Supplementary Information

Design and development of Imidazo[4,5-f] [1,10] phenanthroline-Zn (II) based fluorescent probes for specific recognition of ATP with tunable optical responses and probing the enzymatic hydrolysis of ATP by alkaline phosphatase

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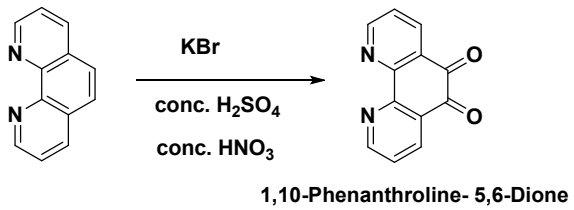
Experimental section

Synthesis of 1,10-Phenanthroline-5,6-Dione: A mixture of 1,10-phenanthroline monohydrate (3gm, 15.5 mmol) and potassium bromide (3g, 25.2 mmol) were added into a two neck round bottom flask. Then ice-cold mixture of conc. HNO_3 (15ml) and conc. H_2SO_4 (30ml) were mixed dropwise at 0°C for 1h. This reaction mixture was heated at 100°C for 30 minutes with stirring. The hot reaction mixture was cooled to room temperature and neutralized by NaOH solution. A yellow colour precipitate was formed. The precipitate was separated, dried, and purified by column chromatography on silica gel eluting with $CH_3OH/CHCl_3$ (2:98, v/v). Yield = 2.1 gm, (9.40 mmol, 60.86 %) (Scheme S1). (^{1}H NMR, DMSO-d_6, 500 MHz, δppm): 9.00-8.98 (m,2H), 8.40-8.98 (m, 2H), 7.69-7.66 (m, 2H).



Scheme S1: Synthetic methodologies adopted for the synthesis of 1,10-Phenanthroline-5,6-Dione.

Synthesis of P1: A mixture of p-N, N dimethyl amino benzaldehyde (462 mg, 3.1 mmol), 1,10-Phenanthroline-5,6-Dione (650 mg, 3.1 mmol), and ammonium acetate (3.1 gm, 40.21 mmol) in glacial acetic acid (15.5 mL) was heated at 100°C for 12 h with continuous stirring. The hot reaction mixture was cooled to room temperature, whereupon 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 $CH_3OH/CHCl_3$ (3:97, v/v). Yield = 700.05 mg, (1.97 mmol, 63.76 %) (Scheme S2). (^{1}H NMR, DMSO-d_6, 500 MHz, δppm):8.98 (d, *J*=6.5 Hz, 2H), 8.92 (s, 2H), 8.08 (d, *J* = 6.5 Hz, 2H), 7.82-7.80 (m, 2H), 6.85 (d, *J* = 6.5 Hz, 2H), 2.98 (s, 6H). FTIR (CaF_2, νmax, cm^{-1}): 733, 811, 952, 1070, 1195, 1358, 1433, 1522, 1607 (Phenanthroline, C=N str), 3178 (Imidazole, N-H str).

Synthesis of P2: A mixture of p-chloro benzaldehyde (450 gm, 3.1 mmol), 1,10-Phenanthroline-5,6-Dione (650 mg, 3.1 mmol), and ammonium acetate (3.1g, 40.21 mmol) in glacial acetic acid (15.5 mL) was heated at 100°C for 12 h with stirring. The hot reaction mixture was cooled to room temperature, whereupon a yellow solid separated. The yellow solid was collected by filtration and washed with dilute aqueous $NaHCO_3$ solution, and finally with water. This yellow residue was dried and purified by column chromatography on silica gel eluting with $CH_3OH/CHCl_3$ (3:97, v/v). Yield = 720.25 mg, (2.14 mmol, 70.24 %) (Scheme S2). (^{1}H NMR, DMSO-d_6, 500 MHz, δppm):8.98 (s,2H), 8.82 (d, *J* = 10 Hz, 2H), 8.18 (d, *J* = 10 Hz, 2H), 7.76-7.79 (m, 2H), 7.60 (d, *J* = 5 Hz, 2H). FTIR (CaF_2, νmax, cm^{-1}): 732, 802, 836, 1014, 1088, 1394, 1455, 1472, 1554 (Phenanthroline, C=N str), 3186 (Imidazole, N-H str).

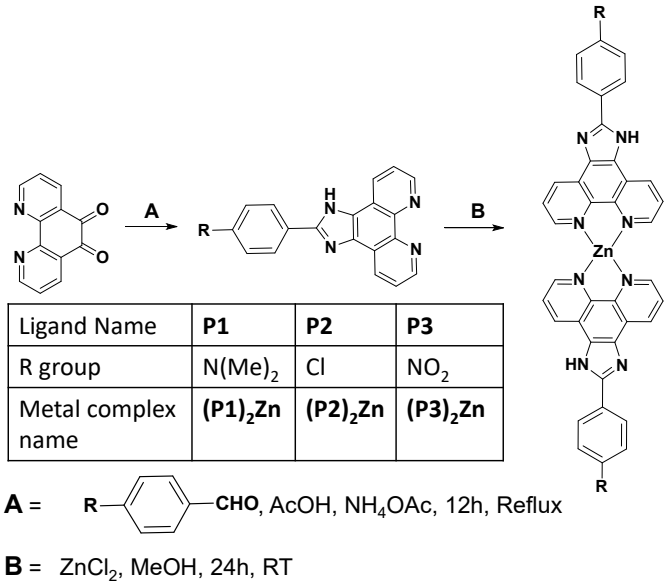
Synthesis of P3: A mixture of p-nitro benzaldehyde (472.8 mg, 3.1 mmol), 1,10-Phenanthroline-5,6-Dione (650 mg, 3.1 mmol), and ammonium acetate (3.1 gm, 40.21 mmol) in glacial acetic acid (15.5 mL) was heated at 100°C for 12 h with stirring. The hot reaction mixture was cooled to room temperature, whereupon a brown solid separated. The yellow solid was collected by filtration and washed with dilute aqueous $NaHCO_3$ solution, and finally with water. This yellow residue was dried and purified by column chromatography on silica gel eluting with $CH_3OH/CHCl_3$ (3:97, v/v). Yield = 801.41 mg, (7.10 mmol, 74.04 %) (Scheme S2). (^{1}H NMR, DMSO-d_6, 500 MHz, δppm): 9.00-8.99 (m,2H), 8.92-8.90 (m, 2H), 8.53 (d, *J* = 8.5 Hz, 2H), 8.42 (d, *J* = 8.5 Hz, 2H), 7.82-7.79

(m, 2H). FTIR (CaF_2, νmax, cm^{-1}): 705, 731, 804, 854, 1106, 1335, 1400, 1514, 1598 (Phenanthroline, C=N str), 3302 (Imidazole, N-H str).

Synthesis of $(P1)_2Zn$: $(P1)_2Zn$ was prepared by a mixture of P1 (200mg, 0.594 mmol) and zinc chloride (52.45mg, 0.297 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: 207.62 mg (0.264mmol, 89.08%) (Scheme S2). ESI-MS (m/z): $[M+1]^+$ =745.17 (calculated); 745.70 (observed). FTIR (CaF_2, νmax, cm^{-1}): 736, 816, 950, 1076, 1198, 1354, 1487, 1610 (Phenanthroline, C=N str), 3344 (Imidazole, N-H str).

Synthesis of $(P2)_2Zn$: **$(P2)_2Zn$** was prepared by a mixture of P2 (160 mg, 0.483 mmol) and zinc chloride (33.11 mg, 0.243 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: 140.2 mg (0.260 mmol, 87.98%) (Scheme S2). ESI-MS (m/z): $[M]^+$ =726.89 (calculated); 726.92 (observed). FTIR (CaF_2, νmax, cm^{-1}): 728, 812, 1072, 1362, 1403, 1448, 1515, 1609 (Phenanthroline, C=N str), 3241 (Imidazole, N-H str).

Synthesis of $(P3)_2Zn$: **$(P3)_2Zn$** was prepared by a mixture of P3 (200mg, 0.594 mmol) and zinc chloride (52.45mg, 0.297 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: 224.27 mg (0.312 mmol, 84.33%) (Scheme S2). ESI-MS (m/z): $[M+1]^+$ =750.04 (calculated); 750.55 (observed). FTIR (CaF_2, νmax, cm^{-1}): 699, 734, 818, 856, 1074, 1100, 1333, 1513, 1603 (Phenanthroline, C=N str), 3367 (Imidazole, N-H str).



Ligand Name	**P1**	**P2**	**P3**
R group	$N(Me)_2$	Cl	NO_2
Metal complex name	**$(P1)_2Zn$**	**$(P2)_2Zn$**	**$(P3)_2Zn$**

A = R—⟨benzene⟩—**CHO**, AcOH, NH_4OAc, 12h, Reflux

B = $ZnCl_2$, MeOH, 24h, RT

Scheme S2: Synthetic methodologies adopted for the synthesis of ligands (P1, P2 and P3) metal complexes (**$(P1)_2Zn$, $(P2)_2Zn$ and $(P3)_2Zn$**).

