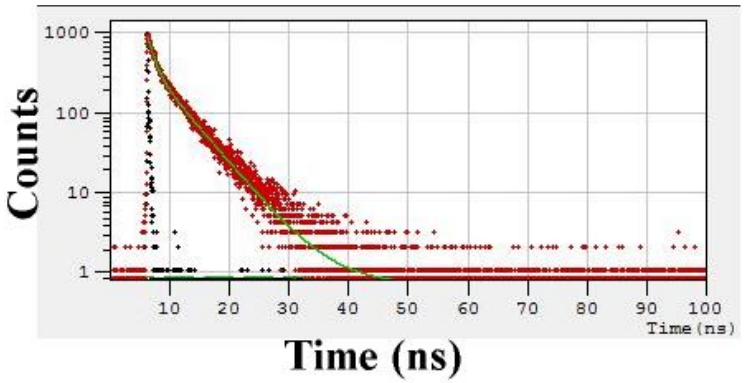


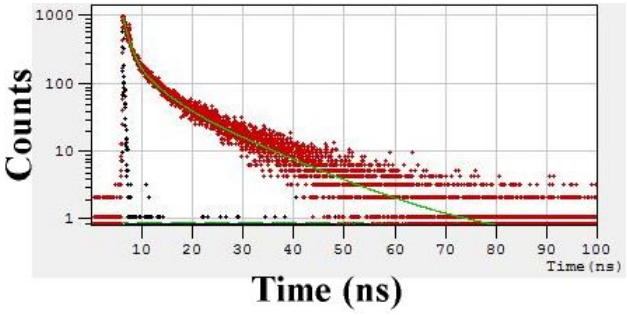
Figure S10: The fluorescence emission spectra of the **(i)** complex **2** and (ii) complex **5** in DMSO solution (λ_{ex} = 385 nm).



	B_i	ΔB_i	f_i (%)	Δf_i (%)	τ_i (ns)	$\Delta\tau_i$ (ns)
1	0.1908	0.0098	4.389	0.224	0.077 fixed	0
2	0.0701	0.0014	22.778	1.022	1.087	0.026
3	0.0491	0.0008	72.834	1.243	4.967	0.002

Goodness of fit χ^2 : 1.036

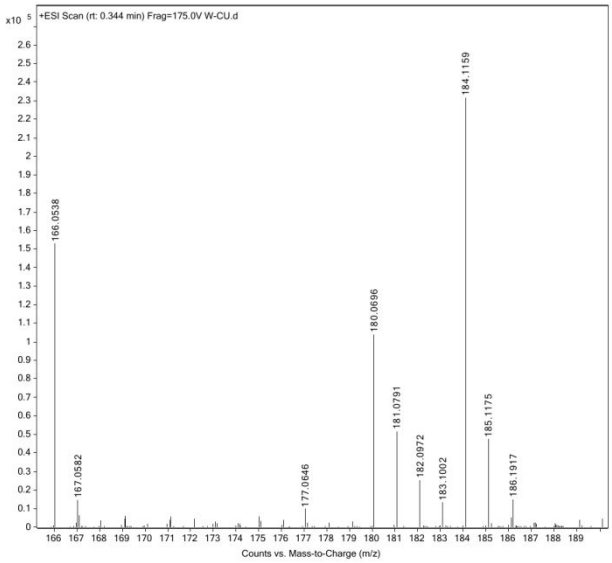
Figure S11: Time resolved fluorescence emission of solid sample of complex **5** (λ_{ex} = 385 nm, λ_{em}= 465 nm).



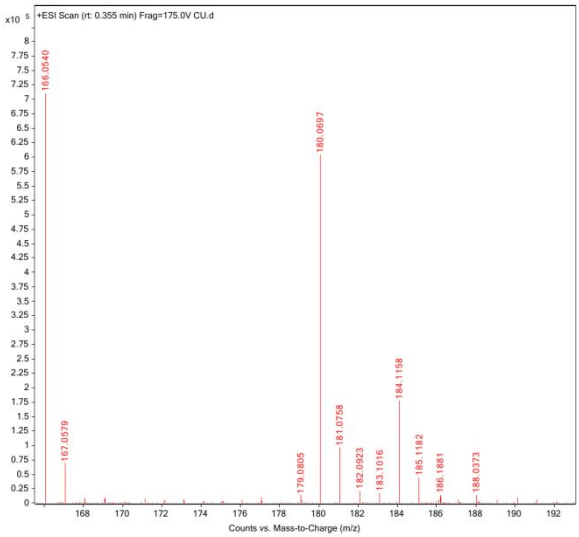
	B_i	ΔB_i	f_i (%)	Δf_i (%)	τ_i (ns)	$\Delta\tau_i$ (ns)
1	0.1310	0.0049	32.768	2.202	1.028	0.031
2	0.0286	0.0017	28.410	1.766	4.086	0.017
3	0.0119	0.0009	38.822	2.817	13.355	0.002

