

Supporting Information

Proton-Coupled Electron Transfer for Photo-induced Generation of Two-electron Reduced Species of Quinone

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Sr. No	Table of contents	Page No.
1	Materials and methods	3
2	Synthesis of ligand L	3
3	Synthesis of 2RuAQ complex	4
4	Analytical methods	4
5	Preparation of sample solutions	5
6	¹ H NMR spectra of ligand L	5
7	¹ H NMR spectra of 2RuAQ complex	6
8	ESI-MS spectra of ligand L and Maldi-ms of 2RuAQ complex	6-7
9	FT-IR spectra of 2RuAQ complex	8
10	Transient absorption spectroscopic study of [Ru(bpy) ₃] ²⁺ complex	8
11	Transient absorption spectroscopic study of ligand L	9
12	Cyclic voltammetric study of 2RuAQ complex	10
13	Cyclic voltammogram of Ferrocene (Fc)	11
14	Steady state spectroscopic study of [Ru(bpy) ₃] ²⁺ and 1,5-Diaminoanthraquinone in different conditions.	11
15	Kinetic Isotope Effect study	12

Experimental section

Materials and methods

4,4'-dimethyl-2,2'-bipyridine, selenium dioxide, silver nitrate, Ruthenium chloride hydrate, 1,5-Diaminoanthraquinone, 2,2'-bipyridine, potassium hexafluorophosphate, lithium chloride, p-Toluenesulphonic acid (PTSA). 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP), DMSO-*d*₆, have been purchased from Sigma Aldrich and used without further purification. Solvents like acetonitrile, toluene have been used spectroscopic grade. Thionyl chloride has been purchased from TCI chemicals and properly distilled before use. Ru(bpy)₂Cl₂ · 2H₂O have been prepared maintaining the literature conditions.¹ IOLAR grade dinitrogen has been used for degassing the standard solutions before the spectroscopic study. 4'-methyl[2,2'-bipyridine]-4-carboxylic acid have been synthesized following the previous literature.²

Synthesis of ligand L

To synthesize the ligand L we followed the literature method and little modification was done.² 4'-methyl[2,2'-bipyridine]-4-carboxylic acid (360 mg, 1.68 mmol) were suspended in 20 ml distilled thionyl chloride. Then the suspension was refluxed for 6h at 110°C temperature. Then excess thionyl chloride was removed by downward distillation and the yellow-coloured residue was dissolved in dry dichloromethane. 1,5-diaminoanthraquinone (200 mg, 0.84 mmol) suspended in 25 ml dry dichloromethane were purged to the yellow colour solution at 0°C. The reaction was stirred for 12 h at room temperature. Finally, we observed red coloured precipitate which was then washed using dichloromethane. After that, the product was dried using a vacuum desiccator and used for the next step. Yield: 344.043 mg (yield 65%)102.18 mg, (38%). ESI-MS (m/z): calculated 631.2088, observed 631.2064 for C₃₈H₂₆N₆O₄ [M + H]⁺, elemental analysis calculated for C₃₈H₂₆N₆O₄ is C, 72.37; H, 4.16; N, 13.33 observed data is C, 72.33; H, 4.18; N, 13.35. ¹H NMR (600 MHz, DMSO – *d*₆) δ (ppm) 10.55 (2H, d, *J* = 5.9 Hz), 10.41 (3H, s), 10.19 (3H, d, *J* = 6.5 Hz), 10.01 (1H, s), 9.44 (1H, d, *J* = 7.7 Hz), 9.33 (3H, t, *J* = 6.8 Hz), 8.83 (2H, dd, *J* = 22.2, 8.2 Hz), 8.72 (1H, t, *J* = 9.8 Hz), 8.59 (1H, d, *J* = 8.7 Hz), 8.24 (1H, d, *J* = 10.4 Hz), 2.54 (6H, s).

