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# Proton Coupled Electron Transfer Processes in Ultrafast Time Domain: Evidence for Effects of H-bond Stabilization on Photoinduced Electron Transfer

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Dedication ((optional))

**Abstract:** Proton coupled electron transfer (PCET) reaction has been investigated for a newly synthesized imidazole-anthraquinone bio mimetic model having a photoactive Ru(II)-polypyridyl moiety that is covalently coupled to the imidazole fragment. Intramolecular hydrogen bonding interaction between imidazole and anthraquinone moieties favoured the PCET process and this could be correlated to an appreciable positive shift of the one-electron reduction potential of the coordinated anthraquinone

moiety functionalized with imidazole fragment. This could also be attributed to the low luminescence quantum yield of Ru(II)-polypyridyl complex that was used for the present study. Dynamics of the intramolecular electron transfer (ET) and PCET processes were studied using femtosecond transient absorption spectroscopy. Consequences of the steady state spectroscopic studies as well as the results of the time resolved absorption studies confirmed that hydrogen bonded

water molecule played a major role in both ET and PCET dynamics as a proton relay in excited state. The electron transfer process was followed by changed in H-bonding equilibrium between AQ and imidazole in acetonitrile solvent and protonation of AQ<sup>•-</sup> from water makes the PCET in presence of water. We observed a slower forward and backward electron transfer rate in presence of D<sub>2</sub>O compared to H<sub>2</sub>O. Our results provide further experimental support for understanding of the PCET process in detail

## Introduction

Proton coupled electron transfer (PCET), is an important process and is generally operational in many natural processes like water driven reduction of CO<sub>2</sub> to methane, nitrogen fixation, and four-electron reduction of dioxygen by cytochrome *c* oxidase in respiration, hydrogenase reductase, water oxidation at the oxygen evolving centre in photosynthesis etc.<sup>[1],[2],[3]</sup> The simplest concept of proton coupled electron transfer can be described as a process wherein an electron and a proton transferred from one redox centre to another redox centre.<sup>[4],[5]</sup> As two species, such as proton and electron are being associated with the PCET process, fundamentally it is more complicated than simple electron transfer or the proton transfer mechanism. The PCET process could be defined by either one of the following processes, namely, proton transfer-electron transfer (PT-ET), stepwise electron transfer-proton transfer (ETPT) and concerted proton-electron transfer (CPET).<sup>[6]</sup> PCET is associated with several crucial biological processes.<sup>[7],[8]</sup> For photosynthesis, quinones play a key role as a primary electron acceptor<sup>[9],[10]</sup> and the reduction process of quinone is facilitated by hydrogen-bond donors or by protonation.<sup>[11]</sup>

In bacterial photosynthetic reaction also the fast electron transfer process occurs through the reduction of quinone,<sup>[12]</sup> which is facilitated due to the formation of a hydrogen bonded adduct with amino acids in immediate vicinity having appropriate spatial orientation. Semiquinone radical, a partially reduced form of quinone, is generally highly reactive and decays quickly when produced through a chemical transformation.<sup>[13],[14]</sup> In biological processes such semiquinone radicals participate in relay process to extend their lifetimes and this also prevent such radicals participating in undesired side reactions. However, such processes are not well understood. The conversion of water to dioxygen in the photo-system(II) is associated with the four electron four proton coupled process and a detailed insight is still lacking. In particular, understanding of PCET process in aqueous medium is even more challenging, as water can act as proton acceptor or donor depending on the media condition as well as the other participating reactant.<sup>[15]</sup> There are attempts in understanding such a process with appropriate synthetic analytes that can mimic the process associated with photosynthesis.

Haga and his co-workers had reported some imidazole functionalised Ru(II)-polypyridyl complexes immobilized on gold surface, which showed the PCET phenomena and the process was studied by cyclic voltammetric technique.<sup>[16],[17]</sup> Hammarström and his co-workers had reported an intramolecular PCET process that happened in micro and nanosecond time domain for ruthenium-tyrosine and tryptophan complexes involving electron transfer from tyrosine and tryptophan to the oxidised Ru-centre and water molecule participated in the process as proton acceptor.<sup>[18],[19]</sup> Costentin *et al.* discussed about mechanistic aspects of the PCET having phenol in the proton relay networks.<sup>[20],[21],[22]</sup> Porphyrin-benzoquinone dyads that mimic the function of P<sub>680</sub> in biological

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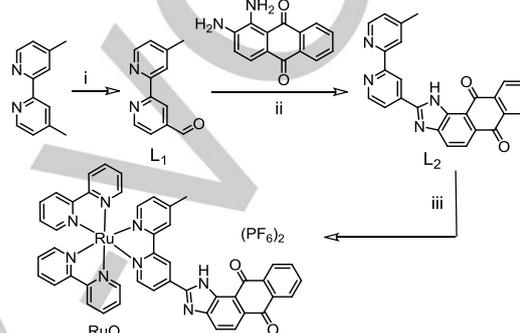
systems were also reported in literature.<sup>[9]</sup> Wenger and co-workers have described an Ir-polypyridyl for achieving long lived charge separated species and other systems to describe the PCET phenomena.<sup>[23],[24]</sup> Many theoretical models have been proposed correlating free energy for reaction, donor-acceptor distance, spatial orientation electronic coupling and biomimetic systems that mimics the tyrosine-histidine pair in PSII, in order to develop better insight in PCET phenomena.<sup>[25]</sup> The range of theoretical and computational treatments of hydrogen tunneling in enzymatic and bio mimetic systems are described in the previously reported literature.<sup>[26]</sup> Despite several literature reports, majority of the studies on the mechanistic understanding of PCET process were focussed on the electronic ground state<sup>[27],[28]</sup> and there are only limited reports that discussed the PCET process associated with electronically excited state.<sup>[29],[30]</sup> Mayer and co-workers<sup>[30]</sup> and others<sup>[31]</sup> had demonstrated the electron transfer and proton coupled electron transfer reaction in Ru(II)-polypyridyl based complexes and many other molecules<sup>[32],[33]</sup> having H<sup>+</sup>-donor fragments through transient absorption studies with nanosecond and micro-second time resolution and cyclic voltammetric studies. Though it has been argued that studies on excited state dynamics and femtosecond transient absorption spectroscopy are crucial for developing a better insight in PCET process, systematic studies in the ultrafast time domain is still lacking. Most of the literature reports unable to observe the transient absorption photoproducts.<sup>[34],[35]</sup>

In general, the electronic absorption spectra of transition metal complexes depends on the oxidation state of the corresponding metal ion and such complexes with well defined redox and excited state properties are ideal for developing a better insight on PCET process. Ru(II)-polypyridyl based complexes comply with both such requirements. However, to the best of our knowledge, no such reports are available in the contemporary literature that describes the excited state dynamics of the PCET process involving Ruthenium(II)-polypyridyl complex in ultrafast time scale. Keeping these in mind, we have designed and synthesized a Ru(II)-polypyridyl complex (RuQ) functionalized with an imidazole moiety, covalently linked to a quinone moiety for studying the PCET process in the ultrafast time domain.