Goodness of fit χ: 1.081

Figure S12: Time resolved fluorescence emission of solid sample of the complex **2** (λ_{ex} = 385nm, λ_{em}= 465 nm).



(a)



(b)

Figure S13: ESI mass in the range of m/z 160 - m/z 190 of reaction mixture of the reaction between hydroxylamine hydrochloride, 1,10-phenanthroline, copper(II) acetate in the presence of sodium acetate carried out by adding (a) isotopic labeled H_2O (labeled with isotope with atomic mass 18) and (b) H_2O.

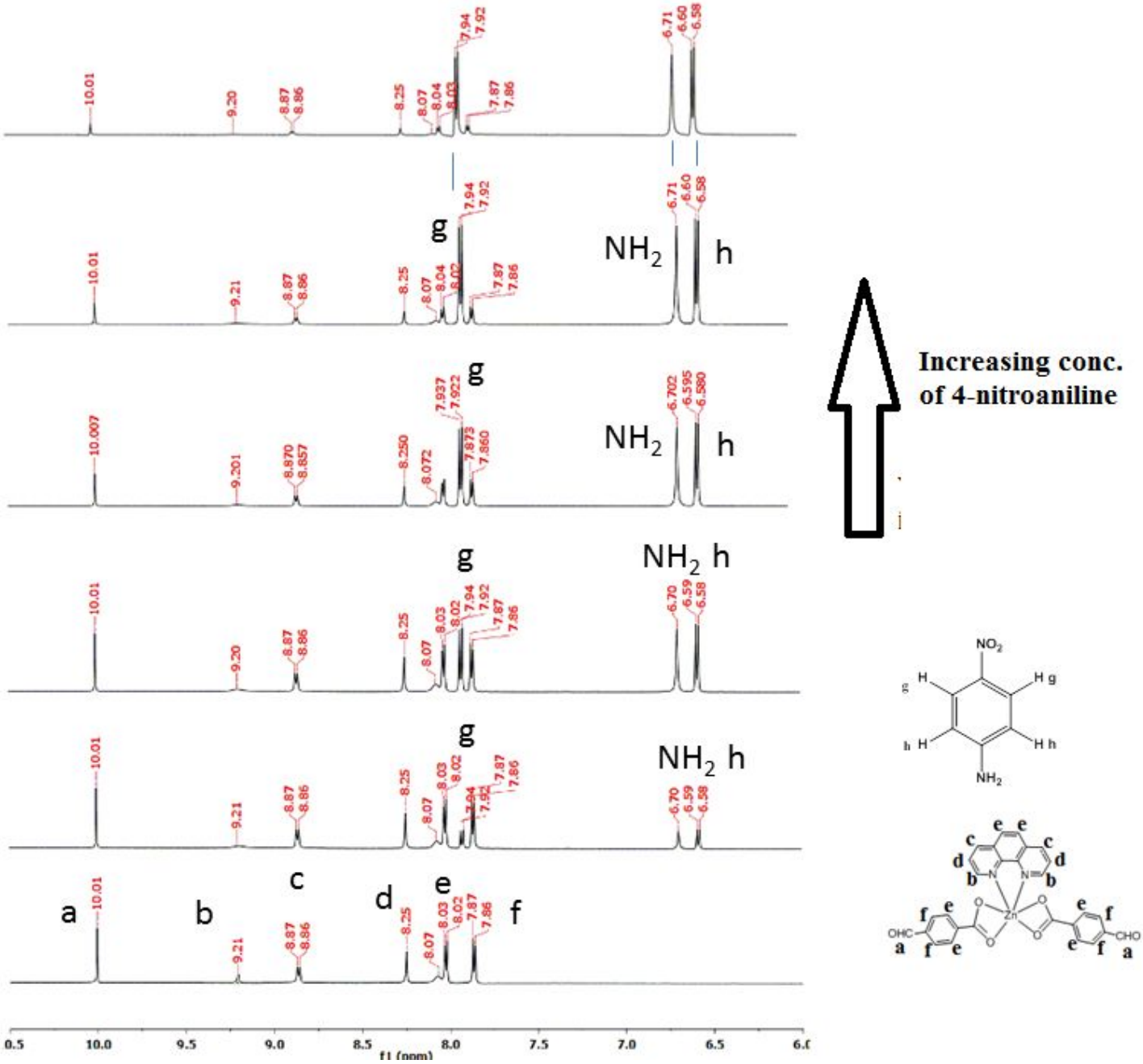


Figure S14: ^{1}H-NMR (6 ppm to10.5 ppm) titration of complex **2** by adding different amounts of 4-nitroaniline (a-h are chemical-shift positions of the protons as per the labels shown in the structures).