Spectroscopic characterization:

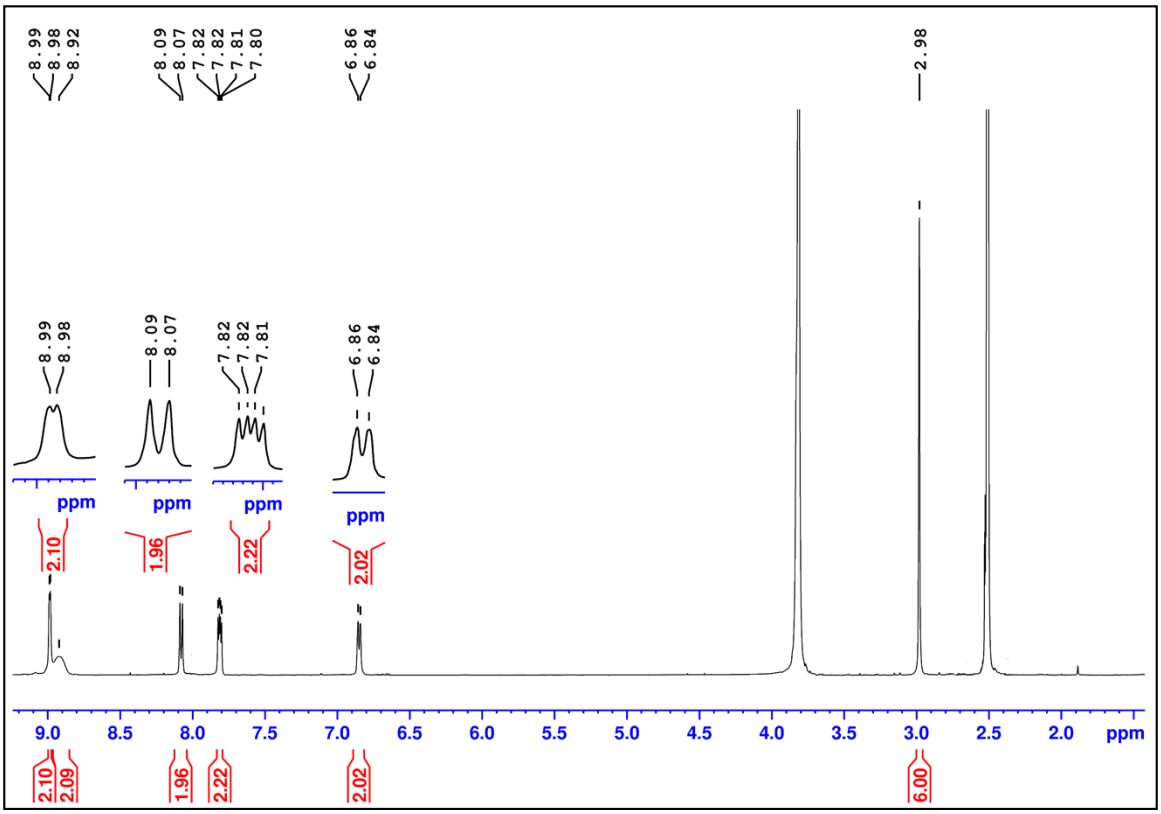


Figure S1. ^1H NMR (DMSO-d_6, 500 MHz, δppm) of P1.

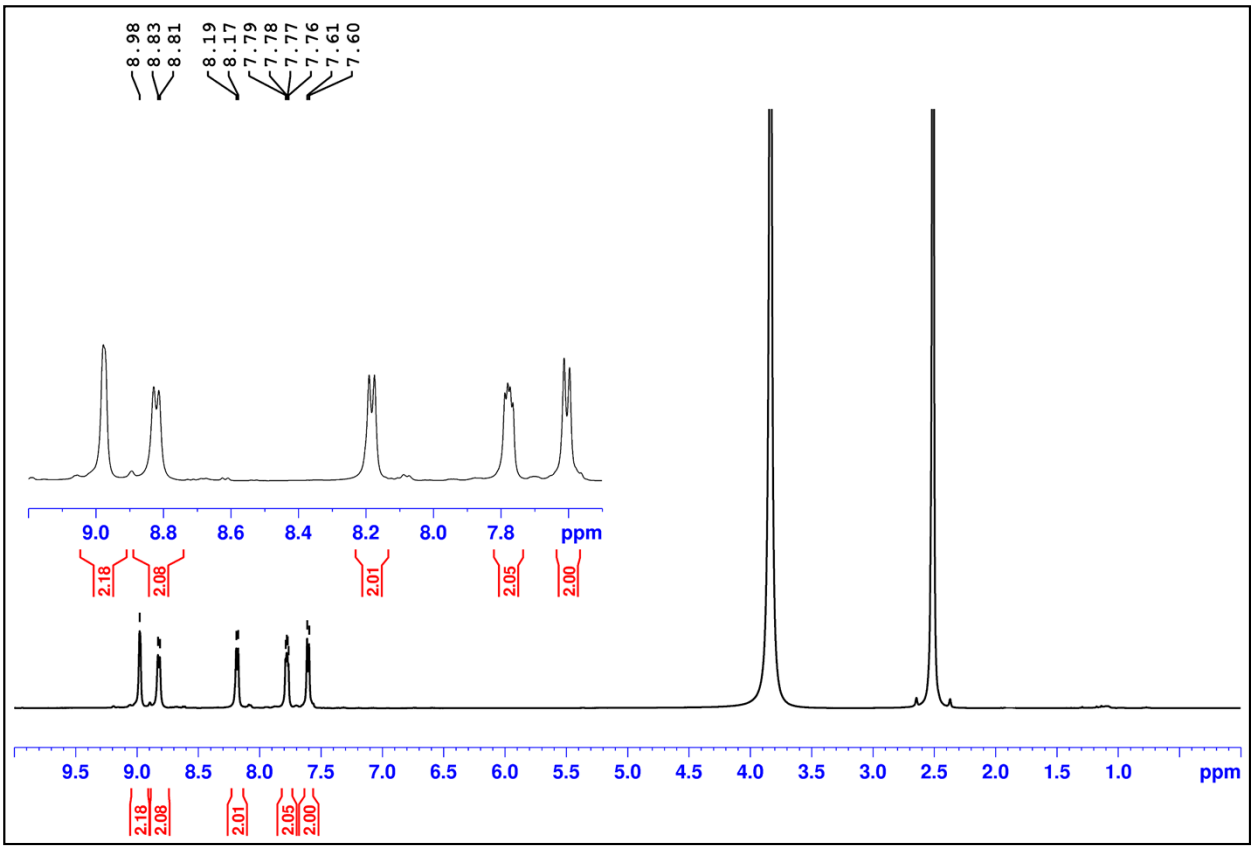


Figure S2. ^{1}H NMR (DMSO-d_6, 500 MHz, δppm) of P2.

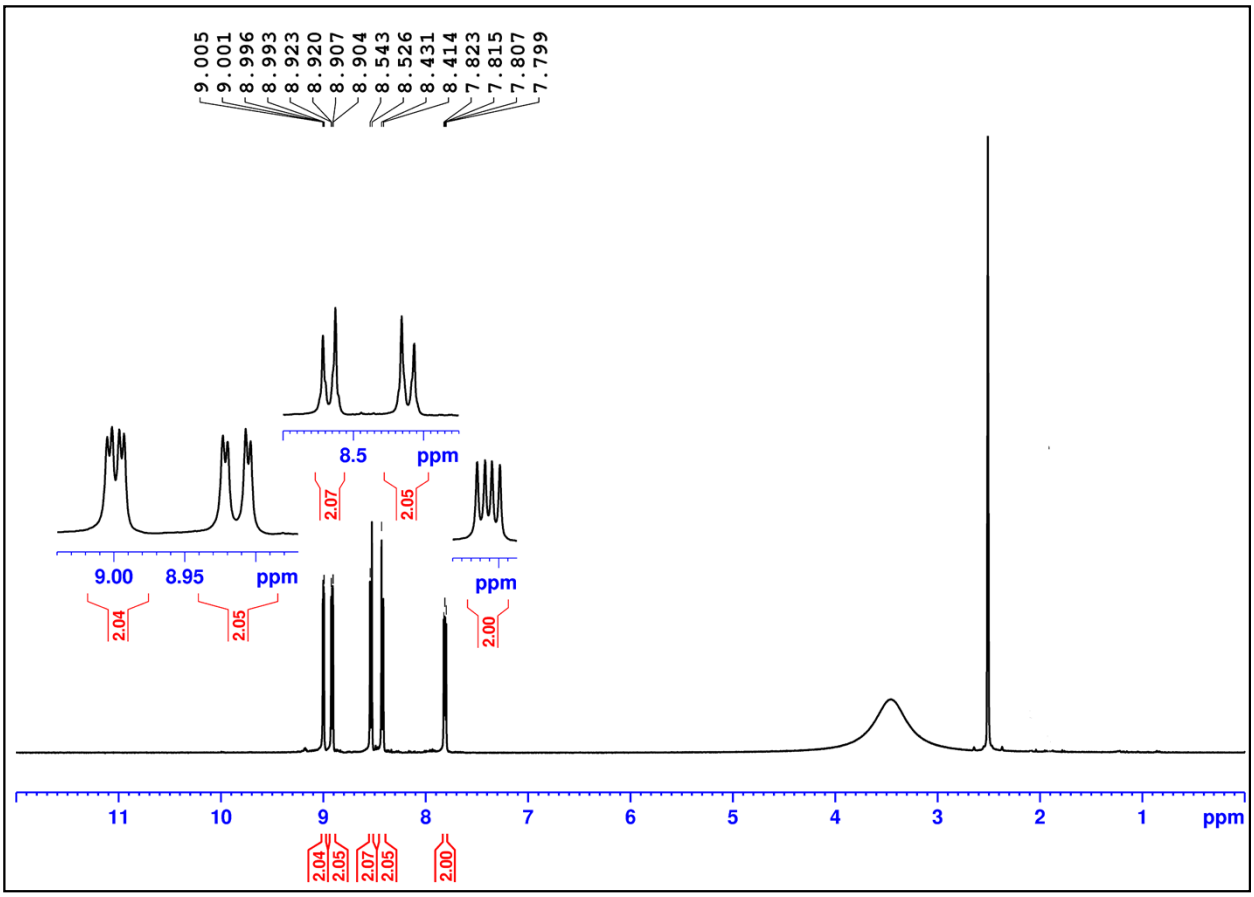


Figure S3. ^{1}H NMR (DMSO-d_6, 500 MHz, δppm) of P3.

