

Electronic Supplementary Information

Modulation of ground and excited state properties of ruthenium complexes through sequential incorporation of metal in polypyridyl-imidazole bridging ligand

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Experimental details

Synthesis of the bridging ligand, 2-(4-(4,5-di(pyridine-2-yl)-1*H*-imidazole-2-yl)phenyl)-1*H*-imidazo[4,5-*f*][1,10]phenanthroline (phen-H₂PhImz-bpy)

A mixture of 4-(1*H*-imidazo[4,5-*f*][1,10]phenanthrolin-2-yl)benzaldehyde (0.32 g, 1.0 mmol), 2,2'-pyridil (0.21 g, 1.0 mmol), and ammonium acetate (2.3 g, 0.03 mol) were taken in acetic acid (25 mL) and was refluxed for 2h. The resulting solution upon pouring on crushed ice produces a yellow colored precipitate which was filtered and washed thoroughly with water. The compound was purified upon recrystallization from a methanol-chloroform (1:1, v/v) mixture and the desired compound was collected as microcrystalline yellow solid (198 mg, yield 40%), mp >300 °C. Anal. Calcd. for C₃₂H₂₀N₈: C, 74.23; H, 3.89; N, 21.65. Found: C, 74.18; H, 3.91; N, 21.61. ¹H NMR (300 MHz, DMSO-*d*₆, δ/ppm): 13.82 (s, 1H, imidazole NH), 8.78 (d, 2H, *J*=3.9 Hz, 2H₁), 8.74 (d, 4H, *J*=6.0 Hz, 2H₆+2H₃), 8.14-8.24 (m, 4H, 2H₈+2H₉), 7.88 (m, 4H, 2H₄+H₅), 7.69-7.73 (m, 2H, 2H₇), 7.61 (t, 2H, *J*=6.0 Hz, 2H₂), ESI-MS (positive, CH₃CN) *m/z* = 517.26 (100 %) [(phen-H₂PhImz-bpy)+H⁺].

Synthesis of the metal complexes

[(bpy)₂Ru(phen-H₂PhImz-bpy)](ClO₄)₂·H₂O (1). [Ru(bpy)₂Cl₂].2H₂O (0.52 g, 1.0 mmol) was dispersed in 30 mL of ethanol and solid AgClO₄ (0.45 g, 2.1 mmol) was added to it and refluxed for 1h with continuous stirring under argon protection. The white precipitate of AgCl that formed was filtered quickly and to the filtrate containing [Ru(bpy)₂(EtOH)₂]²⁺ was added solid powder of the bridging ligand (H₂L) (0.52 g, 1.0 mmol) and refluxed for 6h, during which time the color changed from red-violet to orange-yellow. The solid compound that was formed during the process was collected by filtration and purified through column chromatography (silica gel) using a mixture of acetonitrile-toluene (1:1, v/v) as the eluent. Upon evaporating the major fraction of the eluent to a small volume (~10 mL), an orange-red compound was obtained which was further purified upon recrystallization from acetonitrile-methanol (1:2 v/v) mixture in the presence of feebly acidic condition (2 drops of 10⁻⁴ M aqueous HClO₄). Yield: 85 mg (43%). Anal. Calcd. for C₅₂H₃₈ N₁₂Cl₂O₉Ru: C, 54.43; H, 3.34; N, 14.65. Found: C, 54.39; H, 3.32; N, 14.60. ¹H NMR (400 MHz, DMSO-*d*₆, δ/ppm): 14.50 and 14.35 (s, 2H, NH imidazole), 9.13 (d, 3H, *J*=8.0Hz, 3H_{3''}), 8.88-8.82 (m, 5H, H_{3''}+2H₁+2H₆), 8.53 (t, 4H, *J*=8.0 Hz, 4H_{4'}), 8.21 (t, 3H, *J*=8.0 Hz, 2H₃+H₆), 8.12-8.07 (m, 6H, 3H₆+2H₈+H₉), 7.95 (t, 2H, *J*=8.40 Hz, H₉+H₅) 7.84 (d, 3H, *J*=5.2Hz, H₅+2H₄), 7.62-7.57 (m, 5H, 2H₇+2H₂+H₅), 7.34 (t, 3H, *J*=6.4 Hz, 3H₅), ESI-MS (positive, CH₃CN)

$[(\text{bpy})_2\text{Ru}(\text{phen-H}_2\text{PhImz-bpy})]^{3+}$ ($m/z=310.45$), $[(\text{bpy})_2\text{Ru}(\text{phen-H}_2\text{PhImz-bpy})]^{2+}$ ($m/z = 465.08$) and $[(\text{bpy})_2\text{Ru}(\text{phen-H}_2\text{PhImz-bpy})]^+$ ($m/z = 929.54$).

