Supporting Information

Hydrogen bond assisted photoinduced intramolecular electron transfer and proton coupled electron transfer in ultrafast time domain using a ruthenium-anthraquinone dyad

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Synthesis of complex 2:

Complex **2** was synthesized following the literature procedure.[1]

^{1}H-NMR spectrum of the ligand (L_1):

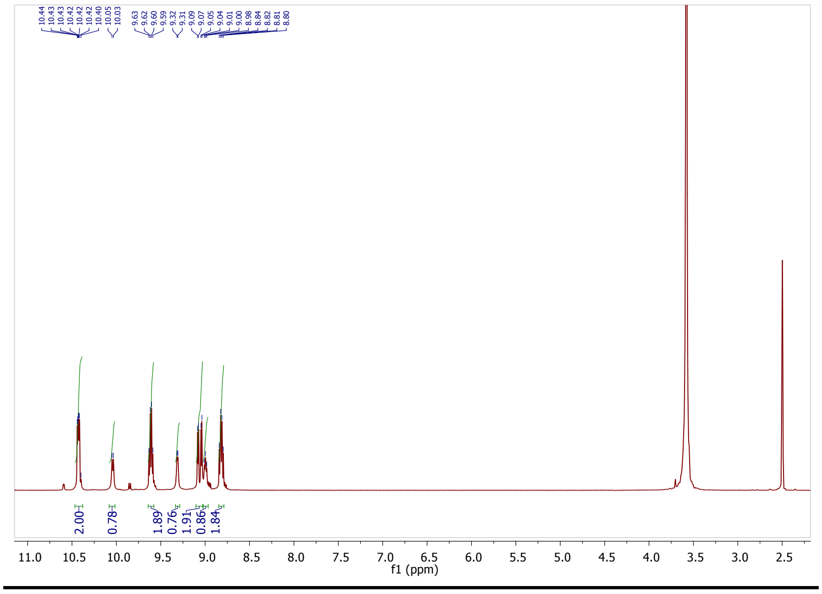

Figure S1: ^{1}H NMR spectrum of ligand $\mathbf{L_1}$ in DMSO-d_6 solvent.

ESI-MS spectrum of ligand (L_1):

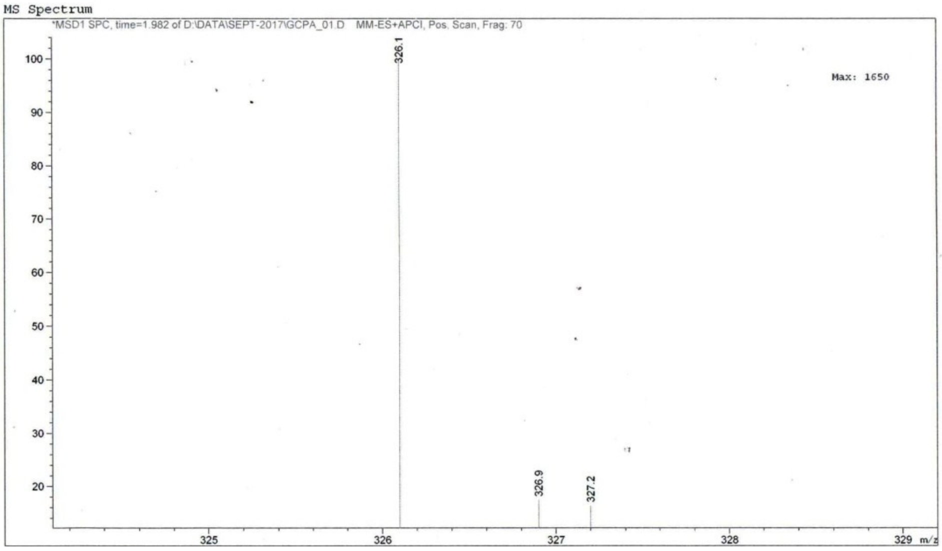

Figure S2: ESI-MS spectrum of the ligand $\mathbf{L_1}$.