Previous reports on the PCET processes involving intermolecular electron and proton transfer process suggest that dynamics of such processes are largely dependent on the rate of diffusion process. To avoid such a problem, we designed a triad system having photoactive Ru(II)-polypyridyl core conjugated with anthraquinone through an imidazole linker (Scheme 1). RuQ was synthesized in 3 steps. Oxidation of 4,4'-dimethyl-2,2'-bipyridine in the presence of SeO<sub>2</sub> resulted in the aldehyde (L<sub>1</sub>). Condensation of L<sub>1</sub> with 1,2-diamino anthraquinone yielded the ligand L<sub>2</sub>. Complexation of L<sub>2</sub> with Ru(bpy)<sub>2</sub>Cl<sub>2</sub> resulted the RuQ complex. All the intermediates and the final compound were well characterized by standard analytical and spectroscopic techniques. We envisioned that in the RuQ complex, Ru acts as a photo-active centre. Imidazole proton is expected to form H-bond with one of the two carbonyl functionalities of the quinone moiety. H-bonding interaction is expected to facilitate the reduction of anthraquinone. H-bonding

also favour the ET process from photo-excited Ru(II)-polypyridyl centre to the anthraquinone moiety (AQ) by lowering the energy level (LUMO) of anthraquinone. We have used different analytical and spectroscopic techniques such as cyclic voltammetry, steady state as well as time-resolved luminescence and femto-second transient absorption spectroscopy to study the ET and PCET process in organic as well as in presence of water.

## Results and Discussion

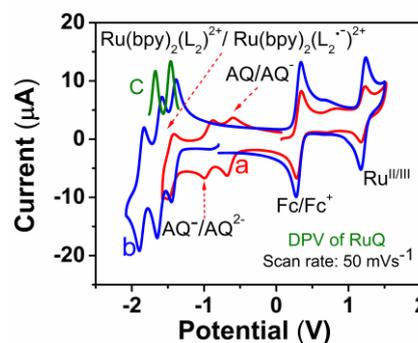


i = SeO<sub>2</sub>, Dioxane, reflux, ii = Ethanol, reflux (48 h); iii = Ru(bpy)<sub>2</sub>Cl<sub>2</sub>, DMF, L<sub>2</sub>, 100°C.

**Scheme 1.** Methodology that was adopted for synthesis of RuQ.

### Cyclic voltammetric studies of RuQ complex

To understand the thermodynamic feasibility of the electron transfer processes in the RuQ complex, the cyclic voltammetric measurements were carried out. Redox potentials for Ru<sup>(II/III)</sup> and bpy/bpy<sup>•+</sup> couples were evaluated and compared with Ru(bpy)<sub>3</sub><sup>2+</sup>. Cyclic voltammograms were recorded using degassed and pre-dried acetonitrile solution of respective complexes and in the presence of tetrabutyl ammoniumhexafluoro phosphate (TBAPF<sub>6</sub>) as the supporting electrolyte.

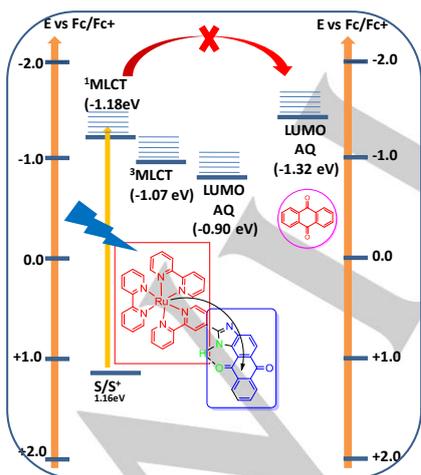


**Figure 1.** Cyclic voltammogram of (a) RuQ (red trace), (b) Ru(bpy)<sub>3</sub><sup>2+</sup> (blue trace) and (c) (olive trace) differential pulsed voltammetry of RuQ in de-oxygenated and pre-dried acetonitrile in the presence of 0.1 (M) tetra butyl ammonium hexafluorophosphate (TBAPF<sub>6</sub>) as supporting electrolyte using Ag/AgCl (saturated KCl) electrode as the reference electrode. Ferrocene (Fc) was used as an internal standard.

It is evident from Figure 1 that Ru<sup>(II/III)</sup> couple appeared at a potential of 0.89 V vs Fc/Fc<sup>+</sup>, which is reversible under these experimental conditions. The two subsequent reversible AQ/AQ<sup>-</sup> and AQ<sup>-</sup>/AQ<sup>2-</sup> couple appeared at -0.95 V and -1.24 V (vs Fc/Fc<sup>+</sup>), respectively. The Ru<sup>II/III</sup> couple provide us some estimate about the HOMO energy level. For RuQ complex, two more bpy-based reductions were observed at -1.77 V and -1.97 V, (vs Fc/Fc<sup>+</sup>) respectively. These two processes are attributed to the two coordinated bpy-ligands in RuQ.<sup>[36]</sup> Please note that second bpy reduction was quasi reversible and for this differential pulsed voltammetry (DPV) plot for these two redox processes are shown in Figure 1. Table 1 shows that reduction potential of Ru(II)/Ru(III) of RuQ dye is similar to that of Ru(bpy)<sub>3</sub><sup>2+</sup> (0.89 V) vs Fc/Fc<sup>+</sup> in acetonitrile, which is rather anticipated. Literature reports suggest that free anthraquinone reduction occurs at -1.32 V (vs Fc/Fc<sup>+</sup>).<sup>[35]</sup> In the present study, AQ/AQ<sup>-</sup> couple appeared at -0.95 V (vs. Fc/Fc<sup>+</sup>) and this facile reduction is attributed to the coordination of L<sub>2</sub> to the cationic Ru(II)-centre. Further, intra-molecular H-bonding interaction between one of the two C=O<sub>imidazole</sub> group and NH<sub>imidazole</sub> facilitates protonation of the resulting radical (AQ<sup>-</sup>) intermediate and we observed the positive shift of the anthraquinone couple.<sup>[37]</sup> Scheme 2 represents the redox relative energy levels of different excited states of Ru-complex (RuQ) and anthraquinone moiety and it is evident that photo-excited electron transfer from Ru(II) to Anthraquinone is thermodynamically feasible.

Table 1. Half-wave potential of the Ru(bpy)<sub>3</sub><sup>2+</sup> and RuQ complex for the oxidation and reduction processes.