$[(\text{bpy})_2\text{Ru}(\text{phen-H}_2\text{PhImz-bpy})\text{Ru}(\text{bpy})_2](\text{ClO}_4)_4 \cdot 2\text{H}_2\text{O}$ (2). Finely powdered form of complex **1** (0.20 g, 0.11 mmol) was dispersed in 30 mL of ethanol and solvated ruthenium(II) precursor complex, $[\text{Ru}(\text{bpy})_2(\text{EtOH})_2]^{2+}$ (obtained upon stoichiometric reaction between $[\text{Ru}(\text{bpy})_2\text{Cl}_2]^{2+}$ and AgClO_4 in ethanol) was added to it and the resulting mixture was refluxed in slightly acidic condition under argon protection for 8h. On cooling down to room temperature, an intense red colored precipitate formed which was collected by filtration. The precipitate was dissolved in small amount of acetonitrile and then loaded into a silica gel column and eluted with solvents with different polarities. The principal fraction on rotary evaporation to a small volume (~5 mL) gives rise to the desired product. Further purification was achieved upon recrystallization from an acetonitrile-methanol (1:1, v/v) mixture in the presence of slightly acidic condition (2 drops of aqueous 10^{-4} M HClO_4). (Yield 90 mg 58%). Anal. Calcd. for $\text{C}_{72}\text{H}_{56}\text{N}_{16}\text{Cl}_4\text{O}_{18}\text{Ru}_2$: C, 48.63; H, 3.17; N, 12.60. Found: C, 48.53; H, 3.13; N, 12.55. ^1H NMR (400 MHz, $\text{DMSO-}d_6$, δ/ppm): 14.40 and 14.21 (s, 2H, NH imidazole), 9.08 (d, 2H, $J=8.4\text{Hz}$, $2\text{H}_{3''}$), 8.88-8.82 (m, 9H, $6\text{H}_{3''}+2\text{H}_1+2\text{H}_6$), 8.69 (d, 1H, $J=7.6$ Hz, H_6), 8.64 (d, 1H, $J=8.0$ Hz, H_3), 8.31 (s, 1H, H_3), 8.23 (t, 3H, $J=7.8$ Hz, $3\text{H}_4'$), 8.11-8.00 (m, 5H, $3\text{H}_4'+2\text{H}_6'$), 7.99-7.90 (m, 2H, $2\text{H}_4'$), 7.85 (d, 4H, $J=5.6$ Hz, $2\text{H}_4'+2\text{H}_5$), 7.72-7.69 (t, 2H, $J=6.2$ Hz, 2H_8), 7.59 (d, 8H, $J=4$ Hz, $2\text{H}_2+4\text{H}_6'+2\text{H}_9$), 7.52 (t, 3H, $J=8.2$ Hz, $\text{H}_6'+2\text{H}_7$), 7.40 (t, 1H, $J=6.8$ Hz, H_5), 7.35 (t, 6H, $J=6.0$ Hz, $5\text{H}_5'+\text{H}_6$), 7.28 (t, 2H, $J=7.6$ Hz, 2H_5), ESI-MS (positive, CH_3CN) $[(\text{bpy})_2\text{Ru}(\text{phen-H}_2\text{PhImz-bpy})\text{Ru}(\text{bpy})_2]^{4+}$ ($m/z=335.86$), $[(\text{bpy})_2\text{Ru}(\text{phen-H}_2\text{PhImz-bpy})\text{Ru}(\text{bpy})_2]^{3+}$ ($m/z = 447.81$) and $[(\text{bpy})_2\text{Ru}(\text{phen-H}_2\text{PhImz-bpy})\text{Ru}(\text{bpy})_2]^{2+}$ ($m/z = 670.72$)

$[(\text{bpy})_2\text{Ru}(\text{phen-HPhImz-bpy})\text{Ru}_2(\text{bpy})_4](\text{ClO}_4)_5 \cdot 4\text{H}_2\text{O}$ (3).

$[\text{Ru}(\text{bpy})_2(\text{EtOH})_2]^{2+}$ and complex **2** (0.05 g, 0.10 mmol) were mixed in 1:1 molar ratio and the mixture was refluxed in presence of triethylamine (0.45g, 0.40 mmol) under argon protection for 8h. On reaching at room temperature, a red-violet compound that deposited was collected by filtration and purified by silica gel column eluting with acetonitrile-water (10:1, v/v) mixture. Upon removal of acetonitrile, the desired compound gets precipitated and filtered. The compound was again recrystallized from 1:1 (v/v) acetonitrile-water mixture. (Yield 78 mg 60%). Anal. Calcd. for $\text{C}_{92}\text{H}_{75}\text{N}_{20}\text{Cl}_5\text{O}_{24}\text{Ru}_3$: C, 47.50; H, 3.25; N, 12.04.