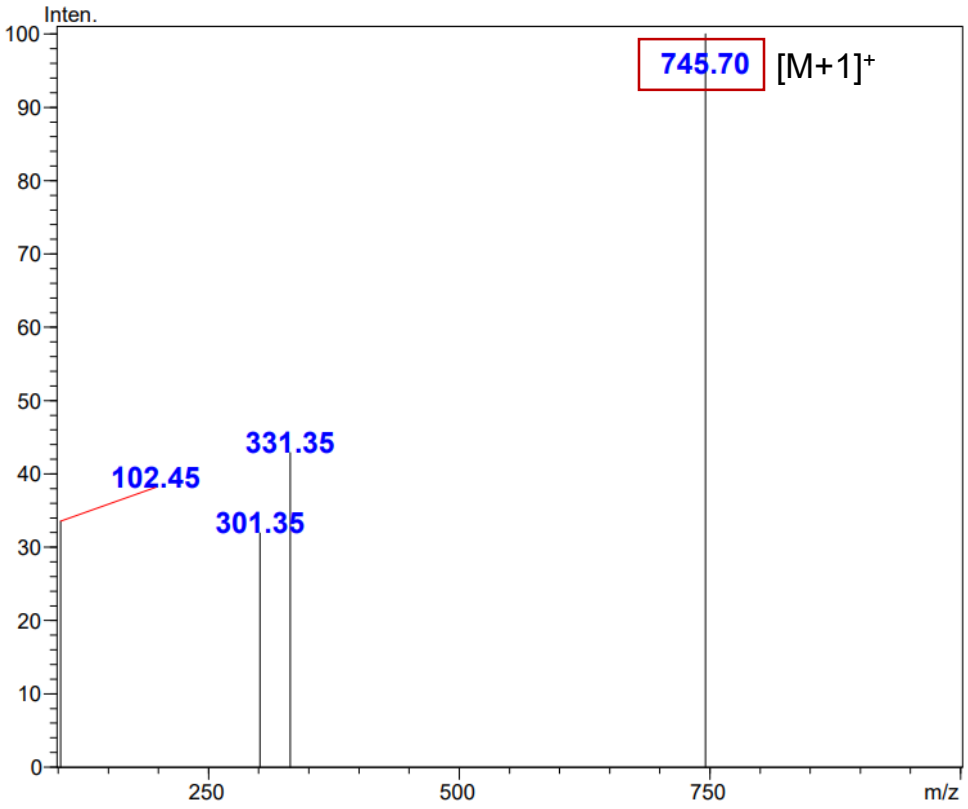


Figure S4. ESI Mass spectra of **$(P1)_2Zn$.**

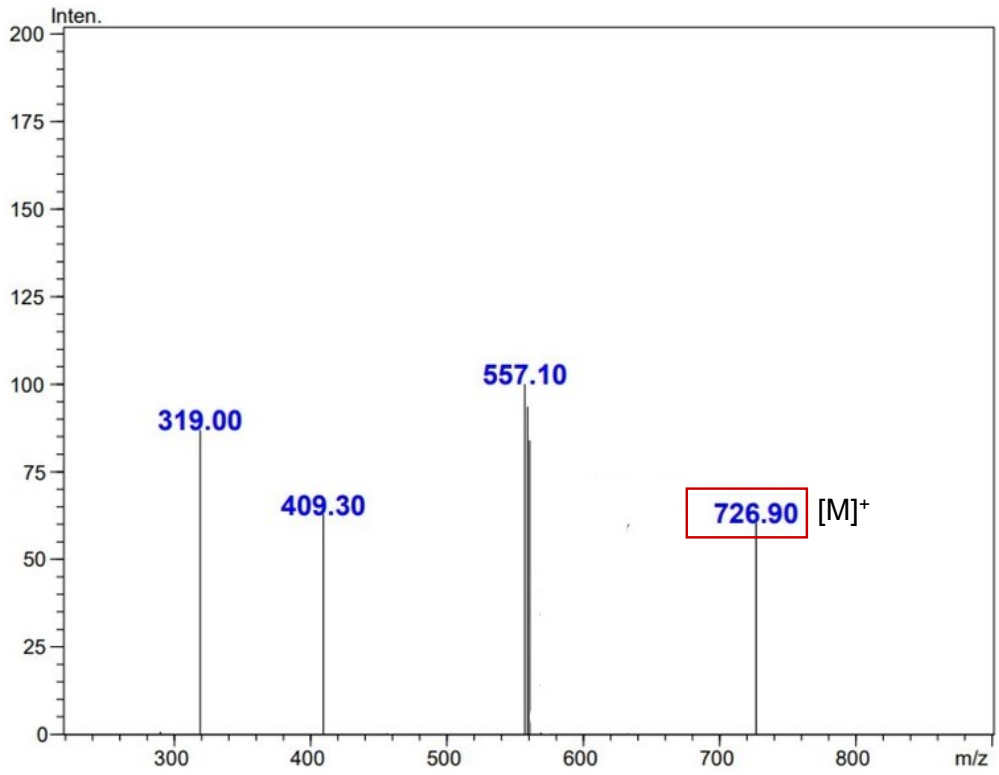


Figure S5. ESI Mass spectra of **$(P2)_2Zn$**.

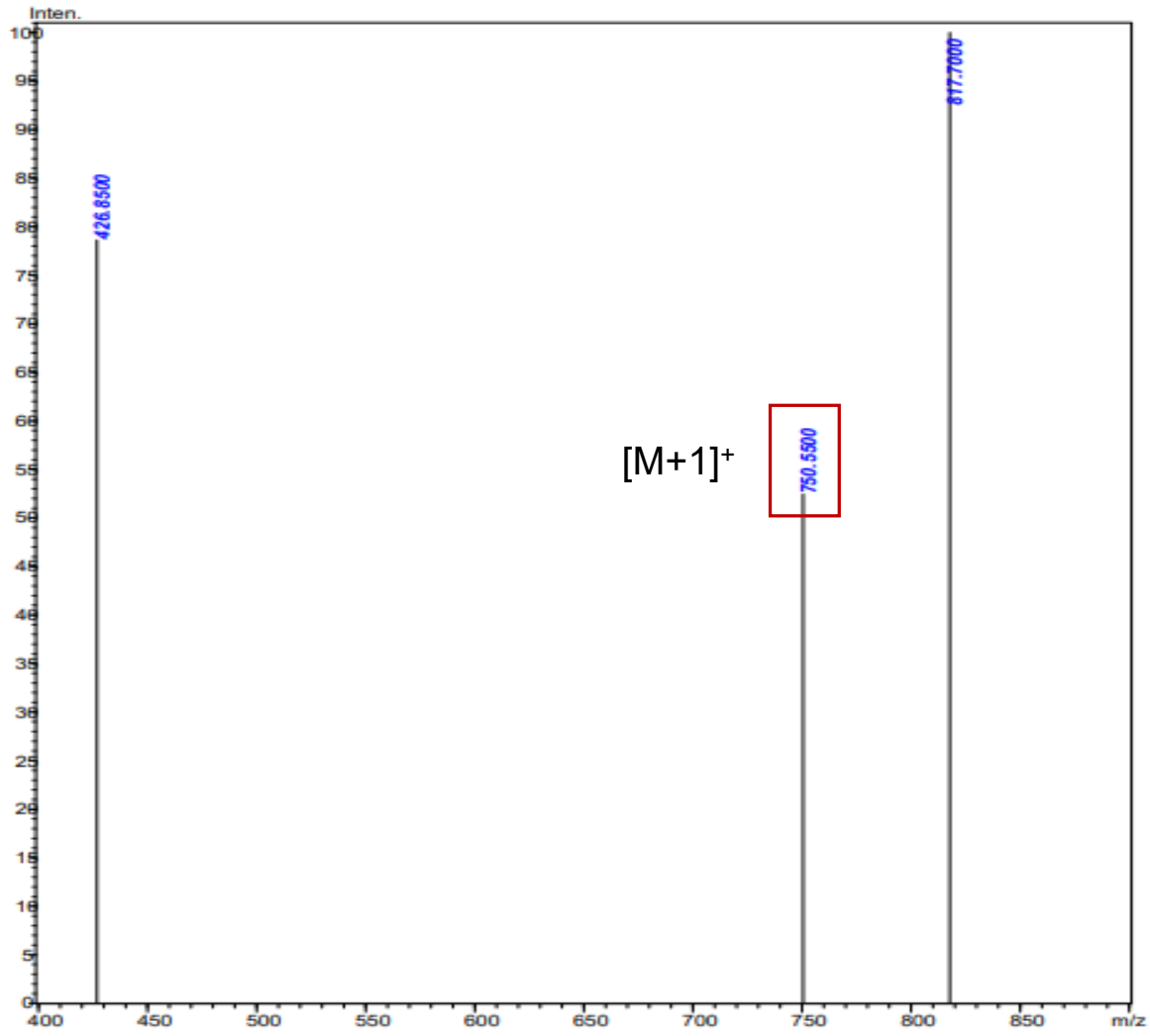


Figure S6. ESI Mass spectra of **$(P3)_2Zn$**.

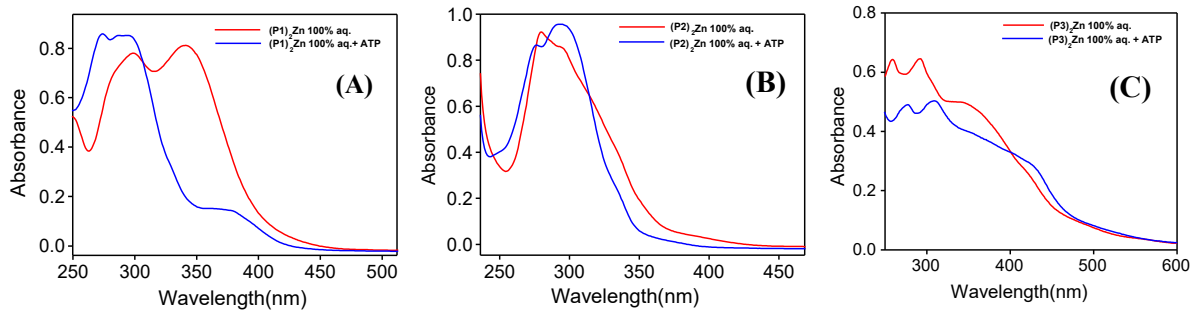


Figure S7. UV-Vis spectra of **(Pn)$_2$Zn** (n=1,2,3) in absence and presence of ATP in aqueous 0.01 M HEPES buffer medium (pH = 7.4).