Species	E <sub>1/2</sub> (Ru <sup>II/III</sup> )	E <sub>1/2</sub> (AQ/AQ <sup>-</sup> )	E <sub>1/2</sub> (AQ <sup>-</sup> /AQ <sup>2-</sup> )	E <sub>1/2</sub> (bpy/bpy <sup>-</sup> )	E <sub>1/2</sub> (bpy <sup>-</sup> /bpy <sup>2-</sup> )	E <sub>1/2</sub> (bpy <sup>2-</sup> /bpy <sup>3-</sup> )
Ru(bpy) <sub>3</sub> <sup>2+</sup>	0.89V	-	-	-1.71V	-1.91V	-2.16V
RuQ	0.89V	-0.95V	-1.24V	-1.77V	-1.97V	-
AQ	-	-1.32V	-	-	-	-

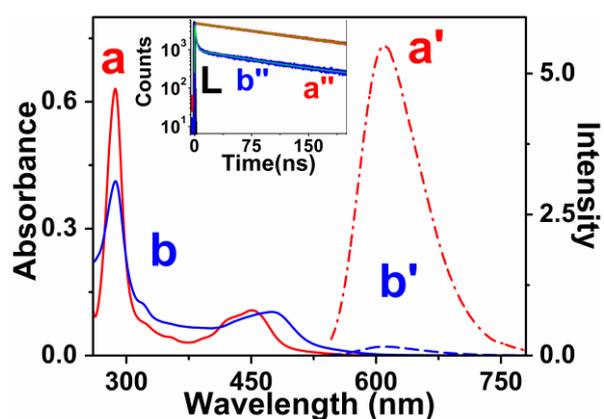


**Scheme 2.** Energy levels of RuQ complex and free anthraquinone from cyclic voltammetry measurements and feasibility of the electron transfer from Ru(II) centre to anthraquinone moiety.

Addition of water to acetonitrile solutions of RuQ complex studied results in positive shifts of both the reduction steps (-0.81V, -0.99V for AQ/AQ<sup>-</sup> and AQ<sup>-</sup>/AQ<sup>2-</sup> respectively) compared to the pure acetonitrile solvent. Representative cyclic voltammograms are shown in Figure S28, S29 (In the supporting information) for the RuQ and Ru(bpy)<sub>3</sub><sup>2+</sup> complexes respectively. In presence of water the positive shift is much larger for the second wave associated with the anthraquinone reduction. The shifts in the potentials of quinone couples caused by the addition of water to aprotic solvent are mainly due to the fast protonation of the dianion. The significant positive shift of the AQ couples in presence of water suggests that the involvement of water molecules plays an important role in the electron transfer phenomena by lowering the LUMO energy level of anthraquinone moiety. This was studied in details by time resolved absorption spectroscopy and is discussed in subsequent sections.

### Optical studies and luminescence spectroscopy of RuQ complex

Prior to the monitoring of ET and PCET processes in RuQ, it was essential to understand and compare the spectral (absorption and emission) properties of RuQ and Ru(bpy)<sub>3</sub><sup>2+</sup>. Figure 2 shows optical absorption and emission spectra of Ru(bpy)<sub>3</sub><sup>2+</sup> (Figure 2a) and RuQ (Figure 2b) in acetonitrile medium. For both the complexes, the absorption band at ~ 290 nm was attributed primarily for π-π\* based transition.<sup>[38]</sup> For Ru(bpy)<sub>3</sub><sup>2+</sup>, band at ~ 450 nm was assigned to a predominant Ru d<sub>π</sub> to bpy π\* based <sup>3</sup>MLCT transition.<sup>[39]</sup> For RuQ, this transition appeared at ~ 480 nm. In addition to that a prominent absorption band was observed at ~ 350 nm for RuQ and this could be attributed to a predominant intra-ligand [bpy]<sub>π-π\*</sub>-[L<sub>2</sub>]<sub>π-π\*</sub> based transition.<sup>[36]</sup>



**Figure 2.** Optical absorption spectra of (a) Ru(bpy)<sub>3</sub><sup>2+</sup> complex and (b) RuQ. Steady state luminescence spectra of (a') Ru(bpy)<sub>3</sub><sup>2+</sup> and (b') RuQ. **Inset:** time-resolved luminescence spectra of (a'') Ru(bpy)<sub>3</sub><sup>2+</sup> and (b'') RuQ after 445 nm laser excitation. All the emission decay traces are monitored at 610 nm. L stands for profile of 445 nm laser excitation source. The concentration of both the complex solutions is 1x10<sup>-5</sup> (M) in acetonitrile solvent.

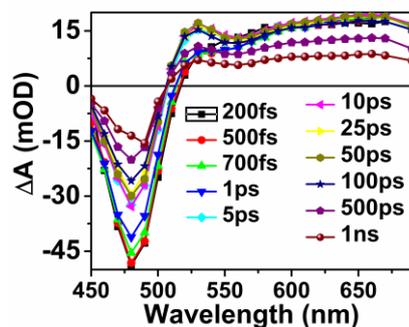
Presence of the extended conjugation and the electron withdrawing groups like imidazole/anthraquinone is expected to lower the  $L_2$ -based LUMO energy in RuQ and this further support the observed longer wavelength absorption band maximum for RuQ as compared to  $\text{Ru}(\text{bpy})_3^{2+}$ . Steady state luminescence spectra for  $\text{Ru}(\text{bpy})_3^{2+}$  (Figure. (2a')) and RuQ (Figure (2b')) in acetonitrile (at 298 K) are shown in Figure 2. Luminescence spectra for  $\text{Ru}(\text{bpy})_3^{2+}$  shows an anticipated broad luminescence band with maximum at 610 nm ( $\phi_{\text{emi}} = 0.1$ ) following excitation at 450 nm. This emission is attributed to  $^3\text{MLCT}$ -based emission.<sup>[40]</sup> For RuQ, luminescence band appears in the same spectral region with much lower emission quantum yield ( $\phi_{\text{emi}} = 0.003$ ). This appreciably lower luminescence quantum yield for RuQ as compared to pure  $\text{Ru}(\text{bpy})_3^{2+}$  could be attributed to energy or electron transfer process involving  $^3\text{MLCT}$  photoexcited state of Ru(II)-centre and the anthraquinone moiety as the acceptor fragment. Steady state redox potential data confirms the thermodynamic feasibility for the electron transfer pathway.<sup>[35]</sup> For RuQ, intramolecular hydrogen bonding between one of the two carbonyl moieties of anthraquinone fragment and  $\text{NH}_{\text{imidazole}}$  further lowers the energy level of anthraquinone LUMO, which eventually favours the possibility of the electron transfer process. These suggest that the decrease in photoluminescence quantum yield for the  $^3\text{MLCT}$ -based excited state in Ru(II)-imidazole-anthraquinone triad is due to intramolecular electron transfer process. In order to check such a possibility and to monitor the intramolecular electron transfer dynamics (if any), time resolved emission studies were carried out for both  $\text{Ru}(\text{bpy})_3^{2+}$  and RuQ following excitation at 445 nm and monitoring the emission decay for respective complex at 610 nm in dry and thoroughly degassed (with argon) acetonitrile solution. These decay profiles are shown as an inset in Figure 2. Figure 2a' shows the emission decay trace of pure  $\text{Ru}(\text{bpy})_3^{2+}$  complex which can be fitted mono-exponentially with time constant of  $\tau = 156.37$  ns. On the other hand Figure 2b' shows the emission decay trace of RuQ, which can be fitted bi-exponentially with time constant  $\tau_1 = 1.772$  ns (81.721%);  $\tau_2 = 111.031$  ns (18.279%). It is interesting to see that the Ru-complex emission decay occurs in much faster rate once it is coupled with H-bonded anthraquinone moiety. This decrement of emission lifetime in RuQ complex suggests a strong electronic interaction between  $\text{Ru}(\text{bpy})_3^{2+}$  and anthraquinone moiety. The fast 1.772 ns component may indicate photoinduced electron transfer process (PET). However, TCSPC cannot resolve the PET timescale as it occurs in ultrafast time domain. To confirm that we have performed femto second transient absorption study which are described later in detail. From the previous report, one can also predict that the  $^3\text{MLCT}$  excited state of  $\text{Ru}(\text{bpy})_3^{2+}$  can also be quenched due to the presence of molecular components through energy transfer. However it is known that anthraquinone moiety absorbs light below 450 nm<sup>[41]</sup> and there will be no overlap between absorption spectra of  $L_2$  and photo-luminescence spectra of Ru-complex, (Figure S10 in the Supporting Information) as a result we can discard Förster energy transfer mechanism. The emissive  $^3\text{MLCT}$  excited states of Ruthenium complexes can be quenched efficiently by triplet – triplet energy transfer when the