Synthesis of 2RuAQ complex

Ligand **L** (250 mg, 0.39 mmol) was reacted with Ru(bpy)₂Cl₂ · 2H₂O (406.38 mg 0.78 mmol) in dry dimethylformamide at 100°C temperature for 8h. After that the reaction mixture was cooled down to room temperature, the dimethylformamide was removed through reduced pressure and the residue was dissolved in distilled water and an excess amount of potassium hexafluorophosphate were added and kept for overnight at 8°C temperature. The obtained precipitate was then filtered and dried. The dried compound was then further purified by column chromatography using acetonitrile- toluene mixture as eluent and silica as the stationary phase. Yield (333.48 mg, yield 42 %). ¹HNMR (600 MHz, DMSO-*d*₆) δ (ppm) 11.22 (2H, s), 10.74 – 10.65 (12H, m), 10.13 (10H, dd, *J* = 17.7, 8.8 Hz), 9.86 (2H, d, *J* = 7.2 Hz), 9.79 (2H, d, *J* = 7.0 Hz), 9.71 (9H, q, *J* = 6.6 Hz), 9.50 (2H, d, *J* = 7.2 Hz), 9.30 (9H, dd, *J* = 16.8, 8.4 Hz), 9.14 (2H, d, *J* = 7.1 Hz), 3.24 (6H, s). Elemental calculated for C₇₈H₅₈N₁₄O₄ is C, 45.98; H, 2.87; N, 9.62; observed data is C, 45.95; H, 2.85; N, 9.65. Maldi-ms for C₇₈H₅₈F₂₄N₁₄O₄P₄Ru₂ Calculated mass for [M – PF₆]⁺ is 1892.44, observed is 1892.33.

Analytical methods

Employing a perkinelmer 883 spectrometer, FT-IR spectra were recorded with a KBr window. Agilent 6545 Q-TOF LC/MS mass spectrometer was used for mass spectroscopic analysis. Geol resonance ECZ600R NMR spectrometer was used for NMR analysis. Shimadzu corp 80109 UV spectrophotometer was used for UV-visible analysis. TCSPC experiments performed using a spectrofluorimeter from IBH (UV which works with a diode laser. A TBX4 detection module (IBH) connected with a Hamamatsu PMT fluorescence detector was used. The instrument response function of 170 ps and excitation of 443 nm laser was employed.³ All the experiments performed at 298 K. A saturated KCl reference electrode (Ag/AgCl), a platinum working electrode, and a platinum wire were used for electrochemical measurements. Before using the cyclic voltammetry experiments, we dried the solvents and thoroughly passed dinitrogen gas. A bi-potentiostat with a traditional three-electrode setup was used for cyclic voltammetry experiments. Horiba Canada QM400 fluorescence instrument was employed for fluorescence study.

Preparation of sample solution

To prepare each sample we have used high-quality spectroscopic grade solvents like acetonitrile, dichloromethane. Before performing the spectroscopic study, we have used N₂ gas to purge the solutions. Cyclic voltammetry experiments were performed using pre-dried acetonitrile.