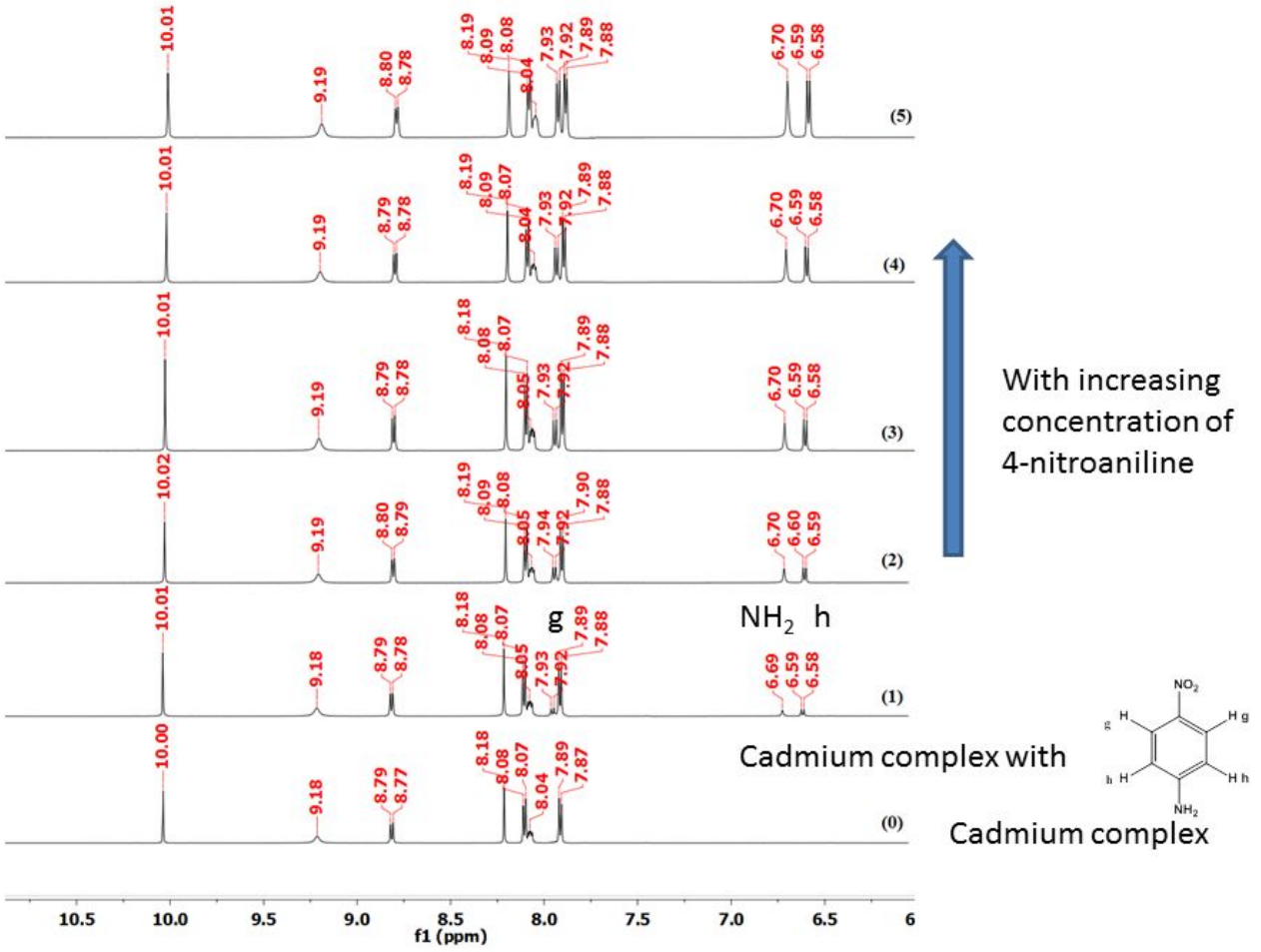


Figure S15: ^{1}H-NMR titration of complex **5** by adding different amounts of 4-nitroaniline (0) cadmium complex (1) to (5) are with increasing amount of 4-nitroaniline (g and h are the signals from the protons marked as g and h in structure of 4-nitroaniline) .

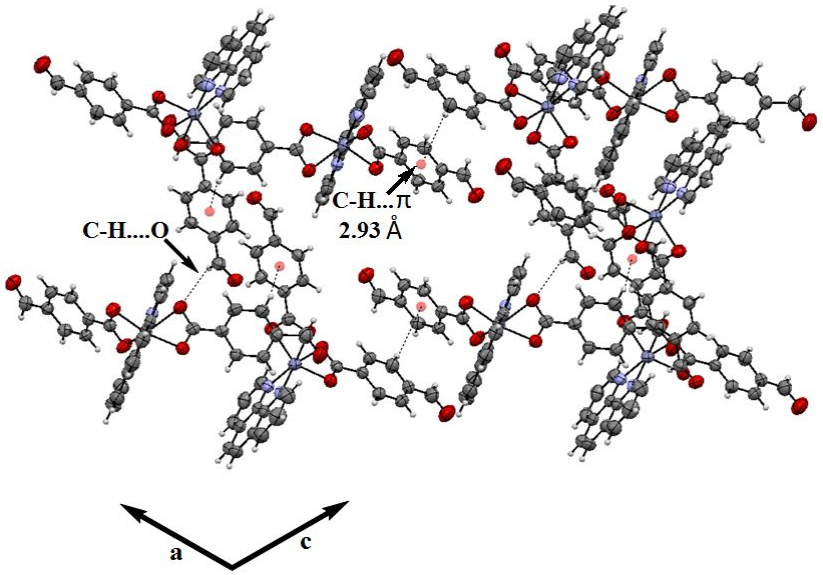


Figure S16: Packing diagram of the zinc complex (**2**)