reaction energetic are favourable (dexter energy transfer). However, the lowest triplet excited state of anthraquinone<sup>[42],[43]</sup> is at 2.72 eV which is much higher than the  $^3\text{MLCT}$  state of the  $\text{Ru}(\text{bpy})_3^{2+}$  complex (2.12 eV). So,  $\text{Ru}(\text{bpy})_3^{2+}$  to anthraquinone triplet-triplet energy transfer is an endergonic process. On the other hand with increasing base concentration the fluorescence intensity of RuQ complex (Figure S13 in the Supporting Information) increases and addition of 2equivalent base (TBAOH) the fluorescence quantum yield increases to  $\phi_{\text{emi}} = 0.004$ . The increased quantum yield in presence of base also suggests that triplet-triplet energy transfer from Ru-centre to anthraquinone is a unlikely quenching process. Here the decrement of emission lifetime can be mainly attributed to photo-excited electron transfer from Ru-complex to anthraquinone moiety which is thermodynamically viable process. While addressing photoluminescence quenching in RuQ, it is clear that charge separation can take place through electron transfer from photo excited  $\text{Ru}(\text{bpy})_3^{2+}$  to anthraquinone forming cation radical of Ru-complex and anion radical of anthraquinone ( $\text{AQ}^{\cdot-}$ ). The ligand  $L_2$  shows a broad emission spectrum (450 nm – 650 nm) with emission maxima at 500 nm. The emission decay trace of  $L_2$  can be best fitted with two time constants  $\tau_1 = 0.071$  ns (95%) and  $\tau_2 = 1.382$  ns (5%) (Figure S11 in the Supporting Information). To understand the intramolecular electron transfer dynamics in shorter time scale we have carried out femtosecond transient absorption studies in the above systems, which are discussed below.

#### Transient absorption studies of RuQ complex

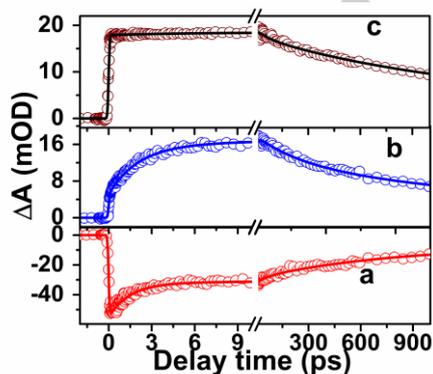
Femtosecond transient absorption studies have been carried out for RuQ,  $\text{Ru}(\text{bpy})_3^{2+}$  complexes and  $L_2$  ligand separately after exciting at 400 nm. For both the complexes, transient absorption due to triplet state in 500-700 nm with very long lifetime ( $\gg 1$  ns) and bleach due to ground state absorption<sup>[44]</sup> below 500 nm were observed (FigureS18 in the Supporting Information). The broad band (580 nm - 700 nm) can be assigned as the excited triplet state absorption of the  $d_{\pi\text{Ru}-\pi^*\text{bpy}}$  based  $^3\text{MLCT}$  state and decays till 1 ns (FigureS20 in the Supporting Information).<sup>[45]</sup> Figure 3 shows transient absorption spectra of RuQ complex at different time delay and these set of time resolved spectra looks completely different as compared to those for  $\text{Ru}(\text{bpy})_3^{2+}$ . Transient absorption spectra of RuQ complex show negative absorption below 515 nm and broad absorption band beyond 515 nm with two peaks at ~ 530 nm and ~ 650 nm respectively. Time-resolved photoluminescence and cyclic voltammetric studies indicated that the intra-molecular electron transfer takes place from Ru-complex to anthraquinone moiety (AQ). In the present study, the transient peak at 530 nm can be attributed to radical anion of anthraquinone ( $\text{AQ}^{\cdot-}$ ) which has been confirmed from earlier reports.<sup>[46],[47],[48]</sup> On the other hand broad transient absorption band 580-700 nm region peaking at 600 nm can be attributed to cation radical of Ru-complex  $\text{Ru}(\text{bpy})_3^{3+}$ . Cation radical band was confirmed on the basis of the data obtained in a complementary pulsed radiolysis experiment (Figure S24 in the Supporting Information) where  $\text{Ru}(\text{bpy})_3^{3+}$  was generated selectively by the reaction of  $\text{Ru}(\text{bpy})_3^{2+}$  with  $\text{N}_3$  radical in  $\text{N}_2\text{O}$

saturated aqueous solution (5% acetonitrile + 95% water). The negative absorption band in 450-500 nm region peaking at 480 nm can be attributed to the bleach due to ground state absorption.



**Figure 3.** Femtosecond transient absorption spectrum of RuQ in acetonitrile solvent after exciting the samples at 400 nm laser light.

Now, to monitor the electron transfer dynamics transient kinetics have been monitored at key wavelengths and shown in Figure 4. The transient decay kinetics at 530 nm can be fitted with tri-exponential growth with time constants of  $\tau_1 = <100 (\pm 15)$  fs (45%),  $\tau_2 = 2 (\pm 0.2)$  ps (50%),  $\tau_3 = 10 (\pm 0.5)$  ps (5%), and bi-exponential decay with time-constants of  $\tau_1 = 250 (\pm 12.5)$  ps (55%),  $\tau_2 = >1 (0.05)$  ns (45%) (Table 2). Here the first growth component  $< 100 (\pm 15)$  fs can be attributed to the formation of triplet state of Ru-complex as the  $^3\text{MLCT}$  state has absorption in this wavelength region. The  $2 (\pm 0.2)$  ps time constant can be attributed to electron transfer from photo-excited Ru-complex to anthraquinone moiety with the formation of anthraquinone radical ( $\text{AQ}^{\cdot-}$ ) (Scheme 3). The important observation in the transient absorption spectrum is that, at 530 nm there is no obvious band at 0.5 ps, but there is a clear peak after 1 ps, and this is essentially fully developed after 5 ps. This observation strongly suggests that the 2 ps is the major component of  $\text{AQ}^{\cdot-}$  formation.