Found: C, 47.45; H, 3.23; N, 11.99. ^1H NMR (400 MHz, $\text{DMSO-}d_6$, δ/ppm): 14.00 (s, 1H, NH imidazole), 9.25 (d, 2H, $J=7.6\text{Hz}$, $2\text{H}_{3''}$), 8.86-8.82 (m, 4H, $4\text{H}_{3''}$), 8.77 (t, 2H, $J=7.8\text{ Hz}$, 2H_1), 8.62-8.58 (m, 7H, $6\text{H}_{3''}+\text{H}_6$), 8.49 (d, 1H, $J=8.4\text{ Hz}$, H_6), 8.29 (t, 1H, $J=5.4\text{ Hz}$, H_4), 8.23-8.20 (t, 4H, $J=7.4\text{ Hz}$, $2\text{H}_3+2\text{H}_4$), 8.11-8.05 (m, 13H, $9\text{H}_4+2\text{H}_6+2\text{H}_9$), 8.00-7.97 (m, 4H, H_4+3H_6), 7.84 (d, 3H, $J=6.0\text{ Hz}$, H_4+2H_5), 7.73 (t, 1H, $J=6.4\text{ Hz}$, H_8), 7.60 (d, 6H, $J=5.6\text{ Hz}$, 6H_6), 7.50 (t, 7H, $J=6.2\text{ Hz}$, $2\text{H}_2+2\text{H}_5+2\text{H}_7+\text{H}_8$), 7.35 (t, 7H, $J=5.6\text{ Hz}$, $6\text{H}_5+\text{H}_6$), 7.27 (t, 4H, $J=6.4\text{ Hz}$, 4H_5). ESI-MS (positive, CH_3CN) $[(\text{bpy})_2\text{Ru}(\text{phen-HPhImz-bpy})\text{Ru}_2(\text{bpy})_4]^{4+}$ ($m/z=438.78$), $[(\text{bpy})_2\text{Ru}(\text{phen-HPhImz-bpy})\text{Ru}_2(\text{bpy})_4]^{3+}$ ($m/z=618.13$) and $[(\text{bpy})_2\text{Ru}(\text{phen-HPhImz-bpy})\text{Ru}_2(\text{bpy})_4]^{2+}$ ($m/z=977.88$).

Alternative route for the synthesis of $[(\text{bpy})_2\text{Ru}(\text{phen-HPhImz-bpy})\text{Ru}_2(\text{bpy})_4](\text{ClO}_4)_5\cdot 4\text{H}_2\text{O}$ (3).

A mixture of $[\text{Ru}(\text{bpy})_2(\text{EtOH})_2]^{2+}$ (0.00 g, 0.75 mmol), powered phen- $\text{H}_2\text{PhImz-bpy}$ ligand (0.15 g, 0.25 mmol) and triethylamine (0.05 g, 0.5 mmol) in 50 mL of ethanol-water (1:1) was refluxed for overnight under argon protection. The resulting solution was filtered to remove unreacted ligand and suspended particle and the filtrate on gradual evaporation gives rise to a red-violet solid. The solid was filtered and successively purified through silica gel column chromatography and recrystallization techniques as mentioned earlier. Yield 145 mg (55%).

Physical measurements

Electronic absorption spectra were obtained with a Shimadzu UV 1800 spectrophotometer at room temperature. Quartz cuvettes with a 1 cm path length and a 3 cm^3 volume were used for all measurements.

Emission spectra were recorded on Perkin-Elmer LS55 fluorescence spectrophotometer. The room temperature (298 K) spectra were obtained using a 1 cm path length quartz cell. For all measurements, same slit widths for excitation and emission were maintained. Quantum yields were determined in freeze-thaw-pump degassed solutions of the complexes by a relative method using $[\text{Ru}(\text{bpy})_3]^{2+}$ in the same solvent as the standard. The quantum yields were calculated by using the equation (2),

$$\Phi_{\text{r}} = \Phi_{\text{std}} \frac{A_{\text{std}}}{A_{\text{r}}} \frac{I_{\text{r}}}{I_{\text{std}}} \frac{\eta_{\text{r}}^2}{\eta_{\text{std}}^2} \quad (2)$$

where Φ_r and Φ_{std} are the quantum yields of unknown and standard samples at $\lambda_{\text{ex}} = 450 \text{ nm}$, A_r and A_{std} (<0.1) are the solution absorbances at the excitation wavelength (λ_{ex}), I_r and I_{std} are the integrated emission intensities, and η_r and η_{std} are the refractive indices of the solvent. Experimental errors in the reported luminescence quantum yields were about 20%.

Time-correlated single-photon-counting (TCSPC) measurements were carried out to estimate the lifetime of the compounds. For TCSPC measurement, the photoexcitation was made at 370 nm for the bridging ligand and 440 nm for the Ru(II) complexes using a picoseconds diode laser (IBH Nanoled-07) in an IBH Fluorocube apparatus. The fluorescence decay data were collected on a Hamamatsu MCP photomultiplier (R3809) and were analyzed by using IBH DAS6 software.

The electrochemical measurements were carried out with a BAS 100B electrochemistry system. A three-electrode assembly (BAS) comprising a Pt (for oxidation) or glassy carbon (for reduction) working electrode, Pt auxiliary electrode, and an aqueous Ag/AgCl reference electrode was used. The cyclic voltammetric (CV) and square wave voltammetric (SWV) measurements were carried out at 25°C in acetonitrile solution of the complex (*ca.* 1 mmol dm⁻³) and the concentration of the supporting electrolyte (TEAP) was maintained at 0.1 mol dm⁻³. The potentials recorded were automatically compensated to iR drop in the cell. All of the potentials reported in this study were referenced against the Ag/AgCl electrode, which under the given experimental conditions gave a value of 0.36 V for the ferrocene/ferrocenium couple.