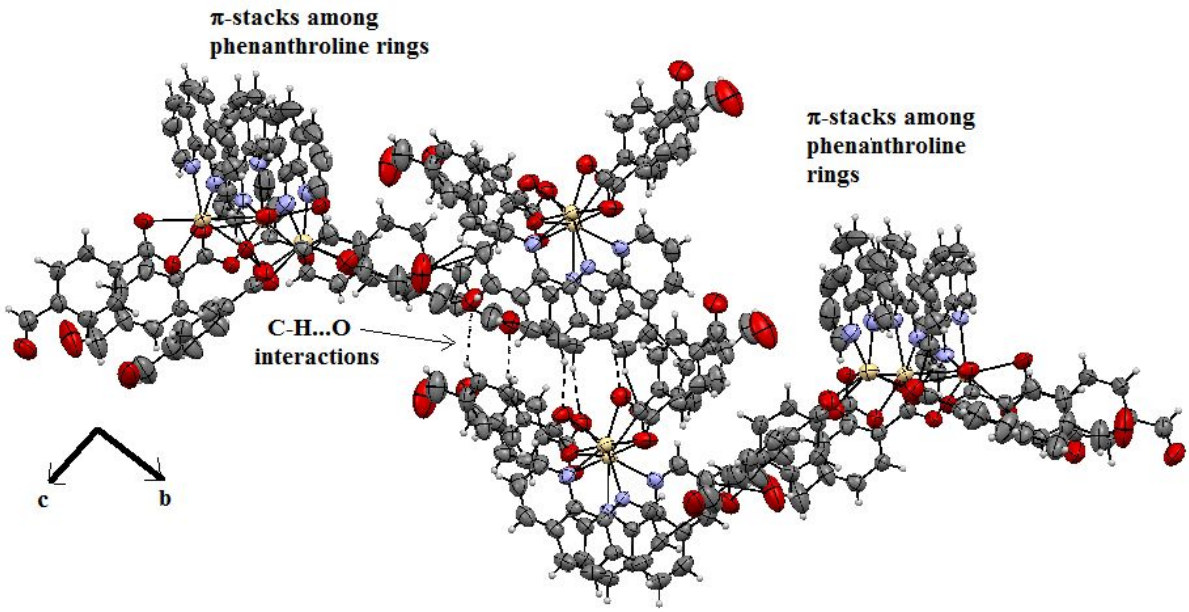


Figure S17: Packing diagram of the molecular complex of cadmium (**5**) showing C-H···O interactions between the neutral molecules.

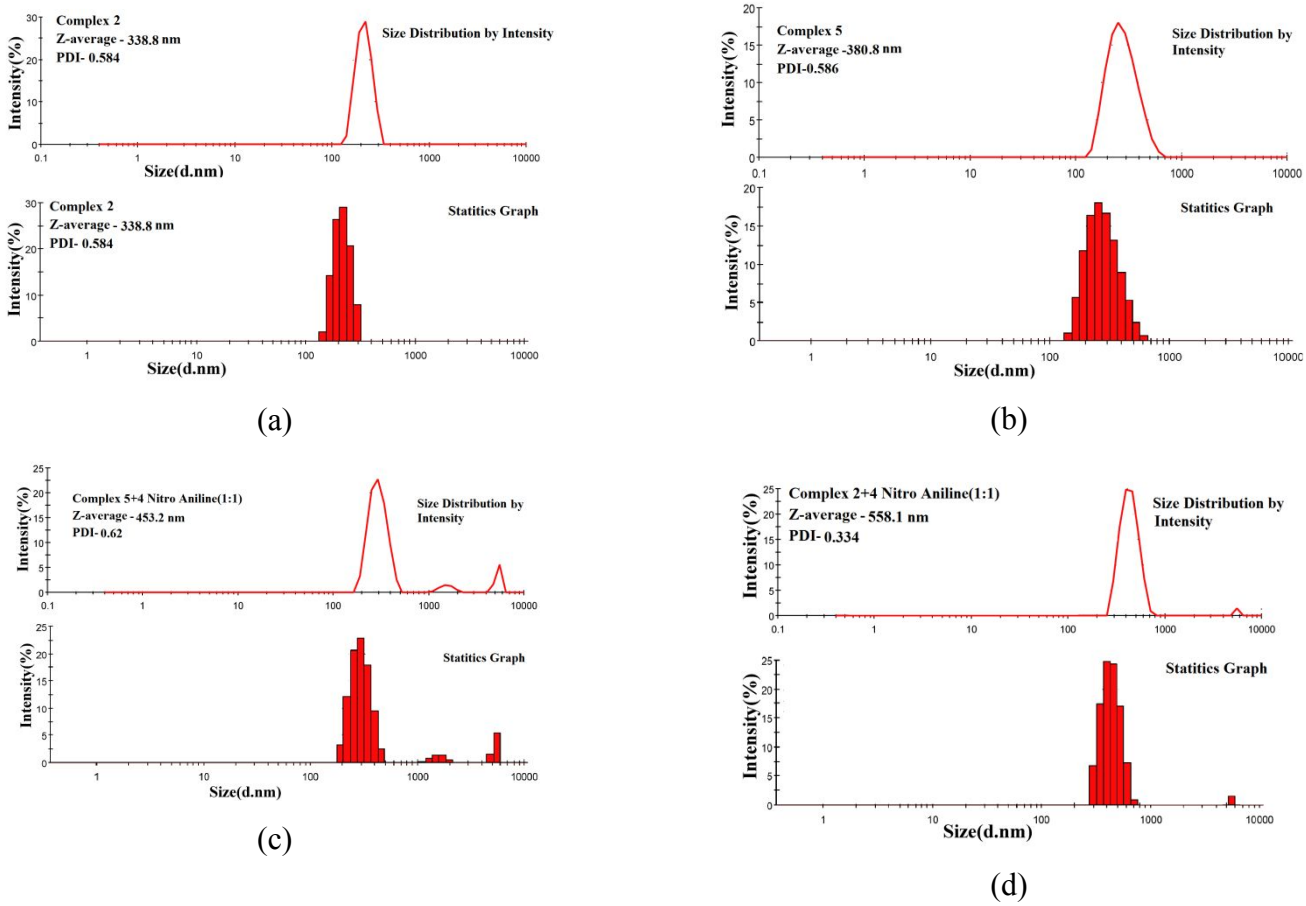


Figure S18: Particle size measurements from plots of intensity vs size from dynamic light-scattering of the (a) zinc complex (**2**) (b) cadmium complex (**5**) (c) the zinc complex with 4-nitroaniline (d) the cadmium complex with 4-nitroaniline.