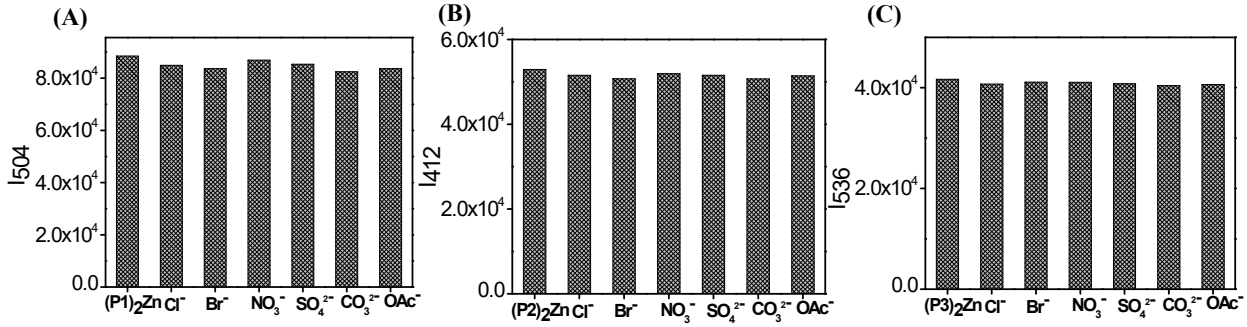


Figure S8. Different anions (Cl^-, Br^-, NO_3^-, SO_4^-, CO_3^{2-} and OAc^-) scanning with (A) **(P1)$_2$Zn**, (B) **(P2)$_2$Zn** and (C) **(P3)$_2$Zn**.

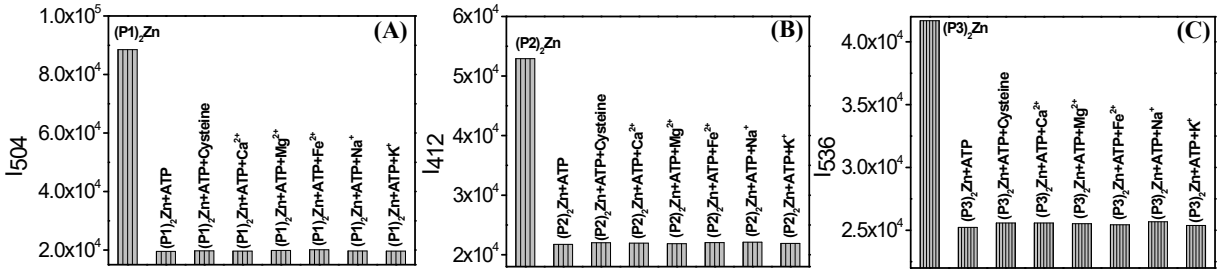


Figure S9. Different cations(cysteine,Ca^{2+},Mg^{2+},Fe^{2+},Na^+ and K^+) scanning with (A) **(P1)$_2$Zn**, (B) **(P2)$_2$Zn** and (C) **(P3)$_2$Zn**.

Calculation of Binding constants:

Binding constant was calculated from changes in fluorescence Intensity with varying [ATP] using nonlinear least-square fitting (SI Equations 1 for 1:1 (**$(Pn)_2Zn$-ATP)** (n = 1,2,3))[1-5].

$$\frac{F_0}{F_c} = 1 + \left(\frac{F_1}{F_0} - 1\right)\left(\frac{K[ATP]}{1+K[ATP]}\right) \quad \text{..... (SIEq.1)}$$

K in SI Equation 1 correspond to binding constant for 1:1 complex formation. In SI Equation 1, F_0 is the fluorescence intensities at specific wavelengths of **$(Pn)_2Zn$** (λ_{Ems} = 504 nm for **$(P1)_2Zn$**, λ_{Ems} = 412 nm for **$(P2)_2Zn$** and λ_{Ems} = 536 nm for **$(P3)_2Zn$)** in absence of ATP. F_1 is maximum fluorescence intensities at these specific wavelengths of **$(Pn)_2Zn$** in presence of ATP. F_c is the fluorescence intensity of **$(Pn)_2Zn$** at particular wavelengths (λ_{Ems} = 504 nm for $(P1)_2Zn$, λ_{Ems} = 412 nm for $(P2)_2Zn$ and λ_{Ems} = 536 nm for **$(P3)_2Zn$)** for a specific [ATP] and this value is restricted for concentration range of (0 – 0.008 M) for SI Equation 1. The concentration of the ATP is denoted by [ATP].

References:

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Table S1. Calculated absorption of **$(Pn)_2Zn$)** (n=1,2,3) complexes in aqueous media at TD-B3LYP level of theory along with experimental values.

	State	λ(nm)/E(eV)	Oscillator	Main configuration	Assign	λexp (nm)
$(P1)_2Zn$	S_{26}	293/ 4.23	0.3036	H-7→L+1 (25%) H-6 →L (26%) H-3 →L+3 (17%) H-2 →L+2 (17%)	PhenA/PhenB →PhenA/PhenB (ILCT) PhenA/PhenB →PhenA/PhenB (ILCT) a-PhN $(CH_3)_2$/b-PhN $(CH_3)_2$→PhenA/PhenB (LLCT) a-PhN$(CH_3)_2$/b-PhN$(CH_3)_2$→PhenA/PhenB (LLCT)	294
	S_{25}	294/ 4.22	0.5200	H-7→L (24%) H-6→L+1 (24%) H-3 →L+2 (16%) H-2 →L+3(16%)	PhenA/PhenB →PhenA/PhenB (ILCT) PhenA/PhenB →PhenA/PhenB (ILCT) a-PhN$(CH_3)_2$/b-PhN$(CH_3)_2$→PhenA/PhenB (LLCT) a-PhN$(CH_3)_2$/b-PhN$(CH_3)_2$→PhenA/PhenB (LLCT)	
	S_9	373/ 3.32	2.1911	H-1→L+5 (49%) H→L+4 (49%)	a-PhN$(CH_3)_2$/b-PhN$(CH_3)_2$→a-PhN$(CH_3)_2$/b-PhN$(CH_3)_2$/PhenA/PhenB (ILCT,LLCT) a-PhN$(CH_3)_2$/b-PhN$(CH_3)_2$→a-PhN$(CH_3)_2$/b-PhN$(CH_3)_2$/PhenA/PhenB (ILCT,LLCT)	349
$(P2)_2Zn$	S_{23}	274/4.52	0.8955	H-7→L (11%) H-6→L+1 (11%) H-3→L+3 (27%) H-2→L+2 (27%)	a-PhCl/b-PhCl→Zn/PhenA/PhenB (LMCT/LLCT) a-PhCl/b-PhCl→Zn/PhenA/PhenB (LMCT/LLCT) a-PhCl/b-PhCl →PhenA/PhenB (LLCT) a-PhCl/b-PhCl →Zn/PhenA/PhenB (LMCT/LLCT)	275

	S_{17}	288/ 4.31	0.2343	H-7→L (27%) H-6→L+1 (27%) H-3→L+3 (11%) H-2→L+2 (11%)	a-PhCl/b-PhCl→Zn/PhenA/PhenB (LMCT/LLCT) a-PhCl/b-PhCl→Zn/PhenA/PhenB (LMCT/LLCT) a-PhCl/b-PhCl →PhenA/PhenB (LLCT) a-PhCl/b-PhCl →Zn/PhenA/PhenB (LMCT/LLCT)	298
	S_{14}	300/ 4.13	0.2574	H-3→L (42%) H-2→L+1 (39%)	a-PhCl/b-PhCl →Zn/PhenA/PhenB (LMCT/LLCT) a-PhCl/b-PhCl →Zn/PhenA/PhenB (LMCT/LLCT)	
	S_9	321/3.87	1.9269	H-1→L+4 (15%) H-1→L+5 (31%) H→L+4 (31%) H→L+5 (15%)	a-PhCl/b-PhCl/PhenA/PhenB →Zn/PhenA/PhenB/a-PhCl/b-PhCl (LMCT, ILCT) a-PhCl/b-PhCl/PhenA/PhenB →Zn/ PhenA/PhenB/a-PhCl/b-PhCl (ILCT, LMCT) a-PhCl/b-PhCl/PhenA/PhenB →Zn/PhenA/PhenB/a-PhCl/b-PhCl (LMCT, ILCT) a-PhCl/b-PhCl/PhenA/PhenB →Zn/PhenA/PhenB/a-PhCl/b-PhCl (LMCT, ILCT)	340
	S_5	359/ 3.45	0.3793	H-1→L+2 (14%) H-1→L+3 (29%) H→L+2 (30%) H→L+3 (14%)	a-PhCl/b-PhCl/PhenA/PhenB →Zn/PhenA/PhenB (LMCT/ILCT) a-PhCl/b-PhCl/PhenA/PhenB →PhenA/PhenB (LLCT/ILCT) a-PhCl/b-PhCl/PhenA/PhenB →Zn/PhenA/PhenB (LMCT/LLCT/ILCT) a-PhCl/b-PhCl/PhenA/PhenB →PhenA/PhenB (LLCT/ILCT)	360

$(P3)_2Zn$	S_{31}	4.61/ 269	1.1632	H-7→L (14%) H-6→L (14%) H-3→L+4 (19%) H-2→L+5 (17%)	b-$PhNO_2$ →Zn/PhenA/PhenB (LMCT/LLCT) a-$PhNO_2$ → Zn/PhenA/PhenB (LMCT/LLCT) a-$PhNO_2$/b-$PhNO_2$→ PhenA/PhenB/ a-$PhNO_2$/b-$PhNO_2$ (LLCT/ILCT) a-$PhNO_2$/b-$PhNO_2$→ PhenA/PhenB/ a-$PhNO_2$/b-$PhNO_2$ (LLCT/ILCT)	
	S_{29}	4.57/271	0.1147	H-5→L+2 (39%) H-4→L+3 (40%)	b-$PhNO_2$→ PhenA/PhenB (LLCT) a-$PhNO_2$→ PhenA/PhenB (LLCT)	240 270
	S_{27}	4.37/ 284	0.1036	H-2→L+5 (13%) H-1→L+7 (16%) H→L+6 (31%)	a-$PhNO_2$/b-$PhNO_2$→ PhenA/PhenB/ a-$PhNO_2$/b-$PhNO_2$ (LLCT/ILCT) a-$PhNO_2$/ PhenA→ PhenA/PhenB/ a-$PhNO_2$/b-$PhNO_2$ (LLCT/ILCT) b-$PhNO_2$/ PhenB→ PhenA/PhenB/ a-$PhNO_2$/b-$PhNO_2$ (LLCT/ILCT)	
	S_{21}	4.21/294	0.4241	H-3→L+2 (21%) H-2→L+3 (22%)	a-$PhNO_2$/b-$PhNO_2$→ PhenA/PhenB (LLCT) a-$PhNO_2$/b-$PhNO_2$→ PhenA/PhenB (LLCT)	350
	S_3	3.24/ 383	1.2025	H-1→L+1 (22%) H-1→L+2 (15%) H→L (25%) H→L+2 (11%) H→L+3 (15%)	a-$PhNO_2$/ PhenA→ Zn/PhenA/PhenB (LMCT/LLCT/ILCT) a-$PhNO_2$/ PhenA→ PhenA/PhenB (LLCT/ILCT) b-$PhNO_2$/ PhenB→ Zn/PhenA/PhenB (LMCT/LLCT) b-$PhNO_2$/ PhenB→ PhenA/PhenB (ILCT/LLCT) b-$PhNO_2$/ PhenB→ PhenA/PhenB (ILCT/LLCT)	