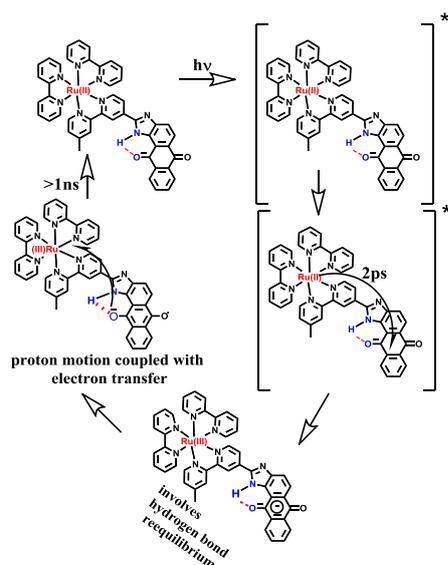
**Figure 4.** Transient kinetic traces of (a) cation radical (at 600 nm) of Ru-complex; (b) anion radical of anthraquinone ( $\text{AQ}^{\cdot-}$ ) (at 530 nm); and (c) bleach recovery kinetics 490 nm of RuQ complex.

After accepting the electron,  $\text{pK}_a$  of  $\text{AQ}^{\cdot-}$  form increases and the H-bonding equilibrium changes with the imidazole proton and forms strong H-bond with  $\text{AQ}^{\cdot-}$ . However the transient decay kinetics at 600 nm can be fitted with bi-exponential growth with time constants of  $\tau_1 = < 100 (\pm 15)$  fs (95%),  $\tau_2 = 10 (\pm 0.5)$  ps (5%), and bi-exponential decay with time-constants of  $\tau_1 = 60 (\pm 3)$  ps (75%),  $\tau_2 = > 1 (\pm 0.05)$  ns (25%) (Table 2). Although we have attributed that transient at 600 nm is due to metal centered oxidation of Ru-complex however it is wondering that  $2 (\pm 0.2)$  ps time constant is absent which we have attributed to forward electron transfer time. This might be due to both photo-excited triplet state ( $^3\text{MLCT}$ ) and oxidised state (cation radical) absorb in the same spectral region.<sup>[49]</sup>

**Table 2.** Parameters for multi-exponential fits for transient kinetics of RuQ dye at different wavelengths after 400 nm laser excitation.

Wavelength (nm)	$\tau_{1 \text{ growth}}$	$\tau_{2 \text{ growth}}$	$\tau_{3 \text{ growth}}$	$\tau_1$	$\tau_2$	$\tau_3$
490	$<100 (\pm 15)$ fs (100%)	-	-	1.5 (0.15) ps (40%)	60 ( $\pm 3$ ) ps (17%)	$>1 (\pm 0.05)$ ns (43%)
530	$<100 (\pm 15)$ fs (45%)	2 ( $\pm 0.2$ ) ps (50%)	10 ( $\pm 0.5$ ) ps (5%)	250 ( $\pm 12.5$ ) ps (55%)	$>1 (\pm 0.05)$ ns (45%)	-
600	$<100 (\pm 15)$ fs (95%)	10 ( $\pm 0.5$ ) ps (5%)	-	60 ( $\pm 3$ ) ps (75%)	$>1 (\pm 0.05)$ ns (25%)	-

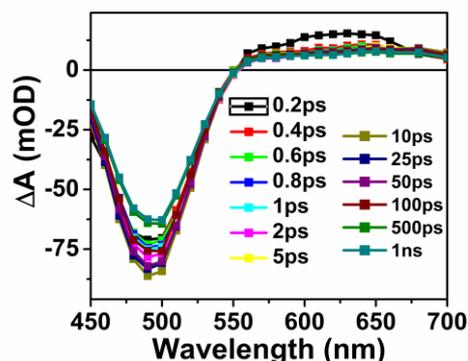
So, on transfer of electron from triplet state, metal centered oxidation of Ru-complex occurs which absorbs in the same spectral region with almost similar molar extinction co-efficient. As a result we do not see much change in transient absorption in early time scale. The bi-exponential decay components at both 530 nm and 600 nm can be attributed to back electron transfer time from anthraquinone radical ( $\text{AQ}^{\cdot-}$ ) to Ru(III). The bi-exponential decay of 530 nm and 600 nm kinetic traces are due to the multiple conformations of the bpy-attached Im-AQ fragment which can rotate around the single bond. The bleach kinetics at 490 nm can be fitted with pulse-width limited growth  $< 100 (\pm 15)$  fs and multi-exponential recovery with time-constants of  $\tau_1 = 1.5$  ps (40%),  $\tau_2 = 60 (\pm 3)$  ps (17%) and  $\tau_3 = > 1 (\pm 0.05)$  ns (43%). Bleach recovery generally gives the indication of back electron transfer however in the present investigation as we are monitoring the bleach at 490 nm which has overlap with the transient spectra of anthraquinone radical  $\text{AQ}^{\cdot-}$  so the faster component 1.5 ( $\pm 0.15$ ) ps can be attributed to electron transfer time from photo-excited Ru-complex to anthraquinone. However, the longer components 60 ( $\pm 3$ ) ps and  $> 1 (\pm 0.05)$  ns are attributed to back electron transfer from anthraquinone radical  $\text{AQ}^{\cdot-}$  to Ru(III).



**Scheme 3.** Mechanistic scheme of electron transfer and proton coupled electron transfer (PCET) pathways and involvement of H-bonding in the transient states.

The above forward and backward electron transfer are demonstrated in Scheme 3. Before discussing the intramolecular electron transfer and back electron transfer process, it is worth noting that FTIR spectra showed the strong evidence for intramolecular H-bonding between anthraquinone carbonyl functional group and adjacent imidazole N-H functional group (Figure S25 in the Supporting Information). In the excited state this H-bonding equilibrium changes followed by easier anthraquinone reduction process. Then subsequently the ground state bleach recovers as Ru(II) is regenerated in the course of intramolecular ET recombination with AQ<sup>•-</sup> unit and Ru(III) (Scheme 3). Ultrafast intramolecular electron transfer transiently produces AQ<sup>•-</sup> and Ru(III). The forward electron transfer reaction initially leads to a charge separated state after photo excitation of Ru(bpy)<sub>3</sub><sup>2+</sup> centre, finally back electron transfer from carbonyl to Ru(III) i.e. the radical recombination occurs. The positive absorption band at 530 nm indicates the formation of additional intermediate (AQ<sup>•-</sup>) shown in Scheme 3. The significant observation is that the 530 nm band decays with the same kinetics as that of the Ru<sup>3+</sup> absorption and ground state recovery. Therefore there is no proton transfer from imidazole to AQ<sup>•-</sup>.

To confirm that there is no interference of the L<sub>2</sub> ligand excited state dynamics in the electron transfer and H-bonding equilibrium dynamics we had taken the transient absorption spectrum of L<sub>2</sub> ligand in acetonitrile separately (Figure S21 in the Supporting Information). The spectrum shows broad positive absorption peaking at 550 nm and the kinetic trace monitored at 550 nm is totally different from the kinetic trace of the RuQ complex monitored at 530 nm.