^{1}H-NMR spectrum of complex 1:

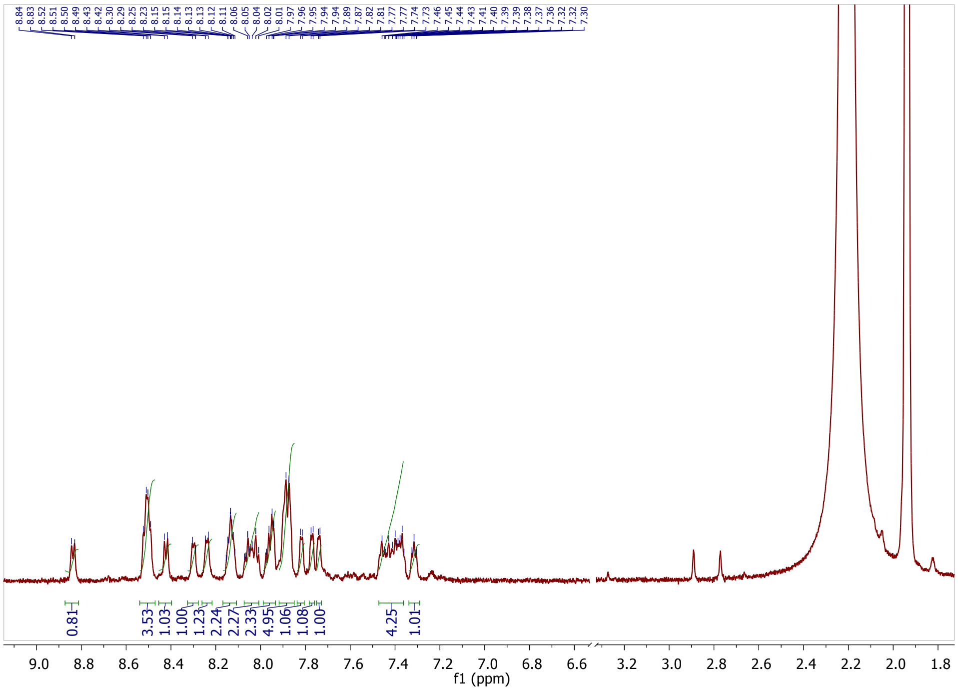

Figure S3: ^{1}H NMR spectrum of complex **1** in CD_3CN solvent.

HRMS spectrum of complex 1:

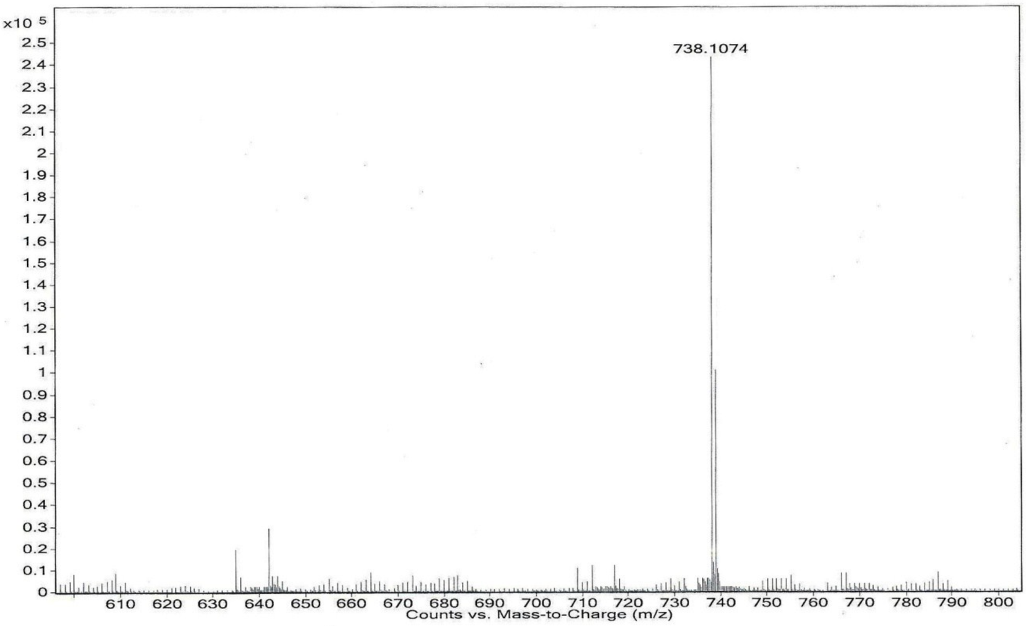

Figure S4: HRMS spectrum of complex **1**.