¹H NMR Spectra of ligand L

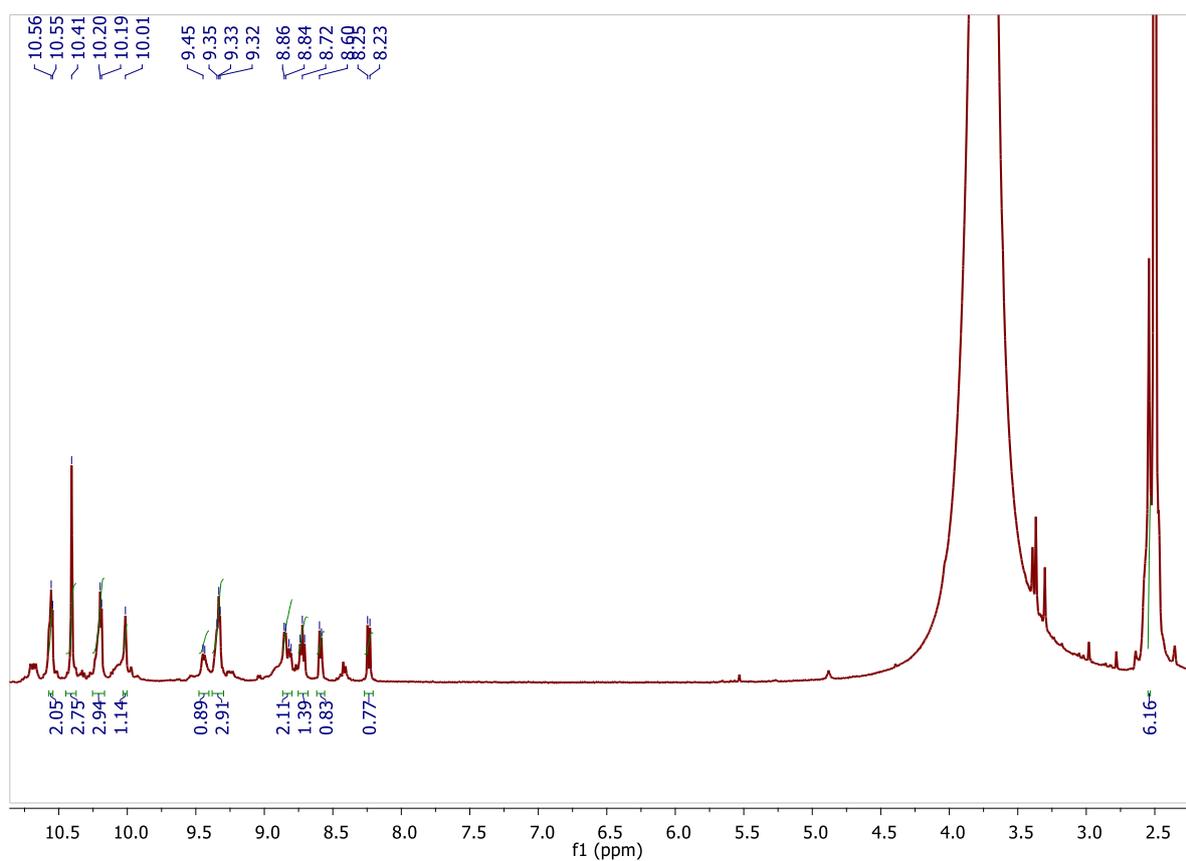


Figure S1. ¹H NMR Spectra of ligand L.