**Figure 5.** Transient absorption spectrum of RuQ complex in presence of tetrabutyl ammonium hydroxide in acetonitrile at different time delay after exciting the sample at 400 nm laser light.

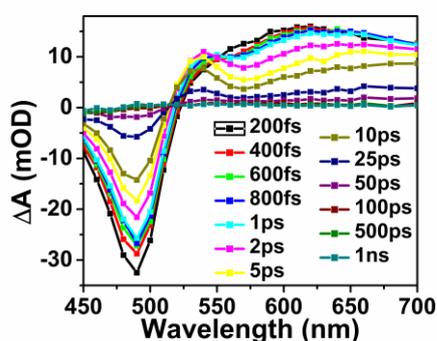
In Scheme 3 we have discussed that the intramolecular H-bonding of imidazole proton and the anthraquinone moiety facilitates the intramolecular electron transfer from Ru(bpy)<sub>3</sub><sup>2+</sup> to the anthraquinone moiety. Now to re-confirm the above process we have carried out transient absorption studies of RuQ in presence of tetra butyl ammonium hydroxide (TBAOH in methanolic solution) and shown in Figure 5. The TA spectra of RuQ in presence of base show broad bleach at 490 nm and a broad positive absorption at (560-700 nm). The transient spectra showed that the bleach slightly shifted to the longer wavelength and there is no signature of AQ<sup>•-</sup> radical. It is interesting to see that the transient spectra of RuQ in presence of TBAOH exactly matches with transient spectra of Ru(bpy)<sub>3</sub><sup>2+</sup> (Figure S18 in the Supporting Information). In addition to that the transient absorption and bleach kinetics also matches exactly as that of Ru(bpy)<sub>3</sub><sup>2+</sup> (Figure S23 in the Supporting Information). This observation clearly suggests that no intramolecular electron transfer takes place from Ru-centre to AQ-centre in RuQ in presence of TBAOH. Herein TBAOH deprotonate the imidazole proton making the electron transfer process energetically unfavourable, as a result no electron transfer takes place from photo-excited Ru-complex to anthraquinone moiety.

Scheme 3 supported by the above experimental results suggested that intra-molecular H-bonding facilitates the excited state electron transfer of RuQ and followed by the proton motion and produces a charge separated state. Electron transfer from photo excited Ru-centre results in the remarkable pK<sub>a</sub> increase at quinone centre, that generates a new state leading to a H-bond rearrangement reaction between imidazole to the anthraquinone moiety.<sup>[50]</sup> So the overall reaction can be considered as a proton coupled electron transfer (PCET) wherein a considerable amount of proton density transferred from imidazole to anthraquinone rather than full proton transfer, finally it goes to ground state due to radical recombination. It has been observed that H-bonding play a major role in PCET reaction of photo-excited RuQ complex.

### Photoinduced electron transfer in the RuQ complex in presence of water

Water is an interesting molecule for H-bonding, it can act as both H-bond donor and H-bond acceptor<sup>[51]</sup> and stabilises many excited state species. After accepting electron, AQ<sup>-</sup> is known to be highly reactive with water molecule<sup>[46]</sup> and the exact mechanism and the photoproduct is not well understood. Mechanistic demonstration of the PCET is always a challenging task. Most of the natural processes which involve PCET reactions avoid intermediate charge build-up states, and follows the accumulation of various types of oxidizing equivalents which can stabilise the high energy intermediates. So in the present study, it is important to monitor both ET and PCET in the presence of water. Literature reports also suggest that both the benzoquinone and anthraquinone are excited state oxidants, and can oxidise aliphatic alcohols, and even water.<sup>[46]</sup>

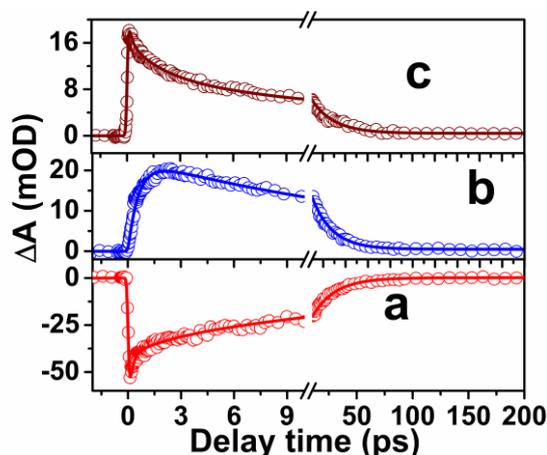
In the present investigation we have carried out steady state absorption and emission spectroscopic study of RuQ complex in presence of water. Figure S7 (In the supporting information) shows the optical absorption spectra of RuQ complex in water-acetonitrile (99:1, v/v) solvent mixture. The ~ 10 nm shift of optical absorption spectra in water-acetonitrile (99:1, v/v) solvent mixture as compared to pure acetonitrile can be attributed to the hydrogen bonding interaction between N-H functional group of the imidazole and water molecules. For better understanding it is necessary to calculate the pK<sub>a</sub> of the RuQ complex. We did the pH titration experiment using photoluminescence technique, exciting the RuQ complex at 450 nm, with increasing pH of the solution from pH 2 to 12 (1:1, v/v) in CH<sub>3</sub>CN–H<sub>2</sub>O mixture. We calculated pK<sub>a</sub> of RuQ complex, from the inflection point of the titration curve monitoring the emission maximum at 612 nm as a function of pH is shown in (Figure S8 in the Supporting Information). The inflection point of the titration curve obtained is at pH<sub>i</sub> = 6.75. The true excited-state ionization constant (pK<sub>a</sub><sup>\*</sup>) is 7.45, obtained from pH<sub>i</sub> while taking into account the different excited-state lifetimes of the protonated (τ<sub>HB</sub>) and deprotonated forms (τ<sub>B</sub>) of the RuQ complex. Since we used PF<sub>6</sub> salt of RuQ complex, the solubility of RuQ is extremely poor in pure water.



**Figure 6.** Femtosecond transient absorption spectra of RuQ in acetonitrile-water (2:3, v/v) solvent mixture at different time delay after 400 nm laser excitation.