Transient absorption study of ligands ($\mathbf{L_1}$):

Figure S6 represents the transient absorption spectrum of $\mathbf{L_1}$. As the benziimidazole-anthraquinone ligand **(**$\mathbf{L_1}$) has ground state absorption in the 400 nm, we did transient absorption study of the ligand $\mathbf{L_1}$ in acetonitrile solvent following 400 nm laser excitation. Ligand $\mathbf{L_1}$ also has positive absorption in 450 nm to 700 nm region but the comparative kinetic traces are very different in nature (figure S6(right side)). This study confirms that there is no interference of the ligand excitation in the intramolecular photo induced electron transfer and H-bonding re-equilibrium process. Scheme 2 represents the advantage of close contact in intramolecular electron transfer as AQ unit is attached with rigid imidazole spacer that facilitates maximizing electronic coupling and minimizing the solvent re-organizational energy. The oxidative quenching by anthraquinone occurs first due to close proximity of metal centre followed by proton motion and then the resulting intermediate decays rapidly by back electron transfer to highly acidic Ru(III) centre.

Transient absorption study of ligand ($\mathbf{L_1}$):

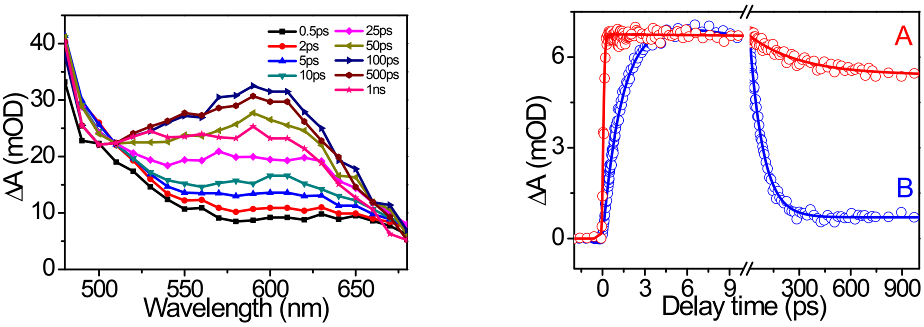

Figure S5: [Left] Femtosecond transient absorption spectrum of ligand ($\mathbf{L_1}$) in acetonitrile solvent after 400 nm laser excitation. [Right side] (a) Kinetic trace monitored at 490 nm.(red trace) of ligand $\mathbf{L_1}$. (b) $AQ^{\cdot -}$ decay of complex **1** (blue trace) monitored at 490 nm.

Transient absorpion spectrum of complex 2:

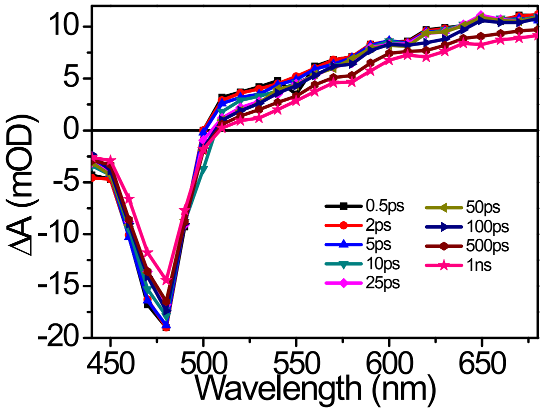

Figure S6: Femtosecond transient absorption spectrum of complex **2** in acetonitrile after 400 nm laser excitation.

Transient absorption study of complex 1 in acetonitrile-water (1:1, v/v) solvent.

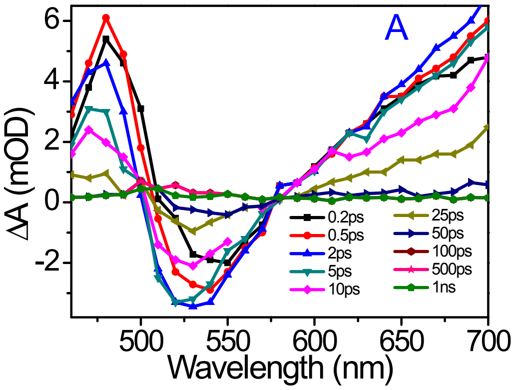

Figure S7. Femtosecond transient absorption spectrum of complex **1** in acetonitrile-water (1:1, v/v) solvent after excitation of the samples with 400 nm laser light at 298 K.