Experimental uncertainties were as follows: absorption maxima, $\pm 2 \text{ nm}$; molar absorption coefficients, 10%; emission maxima, $\pm 5 \text{ nm}$; excited-state lifetimes, 10%; luminescence quantum yields, 20%; redox potentials, $\pm 10 \text{ mV}$.

Tables for electronic supplementary information

Table S1 Photophysical data of complexes **1-3**.

Complex		Absorption λ_{\max}/nm ($\epsilon, \text{M}^{-1}\text{cm}^{-1}$)	Luminescence				
			λ_{\max}/nm	τ/ns	Φ	k_r/s^{-1}	k_{nr}/s^{-1}
1	MeCN (298K)	461(21000),428(br) (19200),385(sh)(39400),360 (54200),287(88000),240(46600)	604	$\tau=150$	1.42×10^{-2}	9.5×10^4	6.6×10^6
		460(33500),430(br) (30150),356(sh)(50300),288 (159200),244(70300)	620	$\tau_1=54.3$ (17%) $\tau_2=124.$ 2 (83%)	1.15×10^{-2}		
		460(41100),430(br)(36400), 360(sh)(41000), 331(sh)(53500),289(170000)	655	$\tau=92$	8.43×10^{-3}	9.1×10^4	1.1×10^7
1	DMSO (298K)	466(12300),372 (34680),290(52600)	613	$\tau=445$	3.1×10^{-2}	6.9×10^4	2.1×10^6
		467(23200),360(sh)(37100), 291(120200)	622	$\tau=412$	2.5×10^{-2}	6.1×10^4	2.3×10^6
		469(37500),432(br)(33900), 360(sh)(49300),336 (58400),291(161000)	660	$\tau=186$	1.07×10^{-2}	5.7×10^4	5.3×10^6
1	H₂O (298K)	462(13400),428(br)(11800), 346(36100),284(56100)	605	$\tau=496$	2.1×10^{-2}	4.1×10^4	1.9×10^6
		460(29300),422(br)(25500), 332(sh)(49500),286(143200)	617	$\tau_1=164$ (66%) $\tau_2=425$ (34%)	1.35×10^{-2}		
		461(36600),427(br)(33200), 355(sh)(36300),329(sh)(50200), 285(153400)	651	$\tau_1=127$ (76%) $\tau_2=353$ (24%)	5.1×10^{-3}		
1	EtOH:MeOH (4:1) (77K)		574	$7.42 \mu\text{s}$	0.036	4.8×10^3	1.3×10^5
			594	$6.11 \mu\text{s}$	0.035	5.7×10^3	1.5×10^5
			623	$3.58 \mu\text{s}$	0.038	1.0×10^4	2.7×10^5