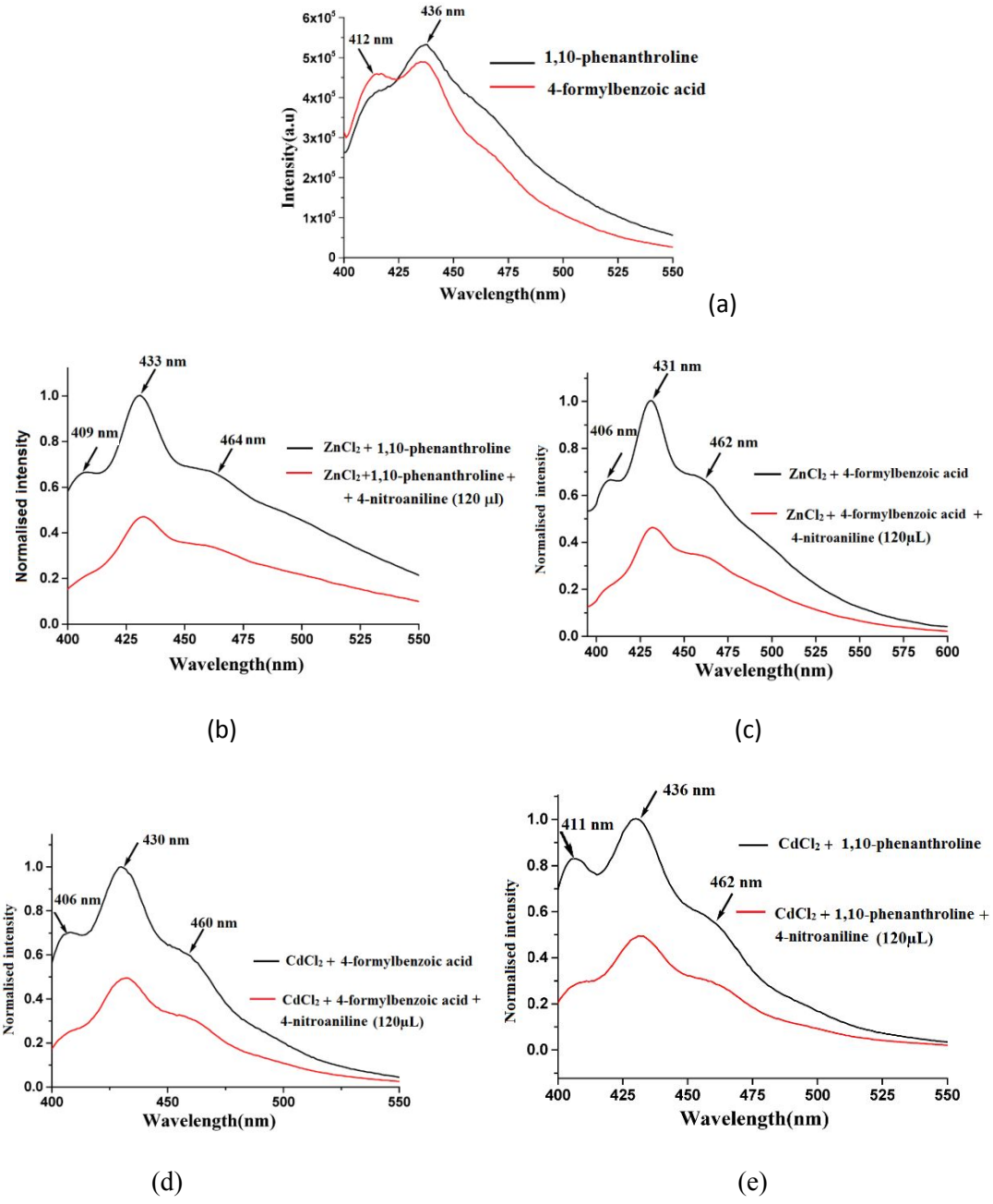


Figure S19: Fluorescence emission spectra (excitation at 385nm) of (a) 1,10-phenanthroline and 4-formylbenzoic acid in DMSO (10^{-4}M). Emission spectra from different solutions of (b) $ZnCl_2$ with 1,10-phenanthroline and 4-nitroaniline; (c) $ZnCl_2$ with 4-formylbenzoic acid; (d) $CdCl_2$ with 1,10-phenanthroline and 4-nitroaniline and (e) $CdCl_2$ with 4-formylbenzoic acid and 4-nitroaniline (in each case 120 µl of 4-nitroaniline added to 2 ml solution of the other components in DMSO of identical concentrations to perform quenching experiment).

Table S1: Photoluminescence quantum yield of the complexes in different solvents

Solvent	Complex **2**	Complex **5**
Dimethylsulphoxide	0.0122	0.0821
Dimethylsulphoxide + Dimethylformamide (4:1)	0.0097	0.0769
Dimethylsulphoxide + acetonitrile (4:1)	0.0061	0.0694
Dimethylsulphoxide + methanol (4:1)	0.0065	0.0728
Dimethylsulphoxide + water (4:1)	0.0062	0.0793

Table S2: Hydrogen bond parameters of the complexes

Complex	D-H···A	d_{D-H} (Å)	$d_{H\cdots A}$ (Å)	$d_{D\cdots A}$ (Å)	∠D-H···A (°)
Complex 1	O(7) -H(7) ···O(5) [x, y, z]	0.82	1.78	2.543(6)	154
	O(7) -H(7G) ···O(2) [x, y, z]	0.87(4)	1.81(5)	2.627(6)	156(5)
	C(26) -H(26) ···O(2) [x,1+y,z]	0.93	2.37	3.290(7)	169
Complex 2	C(9) -H(9) ···O(5) [2-x,1-y,1-z]	0.93	2.52	3.224(4)	133