Therefore, for the transient absorption measurements RuQ was dissolved in acetonitrile-water (2:3, v/v) solvent mixture instead of pure water. Figure 6 shows the transient absorption spectra of RuQ in acetonitrile-water (2:3, v/v) mixture at different time delay after exciting the sample at 400 nm laser. The transient spectra consist of negative absorption below 510 nm peaking at 490 nm and a broad positive absorption band from 520-700 nm and beyond. The negative absorption band is attributed to bleach due to ground state absorption which matches with steady state optical absorption spectra (Figure S7 in the Supporting Information). It is interesting to see that with time, the broad positive absorption band was converted into two separate transient absorption bands peaking at 542 nm and 630 nm, which can be attributed to anthraquinone radical (AQ<sup>-</sup>) and cation radical of Ru-complex respectively. More importantly, the transient absorption band due to AQ<sup>-</sup> in acetonitrile-water (2:3, v/v) was shifted to the red region of spectra (542 nm) as compared to that in pure acetonitrile (530 nm) (Figure 3). This shift could be attributed to strong H-bonding interaction between AQ<sup>-</sup> and water as water is a strong H-bond donor. It is noteworthy to see that both bleach recovery and transient kinetics decay was much faster in acetonitrile-water (2:3, v/v) mixture as compared to pure acetonitrile. This observation clearly suggests that water plays a major role in both ET and PCET reaction in the present investigation. To monitor both ET and PCET dynamics, transient kinetics was monitored at key wavelengths as shown in Figure 7. The transient decay kinetics at 540 nm can be fitted with single exponential growth with time constants of τ<sub>1</sub> = 500 (±50) fs and single exponential decay with time-constants of ~ 20 (±2) ps (Table 3) due to the recombination reaction. We have already mentioned that growth at 540 nm due to anthraquinone radical (AQ<sup>-</sup>) can be attributed to electron transfer time from photo-excited Ru-complex to anthraquinone moiety.

It is interesting to see that in the presence of water, electron transfer become faster 500 (±50) fs. CH<sub>3</sub>CN–H<sub>2</sub>O leads to an even more important increase in electron transfer rates. The stabilization of the anthraquinone radical anion through the formation of H-bonding with water and the considerable positive shifting of the AQ reduction potential compared to pure acetonitrile indicates that LUMO energy level of anthraquinone become further lowers that eventually facilitate both forward and backward electron transfer. The free anthraquinone moiety in RuQ complex cannot be protonated by water (pK<sub>a</sub> = 15.7) or H<sub>3</sub>O<sup>+</sup> (pK<sub>a</sub> = - 1.7) as the conjugate acid of anthraquinone possess the pK<sub>a</sub> = - 8.2 in H<sub>2</sub>O. On the other hand, in N, N'-dimethylformamide solvent medium the conjugate acid form of anthraquinone mono anion has pK<sub>a</sub> = 5.3, hence H<sub>3</sub>O<sup>+</sup> can protonate the anthraquinone mono anion.<sup>[35],[52]</sup> In addition to this as we change the solvent medium from acetonitrile to acetonitrile-water (2:3, v/v) mixture, the dielectric constant of the medium increases from 35.94 to 55.87,<sup>[53]</sup> which in turn increases the driving force for intramolecular electron transfer from Ru-centre to AQ centre in RuQ complex.<sup>[35]</sup>



**Figure 7.** Transient kinetic traces of (c) cation radical of RuQ-complex (at 600 nm); (b) anion radical of anthraquinone ( $AQ^{\bullet-}$ ) (at 540 nm); and (a) bleach recovery kinetics at 490 nm of RuQ complex in acetonitrile-water (2:3, v/v) solvent mixture.

The single exponential decay time constant  $20 (\pm 2)$  ps could be attributed to back electron transfer from  $AQ^{\bullet-}$  radical anion to Ru(III) as shown in Scheme 4. The bleach recovery kinetics at 490 nm can be fitted with pulse-width limited single exponential growth and multi-exponential recovery with time constants of  $\tau_1 = 200 (\pm 26)$  fs (30%),  $\tau_2 = 2 (\pm 0.2)$  ps (30%) and  $\tau_3 = 20 (\pm 2)$  ps (40%). Due to the overlap between transient bleach (at 490 nm) and anthraquinone radical ( $AQ^{\bullet-}$ ) (at 540 nm), both the faster components at 490 nm can be attributed to forward electron transfer. However, the longer component can be attributed to back electron transfer from  $AQ^{\bullet-}$  to Ru(III) (Scheme 4). Kinetics at 600 nm can be fitted with pulse-width limited  $< 100 (\pm 15)$  fs growth and multi-exponential decay with time constants of  $\tau_1 = 200 (\pm 26)$  fs (24%),  $\tau_2 = 2 (\pm 0.2)$  ps (43.7%) and  $\tau_3 = 20 (\pm 2)$  ps (32.3%). Here the faster components can be attributed to electron transfer from the triplet state of Ru-complex to anthraquinone however the longer component can be attributed to back electron transfer time due to ground state recombination. Probable reaction mechanism was predicted (Scheme 4) and the effect of water molecule has been demonstrated in both forward ET and back ET reaction. Upon photo-excitation, electron will be transferred to anthraquinone moiety. After this electron transfer reaction, electron will be localized on oxygen atom of anthraquinone, and there occurs an inter molecular proton relay with anthraquinone and water molecules.

To confirm that, if there is any effect of pH in the forward electron transfer rate we also performed the Transient absorption experiment in presence of acidic pH solution (pH 4), using aqueous HCl. Literature reports suggest that the  $AQ^{\bullet-}$  is stable only in the pH range of 10-4. With decrease in the pH below 2, the transient absorption spectrum of  $AQ^{\bullet-}$  decreases and finally vanishes.<sup>[47]</sup> The transient absorption measurements in acetonitrile-water (2:3, v/v) mixture at pH 4 are shown in (Figure S14 in the Supporting Information). It is interesting to see that at pH 4 there is no change in transient absorption

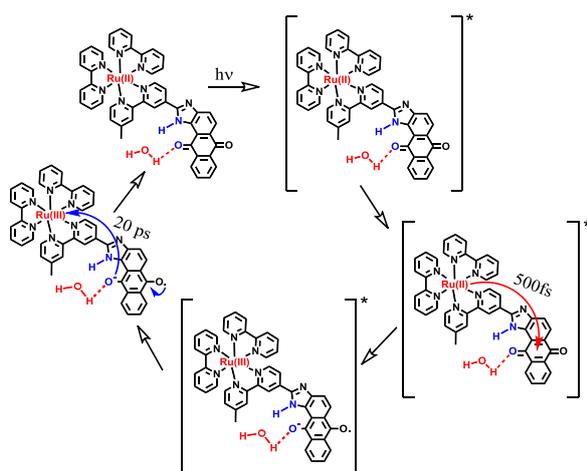
spectra and transient kinetics are similar with acetonitrile-water (2:3, v/v) mixture. This observation clearly suggests that, if the protonation of the anthraquinone takes place after forward electron transfer from Ru-centre to AQ unit, and there is no influence of pH in the forward electron transfer rate.

Scheme 4 demonstrates the involvement of hydrogen-bonding of water molecules to AQ and  $AQ^{\bullet-}$ . Water acts as proton relay in the forward electron transfer from Ru(II) to anthraquinone moiety.

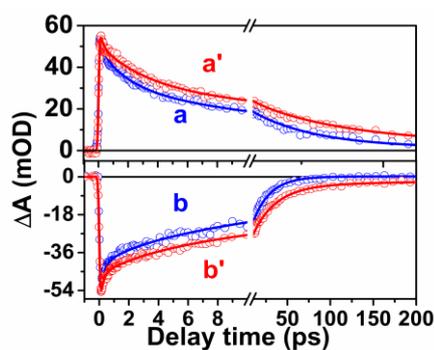
**Table 3.** Parameters for multi-exponential fits for the transient of RuQ dye in acetonitrile-Water (2:3, v/v) mixture at different wavelengths after 400 nm laser excitation.