Figures for electronic supplementary information

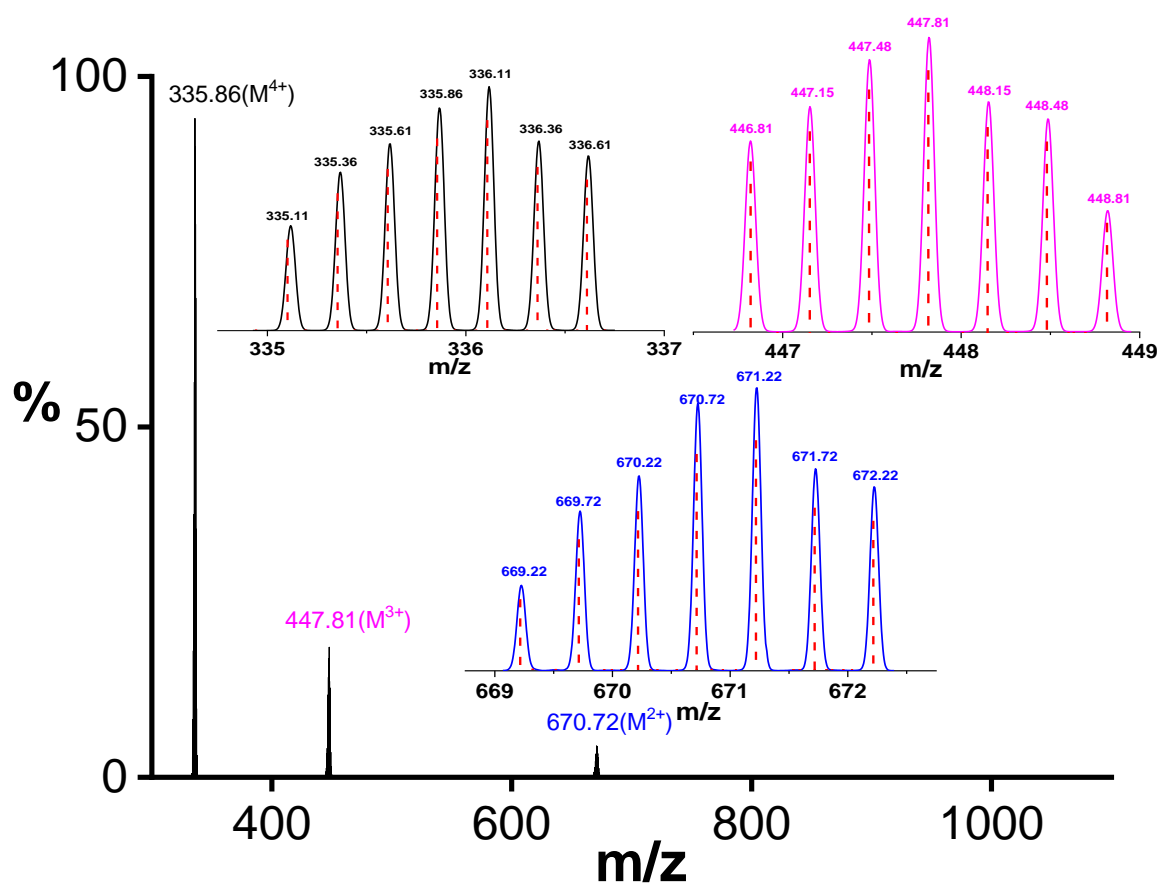


Fig. S1 ESI (positive) mass spectrum for the complex cation of 2 $[(bpy)_2Ru(phen-H_2PhImz-bpy)Ru(bpy)_2]^{4+}$ ($m/z = 335.86$), $[(bpy)_2Ru(phen-H_2PhImz-bpy)Ru(bpy)_2]^{3+}$ ($m/z = 447.81$) and $[(bpy)_2Ru(phen-H_2PhImz-bpy)Ru(bpy)_2]^{2+}$ ($m/z = 670.72$) in MeCN showing both observed and simulated isotopic distribution patterns.

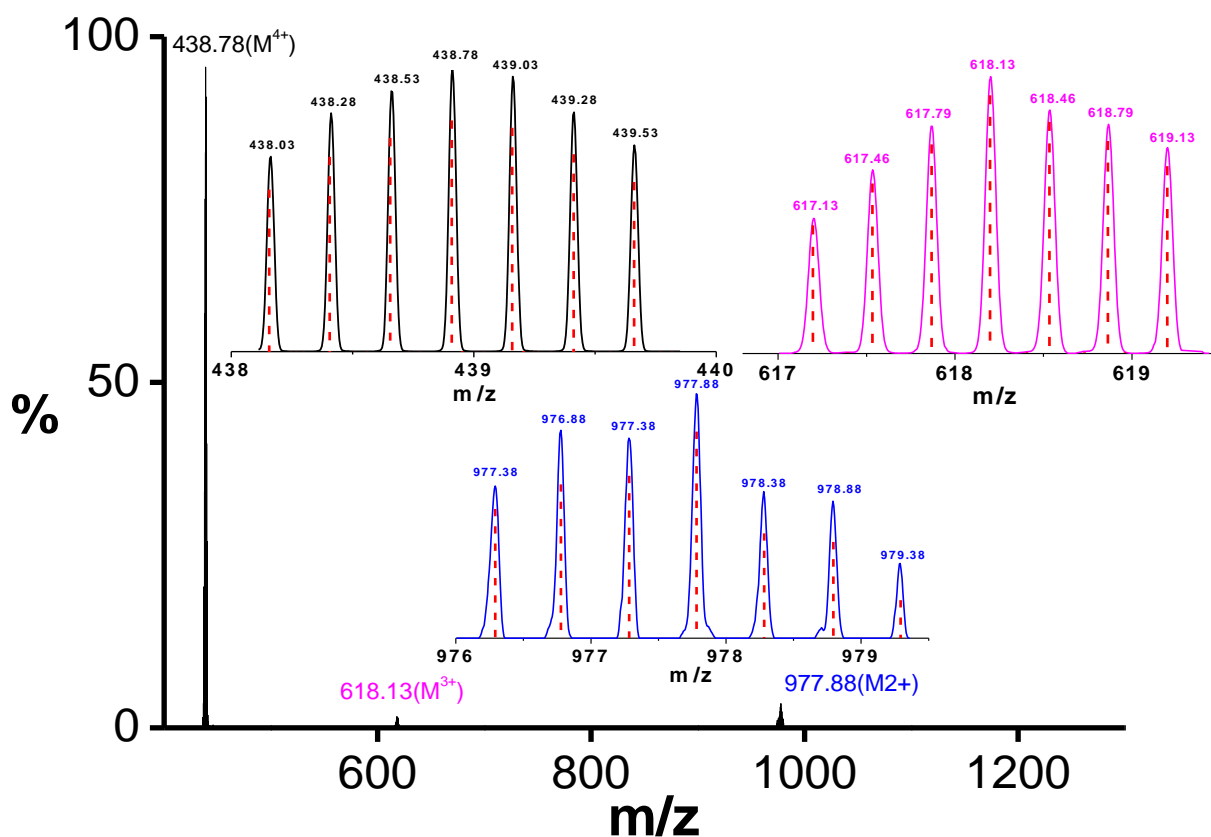


Fig. S2 ESI (positive) mass spectrum for the complex cation of 3 [(bpy)₂Ru(phen-HPhImz-bpy)Ru₂(bpy)₄]⁴⁺ ($m/z = 438.78$), [(bpy)₂Ru(phen-HPhImz-bpy)Ru₂(bpy)₄]³⁺ ($m/z = 618.13$) and [(bpy)₂Ru(phen-HPhImz-bpy)Ru₂(bpy)₄]²⁺ ($m/z = 977.88$) in MeCN showing both observed and simulated isotopic distribution patterns.