¹H NMR spectra of 2RuAQ complex

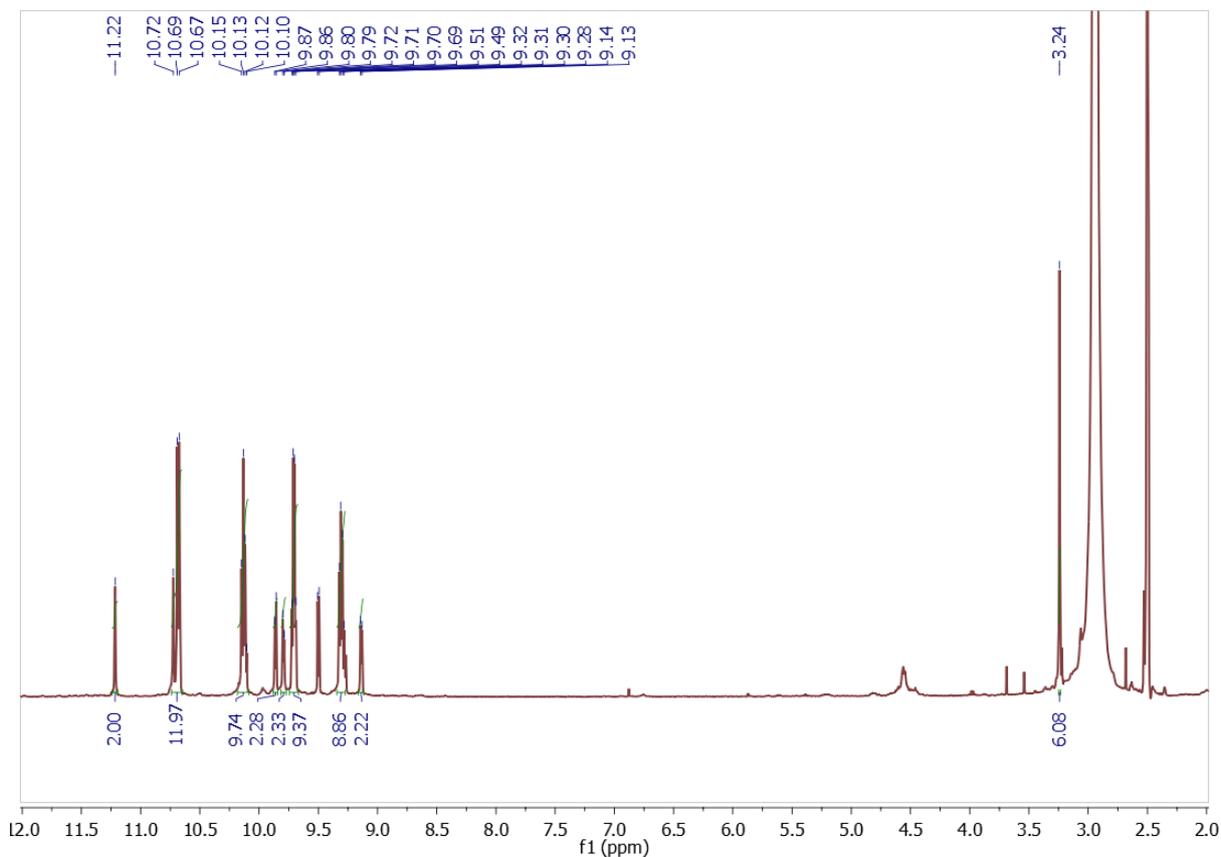


Figure S2. ¹H NMR spectra of 2RuAQ complex

ESI-MS spectra of Ligand (L) and 2RuAQ complex

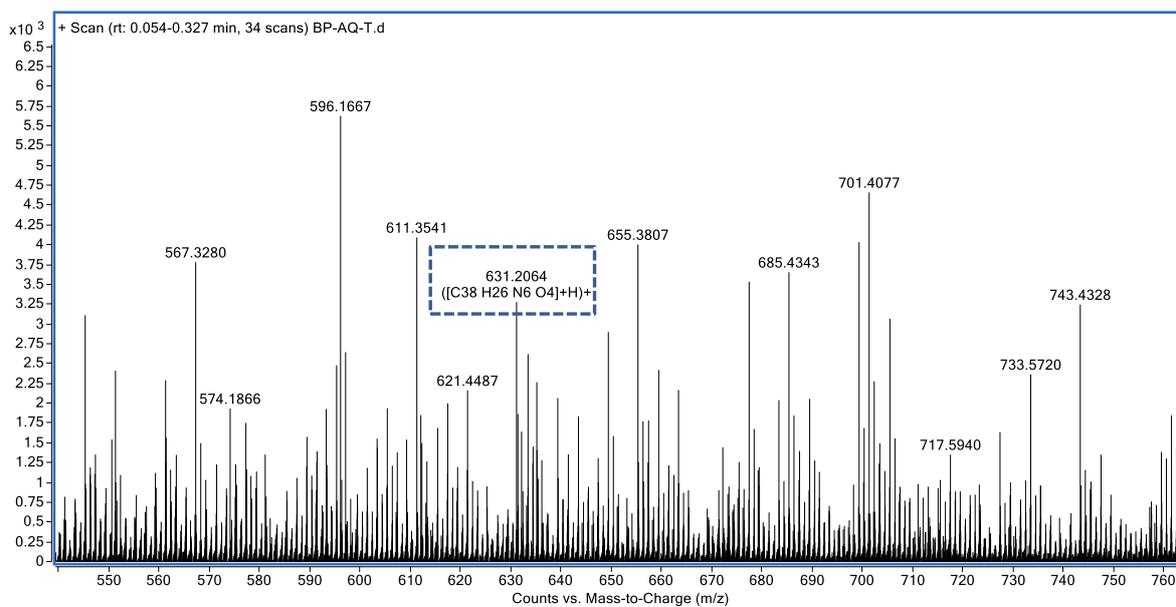
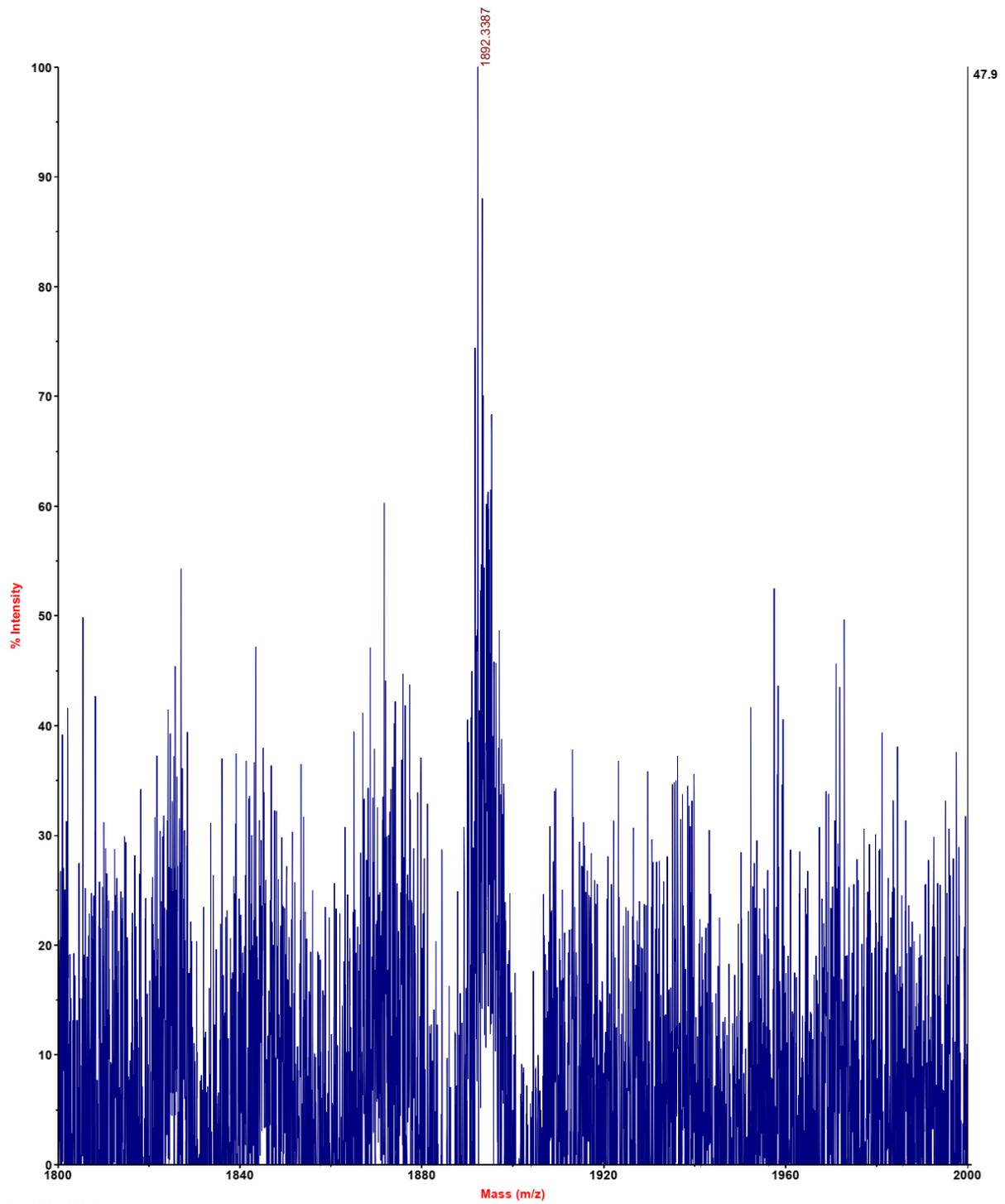