	S_1	3.09/ 402	0.6661	H-1→L+1 (25%) H-1→L+2 (14%) H→L (26%) H→L+3 (14%)	a-$PhNO_2$/ PhenA→ Zn/PhenA/PhenB (LMCT/LLCT/ILCT) a-$PhNO_2$/ PhenA→ PhenA/PhenB (ILCT/LLCT) b-$PhNO_2$/ PhenB→ Zn/PhenA/PhenB (LMCT/LLCT) b-$PhNO_2$/ PhenB→ PhenA/PhenB (ILCT/LLCT)	420

* PhenA(B), a(b)-PhPn represent the imidazoline fused phenanthroline and substituted phenyl units, respectively of ligand A(B)

Table S2. Calculated absorption of **$(Pn)_2Zn$) (n=1,2,3)** complexes in aqueous media at TD-PBE1PBE level of theory along with experimental values.

	State	λ(nm)/E(eV)	Oscillator	Main configuration	Assign	λexp (nm)
$(P1)_2Zn$	S_{23}	282/ 4.40	0.3185	H-7→L (19%) H-6 →L+1 (17%)	PhenA/PhenB →PhenA/PhenB (ILCT) PhenA/PhenB →PhenA/PhenB (ILCT)	
	S_{20}	286/ 4.34	0.2336	H-5→L (28%) H-4→L+1 (27%) H-3 →L+3 (17%) H-2→L+2 (17%)	PhenA/a-$PhN(CH_3)_2$/b-$PhN(CH_3)_2$/PhenB →PhenA/PhenB (ILCT/LLCT) a-$PhN(CH_3)_2$/b-$PhN(CH_3)_2$/PhenA/PhenB →PhenA/PhenB (LLCT, ILCT) a-$PhN(CH_3)_2$/b-$PhN(CH_3)_2$→PhenA/PhenB (LLCT) a-$PhN(CH_3)_2$/b-$PhN(CH_3)_2$→PhenA/PhenB (LLCT)	
	S_{19}	286/ 4.34	0.2724	H-5→L+1(26%)	PhenA/a-$PhN(CH_3)_2$/b-$PhN(CH_3)_2$/PhenB→PhenA/PhenB (LLCT, ILCT) a-$PhN(CH_3)_2$/b-$PhN(CH_3)_2$/PhenA/PhenB	294

				H-4 →L (27%) H-3 →L+2 (18%) H-2 →L+3 (18%)	→PhenA/PhenB (LLCT, ILCT) a-PhN$(CH_3)_2$/b-PhN$(CH_3)_2$→PhenA/PhenB (LLCT) a-PhN$(CH_3)_2$/b-PhN$(CH_3)_2$→PhenA/PhenB (LLCT)	
	S_9	359/ 3.45	2.2719	H-1→L+5 (49%) H→L+4 (49%)	a-PhN$(CH_3)_2$/b-PhN$(CH_3)_2$→a-PhN$(CH_3)_2$/b-PhN$(CH_3)_2$/PhenA/PhenB (ILCT,LLCT) a-PhN$(CH_3)_2$/b-PhN$(CH_3)_2$→a-PhN$(CH_3)_2$/b-PhN$(CH_3)_2$/PhenA/PhenB (ILCT,LLCT)	349
$(P2)_2Zn$	S_{17}	276/ 4.50	0.4522	H-7→L (11%) H-6→L+1 (11%) H-5→L (12%) H-4→L+1 (13%) H-3→L+3 (20%) H-2→L+2 (20%)	a-PhCl/b-PhCl→Zn/PhenA/PhenB (LMCT/LLCT) a-PhCl/b-PhCl→Zn/PhenA/PhenB (LMCT/LLCT) a-PhCl/b-PhCl/PhenA/PhenB →Zn/PhenA/PhenB (LLCT/LMCT/ILCT) a-PhCl/b-PhCl/PhenA/PhenB →Zn/PhenA/PhenB (LLCT/LMCT/ILCT) a-PhCl/b-PhCl →PhenA/PhenB (LLCT) a-PhCl/b-PhCl →Zn/PhenA/PhenB (LMCT/LLCT)	275
	S_{12}	291/ 4.27	0. 3293	H-3→L (40%) H-2→L+1 (39%)	a-PhCl/b-PhCl →Zn/PhenA/PhenB (LMCT/LLCT) a-PhCl/b-PhCl →Zn/PhenA/PhenB (LMCT/LLCT)	298
	S_{11}	291/ 4.27	0.3261	H-3→L+1 (40%) H-2→L (39%)	a-PhCl/b-PhCl →Zn/PhenA/PhenB (LMCT/LLCT) a-PhCl/b-PhCl →Zn/PhenA/PhenB	

					(LMCT/LLCT)	
	S_5	345/ 3.59	0.4540	H-1→L+2 (30%) H-1→L+3 (14%) H→L+2 (14%) H→L+3 (29%)	a-PhCl/b-PhCl/PhenA/PhenB →Zn/PhenA/PhenB (LMCT/LLCT/ILCT) a-PhCl/b-PhCl/PhenA/PhenB →PhenA/PhenB (LLCT/ILCT) a-PhCl/b-PhCl/PhenA/PhenB →Zn/PhenA/PhenB (LMCT/LLCT/ILCT) a-PhCl/b-PhCl/PhenA/PhenB →PhenA/PhenB (LLCT/ILCT)	340
	S_4	367/ 3.37	0.0000	H-1→L (16%) H-1→L+1 (33%) H→L (33%) H→L+1 (16%)	a-PhCl/b-PhCl/PhenA/PhenB →Zn/PhenA/PhenB (LMCT/LLCT/ILCT) a-PhCl/b-PhCl/PhenA/PhenB →Zn/PhenA/PhenB (LMCT/LLCT/ILCT) a-PhCl/b-PhCl/PhenA/PhenB →Zn/PhenA/PhenB (LMCT/LLCT/ILCT) a-PhCl/b-PhCl/PhenA/PhenB →Zn/PhenA/PhenB (LMCT/LLCT/ILCT)	360
$(P3)_2Zn$	S_{39}	5.03/ 247	0.0170	H-7→L (24%) H-6→L+1 (23%)	b-$PhNO_2$ →Zn/PhenA/PhenB (LMCT/LLCT) a-$PhNO_2$ → Zn/PhenA/PhenB (LMCT/LLCT)	240
	S_{29}	4.80/ 259	1.2040	H-7→L (11%) H-3→L+4 (17%) H-2→L+5 (17%)	b-$PhNO_2$ →Zn/PhenA/PhenB (LMCT/LLCT) a-$PhNO_2$/b-$PhNO_2$→ PhenA/PhenB/ a-$PhNO_2$/b-$PhNO_2$ (LLCT/ILCT) a-$PhNO_2$/b-$PhNO_2$→ PhenA/PhenB/ a-$PhNO_2$/b-$PhNO_2$ (LLCT/ILCT)	
	S_{25}	4.56/ 272	0.0625	H-2→L+5 (12%) H→L+6(28%)	a-$PhNO_2$/b-$PhNO_2$→ PhenA/PhenB/ a-$PhNO_2$/b-$PhNO_2$ (LLCT/ILCT) b-$PhNO_2$/ PhenB→ PhenA/PhenB/ a-$PhNO_2$/b-$PhNO_2$ (LLCT/ILCT)	

	S_{18}	4.33/ 286	0.3668	H-3→L+3 (33%) H-2→L+2 (33%)	a-$PhNO_2$/b-$PhNO_2$→ PhenA/PhenB (LLCT) a-$PhNO_2$/b-$PhNO_2$→ PhenA/PhenB (LLCT)	270
	S_{17}	4.33/ 286	0.3960	H-3→L+3 (30%) H-2→L+3 (30%)	a-$PhNO_2$/b-$PhNO_2$→ PhenA/PhenB (LLCT) a-$PhNO_2$/b-$PhNO_2$→ PhenA/PhenB (LLCT)	
	S_3	3.41/364	1.3587	H-1→L+1 (19%) H-1→L+2 (17%) H-1→L+3 (12%) H→L (21%) H→L+2 (13%) H→L+3 (17%)	a-$PhNO_2$/ PhenA→ Zn/PhenA/PhenB (LMCT/LLCT/ILCT) a-$PhNO_2$/ PhenA→ PhenA/PhenB (LLCT/ILCT) a-$PhNO_2$/ PhenA→ PhenA/PhenB (LLCT/ILCT) b-$PhNO_2$/ PhenB→ Zn/PhenA/PhenB (LMCT/LLCT) b-$PhNO_2$/ PhenB→ PhenA/PhenB (ILCT/LLCT) b-$PhNO_2$/ PhenB→ PhenA/PhenB (ILCT/LLCT)	350
	S_1	3.22/ 385	0.6854	H-1→L+1 (29%) H-1→L+2 (11%) H→L (30%)	a-$PhNO_2$/ PhenA→ Zn/PhenA/PhenB (LMCT/LLCT/ILCT) a-$PhNO_2$/ PhenA→ PhenA/PhenB (ILCT/LLCT) b-$PhNO_2$/ PhenB→ Zn/PhenA/PhenB	420

				H→L+3 (12%)	(LMCT/LLCT) b-$PhNO_2$/ PhenB→ PhenA/PhenB (ILCT/LLCT)	

* PhenA(B), a(b)-PhPn represent the imidazoline fused phenanthroline and substituted phenyl units, respectively of ligand A(B)

Table S3. Calculated absorption of **$(Pn)_2Zn$ (n=1,2,3)** complexes in aqueous media at TD-M06-2X level of theory along with experimental values.