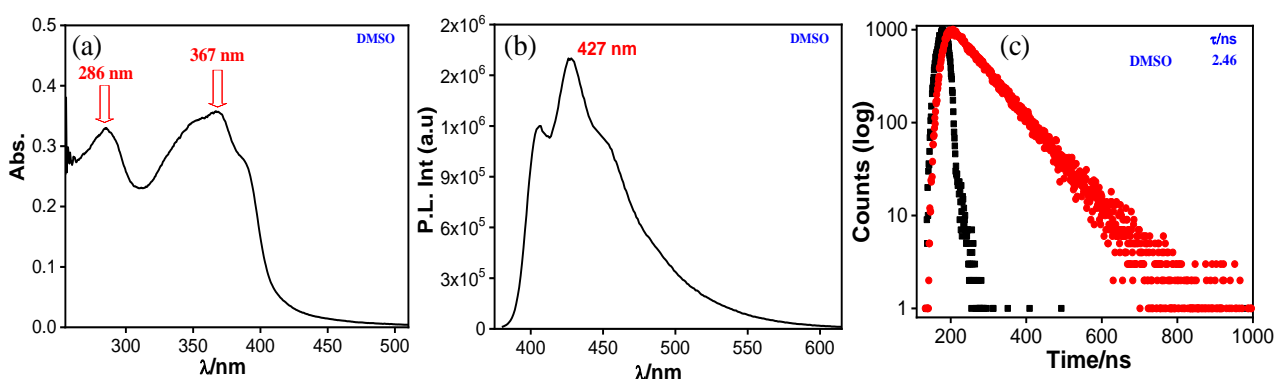


Fig. S3 UV-vis absorption (a) and emission ($\lambda_{\text{ex}}=367$ nm) (b) spectrum of phen-H₂PhImz-bpy ligand in DMSO. (c) Excited state decay profile following pulsed excitation with 370 nm NanoLED. Inset shows the lifetime value.

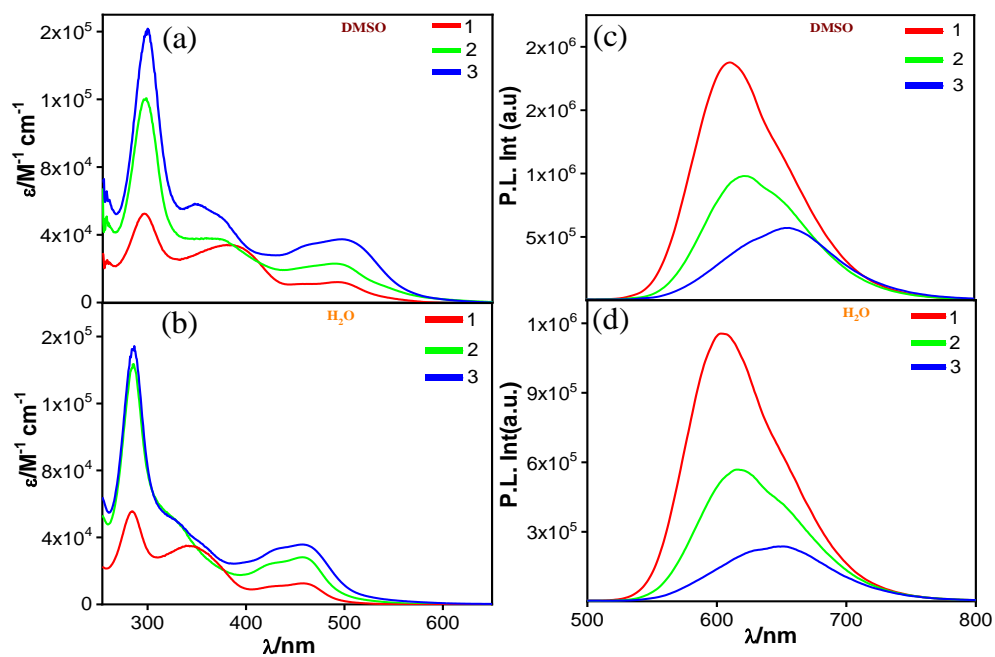


Fig. S4 UV-vis absorption (a-b) and emission ($\lambda_{\text{ex}}=461 \text{ nm}$) (c-d) spectra of **1-3** in DMSO and H₂O.