Figure S3A. Mass spectra of Ligand L.

4700 Reflector Spec #1 MC=>AdvBC(32,0.5,0.1)[BP = 583.5, 84085]



C:\...IP24_MS.t2d
Acquired:

Figure S3B. Maldi-ms spectrum of 2RuAQ complex.

FT-IR spectra of 2RuAQ complex

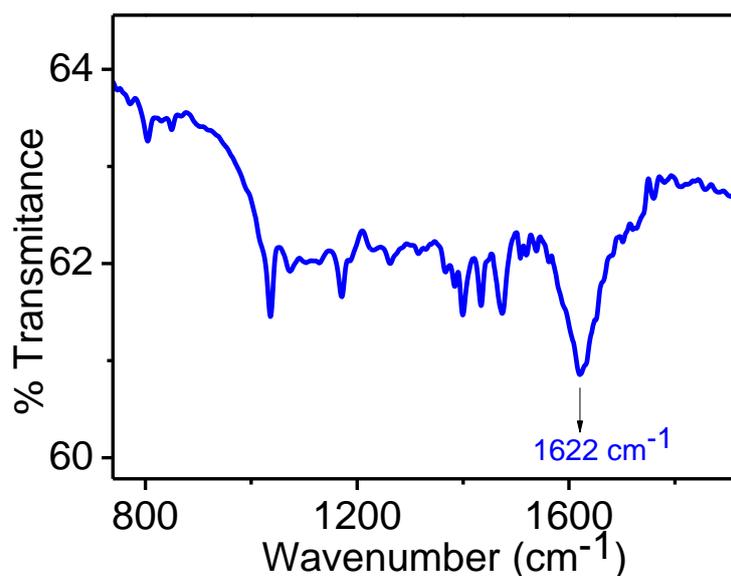


Figure S4. FT-IR spectra of 2RuAQ complex.

The above figure (S4) illustrates strong evidence for intramolecular H-bonding between anthraquinone carbonyl functional group and adjacent amide N-H functional group. FTIR the spectrum shows one distinct peak for CO stretching frequency: the peak at 1622 cm^{-1} can be attributed to the hydrogen bonded CO functional group. The single peak strongly both the CO functional groups has same character and intramolecularly H-bonded.

Transient absorption spectroscopic study of $[\text{Ru}(\text{bpy})_3]^{2+}$ complex