	State	λ(nm)/E(eV)	Oscillator	Main configuration	Assign	λexp (nm)
$(P1)_2Zn$	S_{13}	275/ 4.51	0.2296	H-5→L (27%) H-4→L+1 (27%)	PhenA/a-$PhN(CH_3)_2$/b-$PhN(CH_3)_2$/PhenB→PhenA/PhenB (LLCT, ILCT) a-$PhN(CH_3)_2$/b-$PhN(CH_3)_2$/PhenA/PhenB →PhenA/PhenB (LLCT, ILCT)	294
	S_7	313/ 3.96	1.7008	H-1→L+5 (39%) H →L+4 (39%)	a-$PhN(CH_3)_2$/b-$PhN(CH_3)_2$→a-$PhN(CH_3)_2$/b-$PhN(CH_3)_2$/PhenA/PhenB (ILCT,LLCT) a-$PhN(CH_3)_2$/b-$PhN(CH_3)_2$→a-$PhN(CH_3)_2$/b-$PhN(CH_3)_2$/PhenA/PhenB (ILCT,LLCT)	
	S_3	350/ 3.54	1.1359	H-1→L+3 (40%) H→L+2 (40%)	a-$PhN(CH_3)_2$/b-$PhN(CH_3)_2$→PhenA/PhenB (LLCT) a-$PhN(CH_3)_2$/b-$PhN(CH_3)_2$→PhenA/PhenB (LLCT)	349
$(P2)_2Zn$	S_{11}	250 / 4.95	1.0126	H-3→L+3 (35%) H-2→L+2 (35%)	a-PhCl/b-PhCl→PhenA/PhenB (LLCT) a-PhCl/b-PhCl→Zn/PhenA/PhenB (LMCT/LLCT)	275
	S_{10}	268/4.63	0.4898	H-3→L (29%) H-2→L+1 (29%)	a-PhCl/b-PhCl →Zn/PhenA/PhenB (LMCT/LLCT) a-PhCl/b-PhCl →Zn/PhenA/PhenB (LMCT/LLCT)	

	S_9	268/4.63	0.5645	H-3→L+1 (29%) H-2→L (29%)	a-PhCl/b-PhCl →Zn/PhenA/PhenB (LMCT/LLCT) a-PhCl/b-PhCl→Zn/PhenA/PhenB (LMCT/LLCT)	
	S_5	282/ 4.39	1.5494	H-1→L+4 (22%) H-1→L+5 (14%) H→L+4(14%) H→L+5 (22%)	a-PhCl/b-PhCl/PhenA/PhenB →Zn/a-PhCl/b-PhCl/PhenA/PhenB (LMCT/LLCT/ILCT) a-PhCl/b-PhCl/PhenA/PhenB →Zn/a-PhCl/b-PhCl/PhenA/PhenB (LMCT/LLCT/ILCT) a-PhCl/b-PhCl/PhenA/PhenB →Zn/a-PhCl/b-PhCl/PhenA/PhenB (LMCT/LLCT/ILCT) a-PhCl/b-PhCl/PhenA/PhenB →Zn/a-PhCl/b-PhCl/PhenA/PhenB (LMCT/LLCT/ILCT)	298
	S_3	308/ 4.03	0.7425	H-1→L+2 (25%) H-1→L+3 (16%) H→L+2 (16%) H→L+3 (25%)	a-PhCl/b-PhCl/PhenA/PhenB →Zn/PhenA/PhenB (LMCT/LLCT/ILCT) a-PhCl/b-PhCl/PhenA/PhenB →PhenA/PhenB (LLCT/ILCT) a-PhCl/b-PhCl/PhenA/PhenB →Zn/PhenA/PhenB (LMCT/LLCT/ILCT) a-PhCl/b-PhCl/PhenA/PhenB →PhenA/PhenB (LLCT/ILCT)	
	S_1	346/3.59	0.3926	H-1→L (28%) H-1 →L+1(18%) H →L (18%) H→L+1 (28%)	a-PhCl/b-PhCl/PhenA/PhenB →Zn/PhenA/PhenB (LMCT/LLCT/ILCT) a-PhCl/b-PhCl/PhenA/PhenB →Zn/PhenA/PhenB (LMCT/LLCT/ILCT) a-PhCl/b-PhCl/PhenA/PhenB →Zn/PhenA/PhenB (LMCT/LLCT/ILCT) a-PhCl/b-PhCl/PhenA/PhenB →Zn/PhenA/PhenB (LMCT/LLCT/ILCT)	340 360

$(P3)_2Zn$	S_{21}	5.36/ 231	0.6037	H-1→L+6 (17%) H-1→L+7 (15%) H→L+6 (16%) H→L+7 (18%)	a-$PhNO_2$/ PhenA→ PhenA/PhenB/ a-$PhNO_2$/b-$PhNO_2$ (LLCT/ILCT) a-$PhNO_2$/ PhenA→ PhenA/PhenB/ a-$PhNO_2$/b-$PhNO_2$ (LLCT/ILCT) b-$PhNO_2$/ PhenB→ PhenA/PhenB/ a-$PhNO_2$/b-$PhNO_2$ (LLCT/ILCT) b-$PhNO_2$/ PhenB→ PhenA/PhenB/ a-$PhNO_2$/b-$PhNO_2$ (LLCT/ILCT)	240
	S_{17}	4.93/ 252	0.4260	H+3→L+5 (22%) H+2→L+4 (22%)	a-$PhNO_2$/b-$PhNO_2$→ PhenA/PhenB/ a-$PhNO_2$/b-$PhNO_2$ (LLCT/ILCT) a-$PhNO_2$/b-$PhNO_2$→ PhenA/PhenB/ a-$PhNO_2$/b-$PhNO_2$ (LLCT/ILCT)	
	S_{11}	4.66/ 266	0.5779	H+3→L+3 (15%) H+2→L+2 (19%) H→L+5 (14%)	a-$PhNO_2$/b-$PhNO_2$→ PhenA/PhenB (LLCT) a-$PhNO_2$/b-$PhNO_2$→ PhenA/PhenB (LLCT) b-$PhNO_2$/ PhenB→ PhenA/PhenB/ a-$PhNO_2$/b-$PhNO_2$ (LLCT/ILCT)	270
	S_3	3.67/ 337	1.3678	H-1→L+2 (18%) H-1→L+3 (17%) H→L+2 (21%) H→L+3 (20%)	a-$PhNO_2$/ PhenA→ PhenA/PhenB (LLCT) a-$PhNO_2$/ PhenA→ PhenA/PhenB (LLCT) b-$PhNO_2$/ PhenB→ PhenA/PhenB (LLCT) b-$PhNO_2$/ PhenB→ PhenA/PhenB (LLCT)	350 420
	S_1	3.95/ 314	1.0172	H-1→L+1 (40%) H→L (41%)	a-$PhNO_2$/ PhenA→ Zn/PhenA/PhenB (LMCT/LLCT/ILCT) b-$PhNO_2$/ PhenB→ Zn/PhenA/PhenB (LMCT/LLCT/ILCT)	

* PhenA(B), a(b)-PhL*n* represent the imidazoline fused phenanthroline and substituted phenyl units, respectively of ligand A(B)

Table S4. Calculated absorption of ($(Pn)_2Zn$-ATP) (n=1,2,3) complexes in aqueous media at TD-B3LYP level of theory along with experimental values.

	State	λ(nm)/E(eV)	Oscillator	Main configuration	Assign	λexp (nm)
$(P1)_2$Zn-ATP	S_{36}	277/4.48	0.1014	H-13→L (20%) H-11→L+1 (31%) H-6→L+1 (12%)	Zn/ATP/ PhenA/PhenB →PhenA (MLCT/LLCT/ILCT) Zn/ATP→PhenA/PhenB (MLCT/LLCT) ATP →PhenA/PhenB (LLCT)	
	S_{35}	277/4.47	0.1505	H-6→L+2 (16%) H-5→L+3 (22%)	ATP →PhenA/PhenB (LLCT) ATP/Zn/PhenB/b-PhN$(CH_3)_2$ →PhenB/b-PhN$(CH_3)_2$ (MLCT/LLCT/ILCT)	
	S_{34}	278/4.47	0.2473	H-6→L+1 (21%)	ATP →PhenA/PhenB (LLCT)	
	S_{32}	279/ 4.45	0.7078	H-6→L+1 (12%) H-6→L+3 (12%) H-5→L+2 (13%) H→L+8 (17%)	ATP →PhenA/PhenB (LLCT) ATP →PhenB/b-PhN$(CH_3)_2$ (LLCT) ATP/Zn/PhenB/b-PhN$(CH_3)_2$ → PhenA/PhenB/a-PhN$(CH_3)_2$ (MLCT/LLCT/ILCT) PhenB/b-PhN$(CH_3)_2$ →PhenA/a-PhN$(CH_3)_2$ (LLCT)	265 287
	S_{31}	280/ 4.43	0.2072	H-5→L+1 (39%) H-4→L+3 (18%) H-3→L+3 (14%)	ATP/Zn/PhenB/b-PhN$(CH_3)_2$ →PhenA/PhenB (LLCT/ILCT/MLCT) ATP/ PhenB/b-PhN$(CH_3)_2$→PhenB/b-PhN$(CH_3)_2$ (LLCT/ILCT) Zn/ATP→PhenB/b-PhN$(CH_3)_2$ (MLCT/LLCT)	