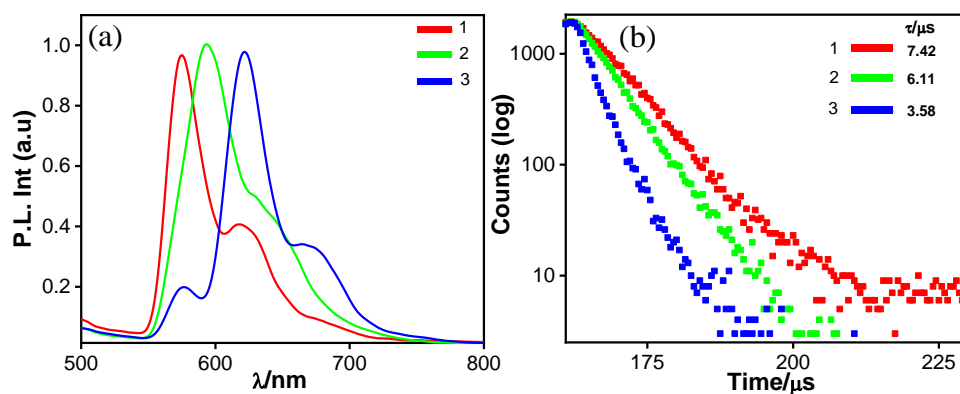


Fig. S5 Normalized emission spectra ($\lambda_{\text{ex}}=460 \text{ nm}$) (a) and excited state decay profiles following pulsed excitation with 450 nm NanoLED of **1-3** in EtOH-MeOH (4:1, v/v) glass at 77 K. The inset to figure b indicates the lifetime values.

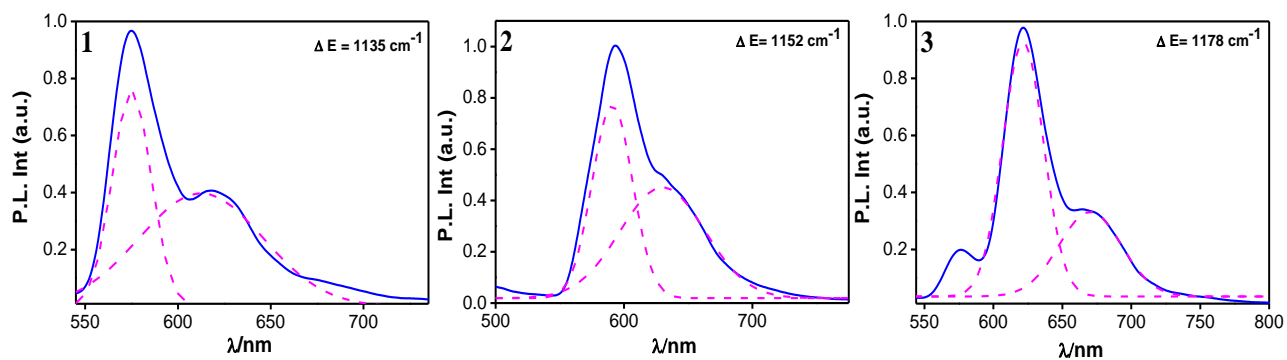


Fig. S6 Experimental (solid line) and deconvoluted (dotted line) emission spectra of **1-3** in EtOH-MeOH (4:1 v/v) at 77K. The inset shows the values of vibrational spacing.

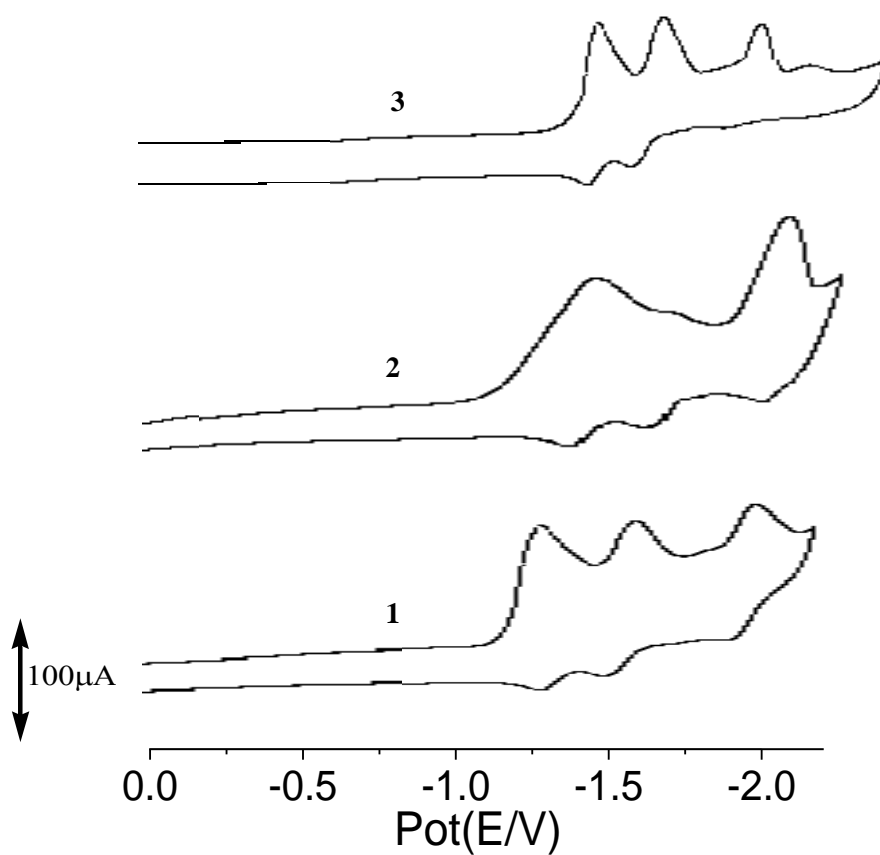


Fig. S7 CVs of **1-3** in acetonitrile showing reduction in negative potential domain.