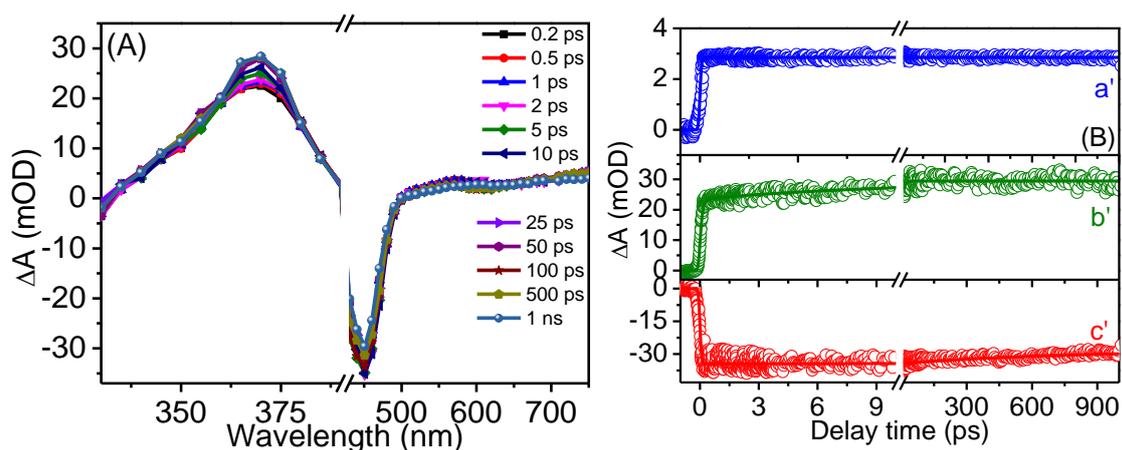


Figure S5. (A) Femtosecond transient absorption spectra of $[\text{Ru}(\text{bpy})_3]^{2+}$ complex in acetonitrile at 298 K after exciting the samples at 400 nm. (B) (a') decay kinetic trace monitored at 600 nm of $[\text{Ru}(\text{bpy})_3]^{2+}$ complex. (b') monitored at 370 nm and (c') monitored at 450 nm decay trace.

Transient absorption spectroscopic study of ligand L

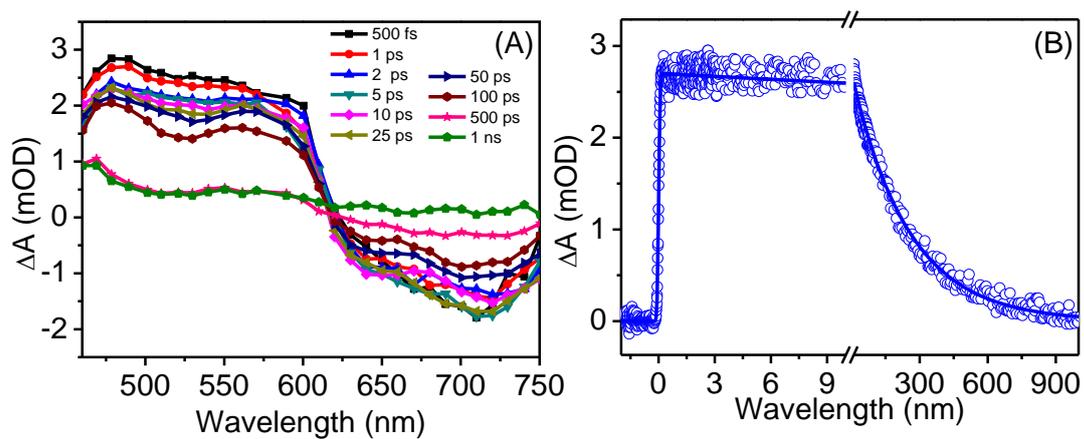


Figure S6. (A) Femtosecond transient absorption spectra of **L** ligand in acetonitrile at 298 K after exciting the samples at 400 nm. (B) decay kinetic trace monitored at 550 nm of **L**.