Transient absorption dynamics of complex 1 in acetonitrile-water (1:1, v/v) (pH 4) solvent mixture:

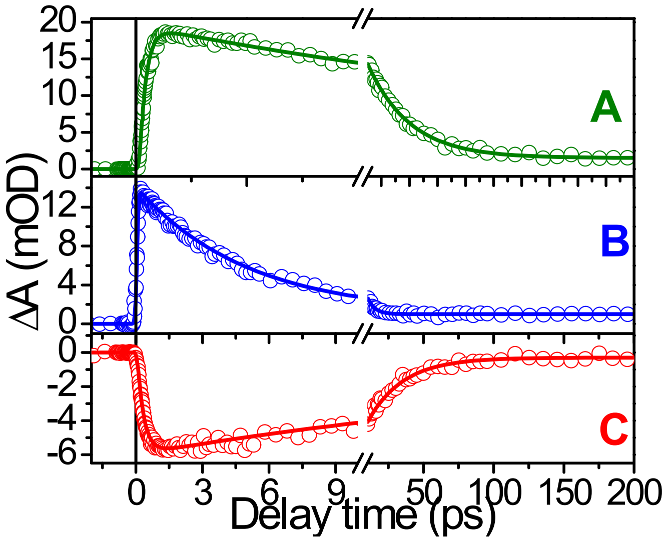

Figure S8. Transient kinetic traces of (a) cation radical (at 690 nm) of complex **1**; (b) $AQ^{\cdot -}$ radical anion decay monitored at 490 nm and (c) bleach recovery kinetics 530 nm of complex **1** in acetonitrile-H_2O (1:1, v/v) pH4 after 400 nm laser excitation.

Transient absorption dynamics of complex 2 in acetonitrile:

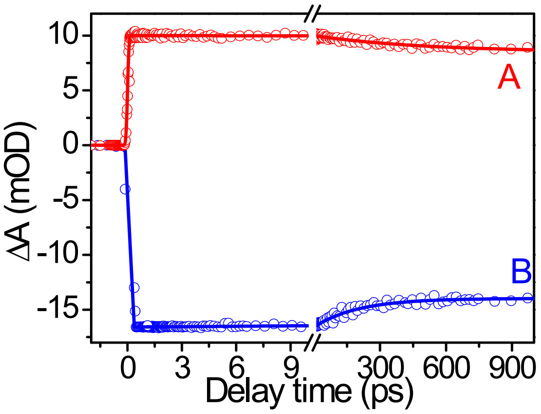

Figure S9. Decay dynamics of complex **2** (a) monitored at 690 nm (red trace). (b) (blue trace) bleach recovery dynamic monitored at 480 nm.

SI Table 1. Parameters for multi-exponential fits for the transient absorption kinetic traces of complex 1 in acetonitrile solvent at different wavelengths after 400 nm laser excitation.

Complex system	Solvent medium	Wavelength (nm)	τ_g	τ_{1decay}
Complex **1**	Acetonitrile	520	1 (±0.1) ps (100%)	105 (± 10) ps (- 100%)
		490	1 (±0.1) ps (100%)	100 (± 10) ps (- 100%)
		690	1 (±0.1) ps (100%)	100 (± 10) ps (- 100%)
	Acetonitrile in presence of Ba^{2+}	520	600 (±60) fs (100%)	50 (± 50) ps (- 100%)
		490	600 (±60) ps (100%)	45 (± 4.5) ps (- 100%)
		690	600 (±60) fs (100%)	50 (± 50) ps (- 100%)

SI Table 2. Parameters for multi exponential fits of transient kinetics monitored at key wavelengths of the complex 1 in different solvents after 400 nm laser excitation.

Complex system	Solvent medium	Wavelength (nm)	τ_g	τ_{1decay}
Complex **1**	Acetonitrile-Water (1:1, v/v)	490	300 (±30) fs (100%)	15 (± 1.5) ps (- 100%)
		520	300 (±30) fs (100%)	20 (± 2) ps (- 100%)
		690	300 (± 30) fs (100%)	20 (± 2) ps (- 100%)
	Acetonitrile-Water (1:1, v/v) pH4	490	< 100 (±15) fs (100%)	20 (±2) ps (- 100%)
		530	200 (±26) fs (100%)	15 (±1.5) ps (- 100%)
		690	200 (± 26) fs (100%)	20 (± 2) ps (- 100%)

Notes and references

1 R. Hönes, M. Kuss-Petermann and O. S. Wenger, Photochemistry between a ruthenium(II) pyridylimidazole complex and benzoquinone: simple electron transfer versus proton-coupled electron transfer, *Photochem. Photobiol. Sci.*, 2013, **12**, 254.