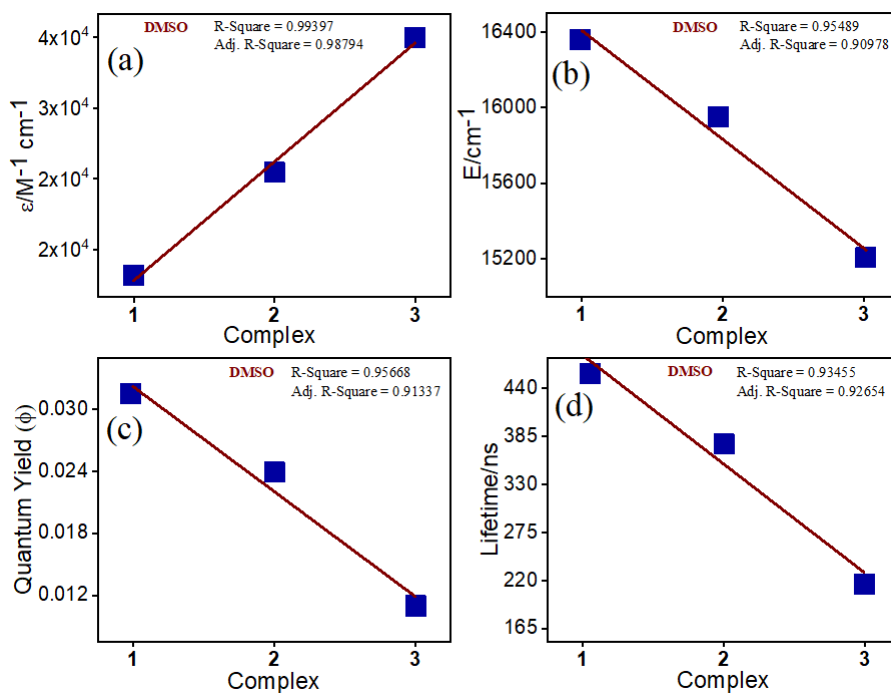


Fig. S8 Variation of molar extinction coefficient (ϵ) (a), emission energy (b), quantum yield (c) and lifetime (d) with the nuclearity of the complexes in DMSO.

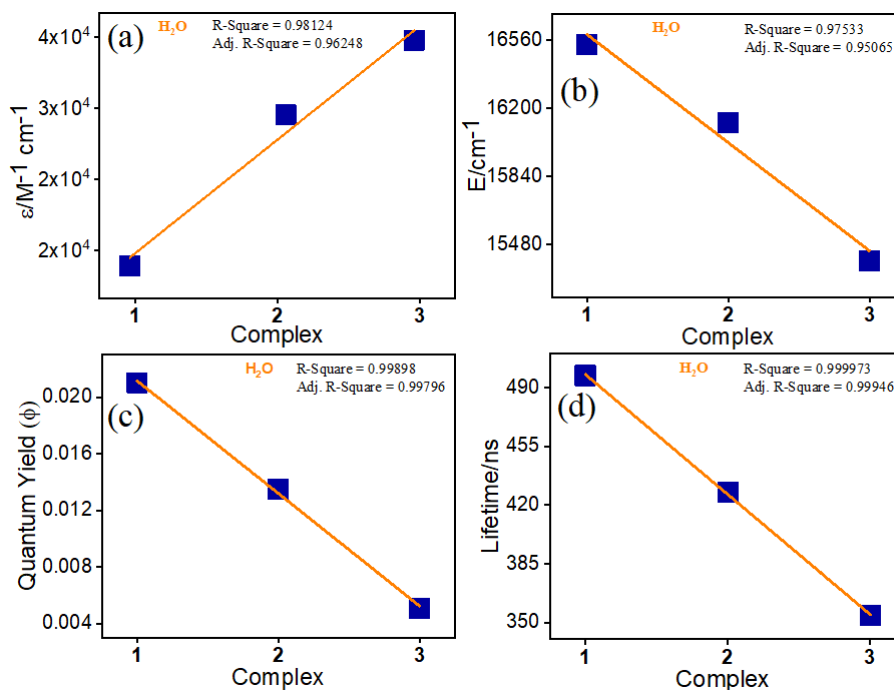


Fig. S9 Variation of molar extinction coefficient (ϵ) (a), emission energy (b), quantum yield (c) and lifetime (d) with the nuclearity of the complexes in H₂O.