Cyclic voltammetry study of 2RuAQ complex and ferrocene

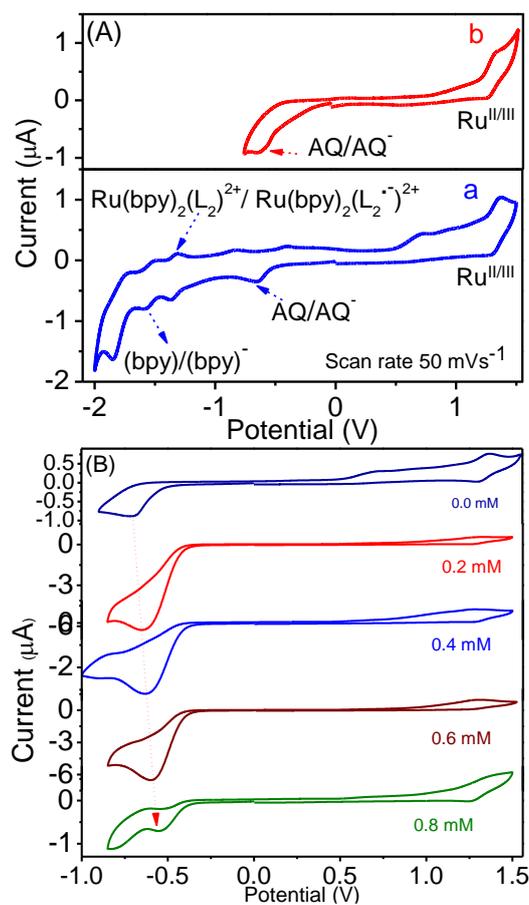


Figure S7. (A) Cyclic voltammograms of (a) 2RuAQ (blue trace), (b) 2RuAQ in presence of PTSA (blue trace), and (B) series of cyclic voltammograms of 2RuAQ with increasing concentration of HFIP. All experiments performed with a scan rate of 50 mV/s, in deoxygenated and pre-dried acetonitrile in the presence of 0.1 M TBAHFPF₆ as supporting electrolyte, by using an Ag/AgCl (saturated KCl) electrode as the reference electrode Ferrocene were used as an internal standard.

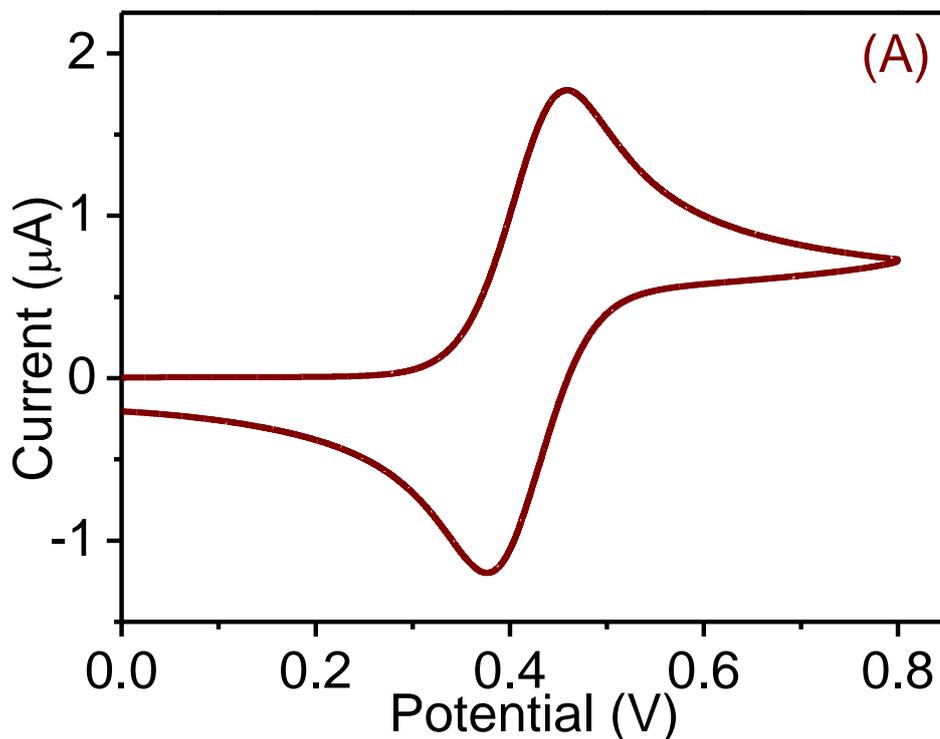


Figure S8. Cyclic voltammogram of ferrocene (Fc).

Steady state spectroscopic study of [Ru(bpy)₃]²⁺ and 1,5-Diaminoanthraquinone in different conditions

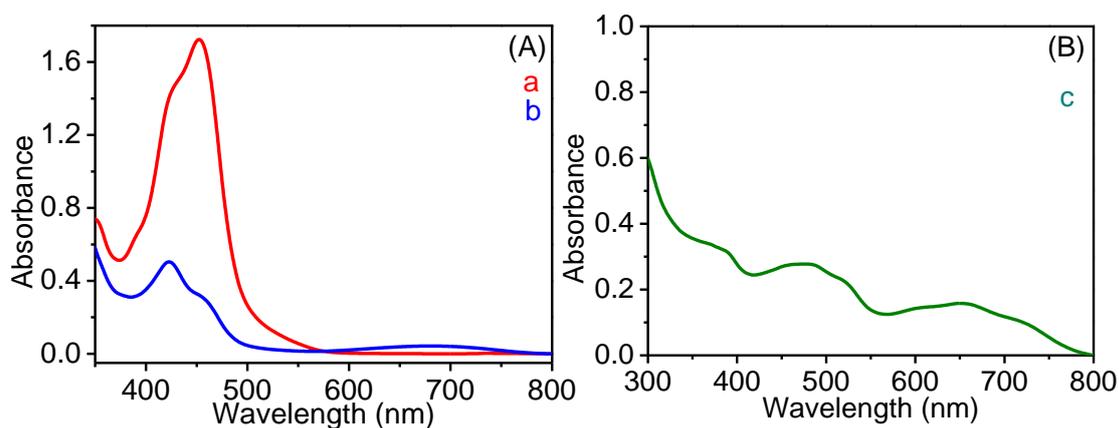


Figure S9: (A) represents the UV-Vis spectral change for a solution of [Ru(bpy)₃]²⁺ in 9 M H₂SO₄ (a) (red trace) a freshly prepared solution in dark and (b) (blue trace) after exposure to sunlight. (B) (c) represents the absorbance spectra of 1,5-Diaminoanthraquinone after treating the compound with NaBH₄ in alkaline medium solvent composition of DMSO/water (1:1, v/v).