	S_{10}	341/3.64	0.5088	H-1→L+4 (26%) H-1→L+5 (62%)	PhenA/a-PhN$(CH_3)_2$ →PhenA/a-PhN$(CH_3)_2$ (ILCT) PhenA/a-PhN$(CH_3)_2$ →PhenB/b-PhN$(CH_3)_2$ (LLCT)	375
	S_9	347/ 3.57	1.5421	H→ L+4 (83%)	PhenB/b-PhN$(CH_3)_2$ →PhenA/a-PhN$(CH_3)_2$ (LLCT)	
	S_6	401/ 3.09	0.1990	H-1→L+2 (56%) H-1 → L+3 (38%)	PhenA/a-PhN$(CH_3)_2$ →PhenA/PhenB/a-PhN$(CH_3)_2$ (ILCT/LLCT) PhenA/a-PhN$(CH_3)_2$ →PhenB/b-PhN$(CH_3)_2$ (LLCT)	
	S_5	405/ 3.06	0.2002	H→ L+2 (73%) H→ L+3 (24%)	PhenB/b-PhN$(CH_3)_2$ →PhenA/PhenB/a-PhN$(CH_3)_2$ (ILCT/LLCT) PhenB/b-PhN$(CH_3)_2$ →PhenB/b-PhN$(CH_3)_2$ (LLCT)	
$(P2)_2$Zn-ATP	S_{25}	275/4.51	0.1958	H-4 →L+2 (52%) H-3 →L+3 (13%)	ATP/Zn/PhenA →PhenA (MLCT/ILCT/LLCT) PhenA/a-PhCl→PhenA/a-PhCl/PhenB/b-PhCl (LLCT/ILCT)	250 279 295
	S_{24}	276/ 4.48	0.5036	H-3→ L+3 (40%)	PhenA/a-PhCl→PhenA/a-PhCl/PhenB/b-PhCl (LLCT/ILCT)	
	S_{19}	283/ 4.39	0.3599	H-4→ L (62%) H-3→ L+1 (11%)	ATP/Zn/PhenA →PhenA (LLCT/MLCT/ILCT) PhenA/a-PhCl →PhenA/a-PhCl (ILCT)	
	S_{18}	285/4.36	0.1307	H-4→ L (12%) H-3→ L+1 (64%)	ATP/Zn/PhenA →PhenA (LLCT/MLCT/ILCT) PhenA/a-PhCl →PhenA/a-PhCl (ILCT)	
	S_{12}	308/ 4.02	0.3932	H→ L+5 (64%)	PhenB/b-PhCl →PhenB/b-PhCl (ILCT)	
	S_{10}	313/ 3.96	0.9664	H-1 → L+4	PhenA/a-PhCl →PhenA/PhenB/a-PhCl/b-	

				(70%) H→ L+4(11%)	PhCl (ILCT/LLCT) PhenB/b-PhCl →PhenA/PhenB/a-PhCl/b-PhCl (ILCT/LLCT)	
	S_6	335/ 3.70	0.2538	H→ L+2 (11%) H → L+3 (68%)	PhenB/b-PhCl → PhenA (LLCT) PhenB/b-PhCl →PhenA/a-PhCl/PhenB/b-PhCl (LLCT/ILCT)	340
	S_5	337/3.68	0.3874	H-1→L+2 (72%) H→L+2 (12%)	PhenA/a-PhCl →PhenA (ILCT/LLCT) PhenB/b-PhCl →PhenA (LLCT)	
	S_1	3.30/ 376	0.1632	H-1→L (55%) H→L+1 (42%)	PhenA/a-PhCl →PhenA (LLCT/ILCT) PhenB/b-PhCl →PhenA/a-PhCl (LLCT)	
$(P3)_2$Zn-ATP	S_{37}	282/4.40	0.2255	H-4 →L+4 (13%) H-1→L+6 (51%)	ATP →PhenB (LLCT) PhenB/b-$PhNO_2$ → PhenA/a-$PhNO_2$ (LLCT)	
	S_{34}	283/ 4.39	0.1541	H-3 →L+3 (43%) H→L+7 (16%)	Zn/ATP → PhenA/a-$PhNO_2$/PhenB (LLCT) ATP→ a-$PhNO_2$ (LLCT)	260 312
	S_{11}	331/ 3.74	0.0325	H-3 → L+1 (73%) H → L+5 (17%)	Zn/ATP → b-$PhNO_2$/PhenB (MLCT/LLCT) ATP→ b-$PhNO_2$/PhenB (LLCT)	330
	S_1	411/3.02	1.3259	H-1 → L (24%) H → L+1 (70%)	b-$PhNO_2$/PhenB → a-$PhNO_2$/PhenA (LLCT) ATP → b-$PhNO_2$/PhenB (LLCT)	440

* PhenA(B), a(b)-PhPn represent the imidazoline fused phenanthroline and substituted phenyl units, respectively of ligand A(B)

Table S5. Calculated absorption of ($(Pn)_2$Zn-ATP) (n=1,2,3) complexes in aqueous media at TD-PBE1PBE level of theory along with experimental values.

	State	λ(nm)/E(eV)	Oscillator	Main configuration	Assign	λexp (nm)
$(P1)_2$Zn-ATP	S_{35}	267/ 4.63	0.1722	H-6→L+1 (48%) H-4→L+3 (14%)	ATP → PhenA/PhenB (LLCT) ATP/ PhenB/b-PhN$(CH_3)_2$→ PhenB/b-PhN$(CH_3)_2$ (LLCT/ILCT)	
	S_{27}	271/4.57	0.5235	H-6→L (12%) H-5→L (29%) H-3→L+3 (12%)	ATP → PhenA (LLCT) ATP/Zn/PhenB/b-PhN$(CH_3)_2$ → PhenA (MLCT/LLCT) Zn/ATP→ PhenB/b-PhN$(CH_3)_2$ (MLCT/LLCT)	265 287
	S_{26}	274/ 4.53	0.2158	H-6→L (17%) H-5→L (19%) H-3→L+2 (42%)	ATP → PhenA (LLCT) ATP/Zn/PhenB/b-PhN$(CH_3)_2$ → PhenA (MLCT/LLCT) Zn/ATP→ PhenA/PhenB/a-PhN$(CH_3)_2$ (MLCT/LLCT)	
	S_{10}	329/3.76	0.5808	H-1→L+4 (21%) H-1→L+5 (67%)	PhenA/a-PhN$(CH_3)_2$ → PhenA/a-PhN$(CH_3)_2$ (ILCT) PhenA/a-PhN$(CH_3)_2$ → PhenB/b-PhN$(CH_3)_2$ (LLCT)	375
	S_9	335/3.70	1.5186	H→L+4 (81%)	PhenB/b-PhN$(CH_3)_2$ → PhenA/a-PhN$(CH_3)_2$ (LLCT)	
	S_6	381/ 3.26	0.2339	H-1→L+2 (81%) H-1→L+3 (43%)	PhenA/a-PhN$(CH_3)_2$ → PhenA/PhenB/a-PhN$(CH_3)_2$ (LLCT/ILCT) PhenA/a-PhN$(CH_3)_2$ → PhenB/b-PhN$(CH_3)_2$ (LLCT)	
	S_5	384/ 3.22	0.2708	H→L+2 (65%) H→L+3 (31%)	PhenB/b-PhN$(CH_3)_2$ → PhenA/PhenB/a-PhN$(CH_3)_2$ (ILCT/LLCT) PhenB/b-PhN$(CH_3)_2$ → PhenB/b-PhN$(CH_3)_2$ (ILCT)	

$(P2)_2$Zn-ATP	S_{40}	243/5.10	0.0616	H-4 → L+4 (48%)	ATP/Zn/PhenA → PhenA/PhenB/a-PhCl/b-PhCl (MLCT/LLCT/ILCT)	
	S_{23}	4.65/267	0.1493	H-4→L+2 (39%) H-3→L+3 (21%)	ATP/Zn/PhenA → PhenA (MCLT/LLCT/ILCT) PhenA/a-PhCl → PhenA/a-PhCl/PhenB/b-PhCl (LLCT/ILCT)	
	S_{22}	4.62/268	0.5921	H-4→L+2 (16%) H-3→L+3 (36%)	ATP/Zn/PhenA → PhenA (MLCT/ILCT/LLCT) PhenA/a-PhCl → PhenA/a-PhCl/PhenB/b-PhCl (ILCT/LLCT)	
	S_{16}	4.52/274	0.4474	H-4→L(54%) H-3→L(13%)	ATP/Zn/PhenA → PhenA (MLCT/ILCT/LLCT) PhenA/a-PhCl → PhenA (ILCT/LLCT)	
	S_{14}	4.47/278	0.2139	H-3→L(15%) H-3→ L+1 (40%) H→L+4(11%)	PhenA/a-PhCl → PhenA (ILCT/LLCT) PhenA/a-PhCl → PhenA/a-PhCl (ILCT) PhenB/b-PhCl → PhenA/PhenB/a-PhCl/b-PhCl (ILCT/LLCT)	250 279 295
	S_{10}	4.15/299	0.4099	H-1→L+3 (29%) H→L+5 (57%)	PhenA/a-PhCl → PhenA/a-PhCl/PhenB/b-PhCl (LLCT/ILCT) PhenB/b-PhCl → PhenB/b-PhCl (LLCT/ILCT)	
	S_8	4.08/304	0.8212	H-1→ L+4 (60%) H →L+4 (13)	PhenA/a-PhCl → PhenA/PhenB/a-PhCl/b-PhCl (ILCT/LLCT) PhenB/b-PhCl → PhenA/PhenB/a-PhCl/b-PhCl (ILCT/LLCT)	
	S_7	4.07/305	0.1264	H-1→L+2 (11%) H→L+2 (70%)	PhenA/a-PhCl → PhenA (ILCT/LLCT) PhenB/b-PhCl → PhenA (LLCT)	340