	C(15) -H(15) ···O(3) [-1+x,y,z]	0.93	2.41	3.332(4)	169
	C(16) -H(16) ···O(5)[-1+x,y,z]	0.93	2.41	3.166(4)	139
	C(18) -H(18) ···O(6) [1+x, y, z]	0.93	2.53	3.438(4)	166
	C(21) -H(21) ···O(1) [-1+x,y,z]	0.93	2.58	3.484(4)	164
	C(24) -H(24) ···O(4) [1+x, y, z]	0.93	2.49	3.394(4)	163
	C(30) -H(30) ···O(4) [1/2-x,-1/2+y,1/2-z]	0.93	2.59	3.367(4)	141
Complex 3	O(1) -H(1) ···O(4) [1/2-x,y,-z]	0.82	1.83	2.625(4)	162
	O(3) -H(3) ···Cl(2) [-1/2+x,1/2+y,1/2+z]	0.82	2.37	3.128(3)	154
	O(4) -H(4A) ···O(2) [x, y, z]	0.87(6)	1.97(6)	2.784(4)	156(4)
	O(4) -H(4B) ···Cl(2) [x, y, z]	0.90(4)	2.35(4)	3.228(3)	166(4)
	C(3) -H(3A) ···N(1) [1/2+x,-y,z]	0.93	2.58	3.412(4)	149
	C(20) -H(20) ···Cl(1) [3/2-x,1/2-y,1/2-z]	0.93	2.83	3.607(3)	142
Complex 4	N(3) -H(3A) ···O(7)) [x,-1+y,z]	0.72(3)	2.07(3)	2.775(6)	166(5)
	O(5) -H(5A) ···O(6) [1-x,1-y,1-z]	0.91(6)	1.88(6))	2.790(5)	175(5)
	O(5) -H(5B) ···O(8) [x, y, z]	0.86(17)	2.08(12)	2.850(6)	149(15)
	O(6) -H(6A) ···O(3) [1+x,1/2-y,1/2+z]	0.89(8)	2.04(8)	2.847(5)	151(7)
	O(6) -H(6B) ···Cl(1) [x,1/2-y,1/2+z]	0.90(6)	2.23(7)	3.108(4)	168(6)
	O(7) -H(7A) ···Cl(1) [-x,1/2+y,1/2-z]	0.85(5)	2.39(6)	3.173(4)	155(5)
	O(7) -H(7B) ···O(6) [x, y, z]	0.85(4)	1.98(4)	2.784(5)	157(5)
	O(8) -H(8B) ···O(3) [-x,-y,-z]	0.85(5)	2.50	3.299(6)	157
	O(8) -H(8B) ···O(4) [-x,-y,-z]	0.85	1.90	2.614(6)	141