Kinetic Isotope Effect study

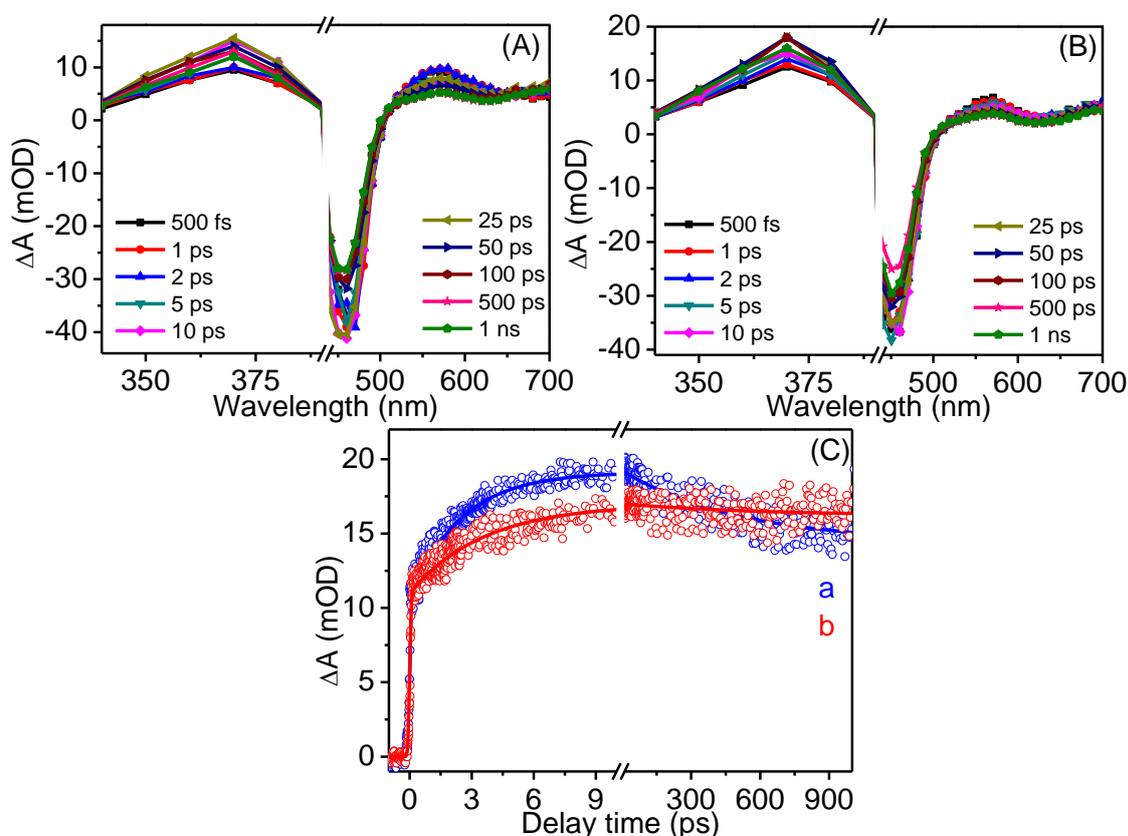


Figure S10. Femtosecond transient absorption spectrum of 2RuAQ (A) in $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ (v/v; 1:1) solvent, (B) in $\text{CH}_3\text{CN}-\text{D}_2\text{O}$ (v/v; 1:1) solvent mixture at different time delay after 400 nm laser excitation. (C) comparative kinetic traces monitored at 370 nm (a) in $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ (v/v; 1:1) and (b) in $\text{CH}_3\text{CN}-\text{D}_2\text{O}$ (v/v; 1:1).

References

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- (3) Aute, S.; Maity, P.; Das, A.; Ghosh, H. N. Demonstrating the Role of Anchoring Functionality in Interfacial Electron Transfer Dynamics in the Newly Synthesized BODIPY- TiO_2 Nanostructure Composite. *New J. Chem.* **2017**, *41*, 5215–5224.