	S_6	3.83/324	0.2326	H→L+3 (66%)	PhenB/b-PhCl → PhenA/a-PhCl/PhenB/b-PhCl (LLCT/ILCT)	
	S_5	3.81/326	0.4165	H-1→L+2 (62%)	PhenA/a-PhCl → PhenA (LLCT/ILCT)	
	S_1	3.43/361	0.2079	H-1→L(56%) H→L+1 (40%)	PhenA/a-PhCl → PhenA (LLCT/ILCT) PhenB/b-PhCl → PhenA/a-PhCl (LLCT)	
$(P3)_2$Zn-ATP	S_{40}	4.74/ 261	0.3444	H-7→L (43%)	PhenA/a-$PhNO_2$ → a-$PhNO_2$/PhenA	
	S_{32}	4.56/ 272	0.4958	H-4 → L+2 (38%) H-1→L+6 (12%)	ATP →PhenA (LLCT) b-$PhNO_2$/PhenB → PhenA/a-$PhNO_2$ (LLCT)	
	S_{30}	4.50/ 275	0.2649	H-3→L+2 (16%) H-3→L+3 (43%) H→L+5 (13%)	Zn/ATP → PhenA (MLCT/LLCT) Zn/ATP → PhenA/a-$PhNO_2$/PhenB (MLCT/LLCT) ATP→b-$PhNO_2$/PhenB (LLCT)	260 312
	S_{13}	3.94/ 315	0.0353	H-3→L+1 (26%) H→L+5 (43%)	Zn/ATP → b-$PhNO_2$/PhenB (MLCT/LLCT) ATP→ b-$PhNO_2$/PhenB (LLCT)	
	S_2	3.24/383	0.1441	H-1→L (58%) H→L+1 (38%)	b-$PhNO_2$/PhenB → a-$PhNO_2$/PhenA (LLCT) ATP→ b-$PhNO_2$/PhenB (LLCT)	330
	S_1	3.20/ 387	1.6000	H-1→L (35%) H→L+1 (57%)	b-$PhNO_2$/PhenB → a-$PhNO_2$/PhenA (LLCT) ATP→ b-$PhNO_2$/PhenB (LLCT)	440

* PhenA(B), a(b)-PhPn represent the imidazoline fused phenanthroline and substituted phenyl units, respectively of ligand A(B)

Table S6. Calculated absorption of (($Pn)_2$Zn-ATP) (n=1,2,3) complexes in aqueous media at TD-M06-2X level of theory along with experimental values.

	State	λ(nm)/E(eV)	Oscillator	Main	Assign	λexp

				configuration		(nm)
$(P1)_2$Zn-ATP	S_{16}	4.80/ 259	0.3024	H-6→L+1 (26%) H-5→L (11%)	ATP → PhenA/PhenB (LLCT) ATP/Zn/PhenB/b-PhN$(CH_3)_2$ → PhenA (MLCT/LLCT)	
	S_{15}	4.77/ 260	0.1154	H-5→L (13%) H-1→L+2 (11%) H-1→L+3 (32%)	ATP/Zn/PhenB/b-PhN$(CH_3)_2$ → PhenA (MLCT/LLCT) PhenA/a-PhN$(CH_3)_2$ → PhenA/PhenB/a-PhN$(CH_3)_2$ (LLCT/ILCT) PhenA/a-PhN$(CH_3)_2$ → PhenB/b-PhN$(CH_3)_2$ (LLCT)	265 287
	S_{13}	4.73/262	0.1554	H-4→L+1 (13%) H→L+3 (22%)	ATP/ PhenB/b-PhN$(CH_3)_2$→ PhenA/PhenB (LLCT/ILCT) PhenB/b-PhN$(CH_3)_2$ → PhenB/b-PhN$(CH_3)_2$ (ILCT)	
	S_9	4.67/265	0.1323	H-6→L (12%) H-5→L+1 (17%) H-5→L+1 (12%) H-3→L (15%)	ATP → PhenA (LLCT) ATP/Zn/PhenB/b-PhN$(CH_3)_2$ → PhenA/PhenB (LLCT/MLCT/ILCT) ATP/Zn/PhenB/b-PhN$(CH_3)_2$ → PhenA/PhenB (LLCT/MLCT/ILCT) Zn/ATP→ PhenA (MLCT/LLCT)	
	S_6	4.27/290	0.5958	H-1→L+4 (20%) H-1→L+5 (52%)	PhenA/a-PhN$(CH_3)_2$ → PhenA/a-PhN$(CH_3)_2$ (ILCT) PhenA/a-PhN$(CH_3)_2$ → PhenB/b-PhN$(CH_3)_2$ (LLCT)	
	S_5	4.21/ 294	0.8526	H→L+4 (55%) H→L+5 (17%)	PhenB/b-PhN$(CH_3)_2$ → PhenA/a-PhN$(CH_3)_2$ (LLCT) PhenB/b-PhN$(CH_3)_2$ → PhenB/b-PhN$(CH_3)_2$ (ILCT)	
	S_4	3.89/ 319	0.4586	H-1→L+2	PhenA/a-PhN$(CH_3)_2$ → PhenA/PhenB/a-	

				(38%) H-1→L+3 (43%)	$PhN(CH_3)_2$ (LLCT/ILCT) PhenA/a-$PhN(CH_3)_2$ → PhenB/b-$PhN(CH_3)_2$ (LLCT)	375
	S_1	3.55/349	0.6041	H-1→L (15%) H→L (12%) H→L+1(48%)	PhenA/a-$PhN(CH_3)_2$ → PhenA (ILCT/LLCT) PhenB/b-$PhN(CH_3)_2$ → PhenA (LLCT) PhenB/b-$PhN(CH_3)_2$ → PhenA/PhenB (LLCT/ILCT)	
$(P2)_2$Zn-ATP	S_{19}	5.35/232	0.4463	H-2→L+7 (83%)	Zn/ATP → PhenA/a-PhCl (LLCT)	250 279 295
	S_{14}	5.08/244	0.1550	H-4→L+2 (42%) H-3→L+3 (18%)	ATP/Zn/PhenA → PhenA (MCLT/LLCT/ILCT) PhenA/a-PhCl→PhenA/a-PhCl/PhenB/b-PhCl (LLCT/ILCT)	
	S_{12}	5.05/246	0.6028	H-4→L+2 (11%) H-3→ L+3 (32%)	ATP/Zn/PhenA → PhenA (MLCT/LLCT/ILCT) PhenA/a-PhCl→PhenA/a-PhCl/PhenB/b-PhCl (LLCT/ILCT)	
	S_8	4.85/255	0.7002	H-4→L (37%)	ATP/Zn/PhenA → PhenA (MLCT/ILCT/LLCT)	
	S_7	4.78/ 259	0.3707	H-4→L (14%) H-1→L+1 (37%)	ATP/Zn/PhenA → PhenA (MLCT/ILCT/LLCT) PhenA/a-PhCl → PhenA/a-PhCl (ILCT)	
	S_6	4.58/ 271	0.4270	H-3→ L+1 (13%) H-1→ L+5 (25%) H→ L+5 (45%)	PhenA/a-PhCl→ PhenA/a-PhCl (ILCT) PhenA/a-PhCl → PhenB/b-PhCl (LLCT) PhenB/b-PhCl → PhenB/b-PhCl (ILCT)	
	S_5	4.53/274	0.8605	H-8→L+4	Zn/ATP→PhenA/PhenB/a-PhCl/b-PhCl	

				(48%) H→L+4 (28%)	(MLCT/LLCT) PhenB/b-PhCl → PhenA/PhenB/a-PhCl/b-PhCl (ILCT/LLCT)	
	S_3	4.21/ 295	0.5845	H-1→L+2 (50%) H→L+2 (26%)	PhenA/a-PhCl → PhenA (ILCT/LLCT) PhenB/b-PhCl → PhenA (LLCT)	
	S_1	3.88/319	0.4633	H-1→L (40%) H→L+1 (45%)	PhenA/a-PhCl → PhenA (LLCT/ILCT) PhenB/b-PhCl → PhenA/a-PhCl (LLCT)	340
$(P3)_2$Zn-ATP	S_{16}	4.87/ 255	0.6515	H-4→L+2 (28%) H-4→L+3 (15%) H-1→L+4 (12%) H→L (11%)	ATP →PhenA (LLCT) ATP →PhenA/a-$PhNO_2$/PhenB (LLCT) b-$PhNO_2$/PhenB → PhenB (LLCT/ILCT) ATP→ a-$PhNO_2$/PhenA (LLCT)	
	S_{15}	4.86/ 255	0.1102	H → L (63%)	ATP→ a-$PhNO_2$/PhenA (LLCT)	
	S_{14}	4.79/ 259	0.3529	H-4→L+2 (12%) H-3→L+2 (15%) H-3→L+3 (37%) H→L+5 (11%)	ATP →PhenA (LLCT) Zn/ATP → PhenA (MLCT/LLCT) Zn/ATP → PhenA/a-$PhNO_2$/PhenB (MLCT/LLCT) ATP→ PhenA/a-$PhNO_2$/PhenB (LLCT)	260 312
	S_5	4.05/ 306	0.1039	H→L+2 (23%) H→L+3 (47%)	ATP→ PhenA (LLCT) ATP→ PhenA/a-$PhNO_2$/PhenB (LLCT)	
	S_2	3.81/ 325	0.1575	H-1→L (22%)	b-$PhNO_2$/PhenB → a-$PhNO_2$/PhenA (LLCT)	

				H→L+1 (52%)	ATP→ b-$PhNO_2$/PhenB (LLCT)	330
	S_1	3.76/ 330	1.9722	H-1→L (55%) H→L+1 (18%)	b-$PhNO_2$/PhenB → a-$PhNO_2$/PhenA (LLCT) ATP→ b-$PhNO_2$/PhenB (LLCT)	440

* PhenA(B), a(b)-PhPn represent the imidazoline fused phenanthroline and substituted phenyl units, respectively of ligand A(B).

Tabel S7. Calculated HOMO-LUMO contours with energy levels (in eV) computed for the optimized geometries of (**$(Pn)_2Zn$** and $(Pn)_2Zn$ -ATP) molecules (n=1,2,3) with isosurface=0.025

	LUMO	GAP	HOMO
$(P1)_2Zn$	-7.131	**1.490**	-8.621
$(P2)_2Zn$	-7.678	**2.429**	-10.106
$(P3)_2Zn$	-7.920	**2.903**	-10.823
$(P1)_2Zn$ -ATP	-2.069	**3.064**	-5.133
$(P2)_2Zn$ -ATP	-2.453	**3.472**	-5.925
$(P3)_2Zn$ -ATP	-3.180	**2.868**	-6.048

at B3LYP/6-31g* level of theory.

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