	C(7) -H(7) ···O(7) [x,-1+y,z]	0.93	2.57	3.461(6)	159
	C(11) -H(11) ···O(6) [x, y, z]	0.93	2.59	3.500(5)	165
Complex 5	C(1) -H(1)···O(4) [x, y, z]	0.93	2.50	3.105(6)	123
	C(3) -H(3) ···O(2) [x,y,1+z]	0.93	2.56	3.349(6)	143
	C(10) -H(10) ···O(8) [1/2-x,1/2+y,1-z]	0.93	2.54	3.096(6)	119
	C(32) --H(32) ···O(10) [1/2-x,1/2+y,-z]	0.93	2.55	3.205(7)	128
	C(42) -H(42) ···O(11) [1/2-x,-1/2+y,2-z]	0.93	2.37	3.240(9)	155
	C(46) -H(46) ···O(11) [x,y,-2+z]	0.93	2.48	3.235(7)	138

Table S3: XYZ coordinates of complex **2**:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	30	-0.106189	0.379032	-0.017487
2	6	0.354547	3.194401	-0.634150
3	6	0.809038	3.042563	0.721875
4	6	1.359961	4.129428	1.392258
5	6	0.468540	4.423810	-1.261492
6	6	1.465376	5.378888	0.716268
7	1	1.828128	6.111460	1.159591
8	6	1.048419	5.517313	-0.550350
9	1	1.138172	6.339440	-0.974553
10	6	-0.599177	2.216540	-2.471360

11	1	-0.960074	1.468602	-2.890346
12	6	1.762115	3.934432	2.719939
13	1	2.125308	4.637266	3.208036
14	6	1.052259	1.684859	2.553764
15	1	0.943022	0.857585	2.963457
16	6	-0.528717	3.424241	-3.187962
17	1	-0.845974	3.476492	-4.060381
18	6	0.008145	4.506302	-2.584804
19	1	0.072778	5.310865	-3.048206
20	6	1.619768	2.715030	3.284861
21	1	1.900613	2.568298	4.158663
22	6	-4.083491	-2.120174	-1.060839
23	1	-3.492928	-2.336911	-1.745525
24	6	-4.569706	-0.987513	0.981938
25	1	-4.309361	-0.410873	1.663878
26	6	-5.820035	-1.549893	1.006201
27	1	-6.388886	-1.378544	1.721541
28	6	-6.236326	-2.363603	-0.018004
29	6	-3.689226	-1.272065	-0.053535
30	6	-5.362810	-2.651262	-1.052764
31	1	-5.636955	-3.206077	-1.748237
32	6	2.964665	-2.195783	0.011049
33	6	3.242772	-3.159715	0.964261
34	1	2.635835	-3.319982	1.650638
35	6	5.012768	-2.746651	-1.124895

36	1	5.596114	-2.622708	-1.838981
37	6	3.852117	-2.015584	-1.047595
38	1	3.656336	-1.392292	-1.709803
39	6	5.310854	-3.667549	-0.138620
40	6	6.578557	-4.406466	-0.153852
41	1	6.733650	-5.005146	0.540508
42	6	4.410654	-3.880277	0.902081
43	1	4.600951	-4.511673	1.556812
44	8	1.572488	-0.449769	-0.735702
45	8	-1.977829	0.094035	0.866623
46	8	-1.593148	-0.823699	-1.062342
47	8	0.963605	-1.479064	1.082460
48	8	7.427963	-4.298949	-0.988421
49	6	-2.349064	-0.630651	-0.088750
50	6	1.750536	-1.339751	0.133855
51	7	-0.173804	2.102214	-1.231913
52	7	0.656088	1.822869	1.297549
53	6	-7.584058	-2.940217	-0.028175
54	1	-7.895320	-3.293596	-0.829502
55	8	-8.315906	-2.990389	0.924924