Wavelength (nm)	$\tau_{1 \text{ growth}}$	$\tau_1$	$\tau_2$	$\tau_3$
490	$< 100 (\pm 15)$ fs (100%)	$200 (\pm 26)$ fs (30%)	$2 (\pm 0.2)$ ps (30%)	$20 (\pm 2)$ ps (40%)
540	$500 (\pm 50)$ fs (100%)	$20 (\pm 2)$ ps (100%)	-	-
600	$< 100 (\pm 15)$ fs (100%)	$200 (\pm 26)$ fs (24%)	$2 (\pm 0.2)$ ps (43.7%)	$20 (\pm 2)$ ps (32.3%)

To examine the proton coupled electron transfer process it is common to distinguish the effect of protonation and deprotonation in presence of  $D_2O$ . Interestingly we observed a slightly slower forward electron transfer rate (700 fs) in presence of  $D_2O$ . Transient absorption spectra of RuQ in acetonitrile- $D_2O$  (2:3, v/v) are shown in (Figure S16 in the Supporting Information). To monitor the difference between  $H_2O$  and  $D_2O$  in the back electron transfer reaction transient kinetics at both 490 nm and at 600 nm are compared and shown in Figure 8. As expected, both the transient decay and bleach recovery were slower in presence of  $D_2O$  as compared to  $H_2O$ . The transient data are fitted multi-exponentially and are shown in Table 4. At both the wavelengths (490 nm and 600 nm) two longer components  $2 (\pm 0.2)$  ps and  $20 (\pm 2)$  ps have been observed in water, which we attributed to back electron transfer reaction from anthraquinone to Ru(III) centre. Additionally in the transient kinetics it is clear from the data shown in Figure 8 that the isotope effect is only present in long time components of 20 ps. While for the shorter timescales the (2 ps and 3 ps) two time-constants are pretty much the same. Interestingly, in  $D_2O$  in both the wavelengths the longer components can be fitted with  $3 (\pm 0.3)$  ps and  $30 (\pm 3)$  ps respectively. T. J. Meyer and his co-workers had reported EPT and PCET phenomena in the sub-picosecond time scale.<sup>[54],[55]</sup> In our Transient Absorption study, we have clearly identified the transient absorption photoproducts even in presence of water. It has been observed that intramolecular H-bonding and H-bonding between  $AQ^{\bullet-}$  and water play a major role in PCET reaction of photo-excited RuQ complex. The experimental observations suggest the unique example of proton coupled electron transfer reaction in presence of water in the ultrafast time scale for the Ru-polypyridyl complex as sensitizer.



**Scheme 4.** Mechanistic scheme for electron transfer and proton coupled electron transfer (PCET) pathways and involvement of water molecule through H-bonding in the transient states.



**Figure 8.** Transient decay kinetics at 600 nm for RuQ in (a) acetonitrile- H<sub>2</sub>O (2:3, v/v) and (a') in acetonitrile- D<sub>2</sub>O (2:3, v/v); bleach recovery kinetics at 490 nm for RuQ in (b) acetonitrile- H<sub>2</sub>O (2:3, v/v) and (b') in acetonitrile- D<sub>2</sub>O (2:3, v/v).

**Table 4.** Parameters for multi-exponential fit for the transients of RuQ dye at different wavelengths in acetonitrile-H<sub>2</sub>O (2:3, v/v) and in acetonitrile-D<sub>2</sub>O (2:3, v/v) solvent mixtures after exciting the sample at 400 nm laser light.

Medium	$\lambda$ (nm)	$\tau_{\text{growth}}$	$\tau_1$	$\tau_2$	$\tau_3$
Acetonitrile- H <sub>2</sub> O (2:3, v/v)	490	<100 ( $\pm$ 15) fs (100%)	200 ( $\pm$ 26) fs (30%)	2 ( $\pm$ 0.2) ps (30%)	20 ( $\pm$ 2) ps (40%)
Acetonitrile- D <sub>2</sub> O (2:3, v/v)	490	<100 ( $\pm$ 15) fs (100%)	200 ( $\pm$ 26) fs (20%)	3 ( $\pm$ 0.3) ps (33%)	30 ( $\pm$ 3) ps (47%)
Acetonitrile- H <sub>2</sub> O (2:3 v/v)	600	<100 ( $\pm$ 15) fs (100%)	200 ( $\pm$ 26) fs (24%)	2 ( $\pm$ 0.2) ps (43.7%)	20 ( $\pm$ 2) ps (32.3%)
Acetonitrile- D <sub>2</sub> O (2:3, v/v)	600	<100 ( $\pm$ 15) fs (100%)	200 ( $\pm$ 26) fs (16.66%)	3 ( $\pm$ 0.3) ps (42.5%)	30 ( $\pm$ 3) ps (40.8%)

## Conclusion

Ruthenium polypyridyl complex covalently linked with imidazole-anthraquinone (RuQ) has been designed, synthesized and characterized by FTIR, Mass and NMR spectroscopy. Imidazole H-atom forms H-bond with carbonyl group which suggests that RuQ molecule is an ideal system for demonstrating proton coupled electron transfer reaction in the photo-excited state. Cyclic voltammetric studies of RuQ complex suggest that photo-excited electron can be transferred from Ru-polypyridyl moiety to anthraquinone moiety (AQ). Water plays an important role in both forward ET and PCET reactions, where both the reaction rate gets facilitated in presence of water. The significant lowering of LUMO energy level of anthraquinone in presence of water facilitates both forward and backward electron transfer process which has been confirmed by femtosecond transient absorption studies. We have successfully identified the transient absorption photo products AQ<sup>•-</sup> and Ru(bpy)<sub>3</sub><sup>3+</sup> in acetonitrile and even in presence of water. Electron transfer time from photo-excited Ru(II) to anthraquinone moiety has been monitored after following growth time of anthraquinone radical (AQ<sup>•-</sup>) at 530 nm resulting time constants of 2 ( $\pm$ 0.2) ps and 10 ( $\pm$ 0.5) ps. Forward ET reaction time has been determined to be 500 ( $\pm$ 50) fs in presence of water. Our study reveals that excitation of the RuQ complex is followed by electron transfer to the anthraquinone. Our results reveal the effects of H-bond stabilization on photoinduced electron transfer. To the best of our knowledge, this type of example is rare in contemporary literature.

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**Keywords:** Proton Coupled Electron Transfer, Intramolecular Electron Transfer, H-bond rearrangement.

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## FULL PAPER

Ultrafast electron transfer (ET) and proton coupled electron transfer (PCET) reaction has been demonstrated in Ru(II)-polypyridyl complex, with the help of Femtosecond transient absorption spectroscopy. Water found to play an active role in both ET and PCET reaction. The electron transfer process was followed by proton reequilibration.



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