

Luminescence Quenching and Upconversion Experiment

CH454 Physical Chemistry Lab #3

Introduction

This laboratory experiment will provide you with an introduction to the study the quantum yield and kinetics of luminescence quenching. One of the most studied molecules in this field is the $\text{Ru}(\text{bpy})_3^{2+}$ complex. This complex is used as a photosensitizer in photoelectrochemistry (solar energy) applications. It is also a nice laboratory example, because it has a long-lived excited state. In order to understand the observations in this experiment you will want to review first order and second order kinetics, fluorescence and phosphorescence, and various quenching mechanisms. It is important to differentiate between energy and the charge transfer mechanisms of quenching. Here we will use energy transfer quenching combined with a second process of triplet-triplet annihilation in the acceptor to make a higher energy singlet state.

The donor for triplet energy transfer used in this experiment is $\text{Ru}(\text{bpy})_3^{2+}$, which is shown in Figure 1.

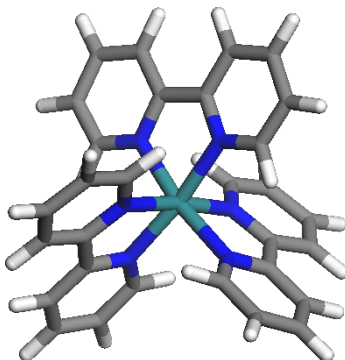
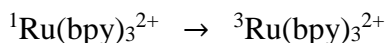


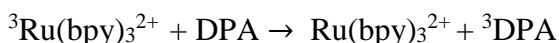
Figure 1. The structure of the $\text{Ru}(\text{bpy})_3^{2+}$ ion

These bidentate ligands form *tris* complexes with Ru(II) that have approximately D_3 point group symmetry. The electronic absorption spectrum of $\text{Ru}(\text{bpy})_3^{2+}$ at room temperature consists of a broad band from 400-460 nm. This transition consists of a (spin allowed) metal-to-ligand charge transfer (MLCT) from a molecular orbital that has mostly Ru(II) *d* orbital character to a molecular orbital that has mostly ligand π orbital character. Since the band is a MLCT band it has a large excited state dipole moment.

Ru(II) complexes are excited by metal-to-ligand charge transfer (MLCT) transitions. For example, in the bipy complex the process initially forms a singlet MLCT state. However, this singlet state forms a triplet state by intersystem crossing.



One reason for this is the heavy atom effect of Ru, which increases the spin-orbit coupling process leading to a spin flip. Once the triplet state is formed the excited state of $^3\text{Ru}(\text{bpy})_3^{2+}$ can be quenched by anthracene. Since $\text{Ru}(\text{bpy})_3^{2+}$ has evolved to the triplet state the luminescence is phosphorescence rather than fluorescence. However, many people mistakenly refer to the luminescence as fluorescence. In this experiment we will use 9,10-diphenylanthracene (DPA) since that molecule cannot undergo photochemical crosslinking reactions.



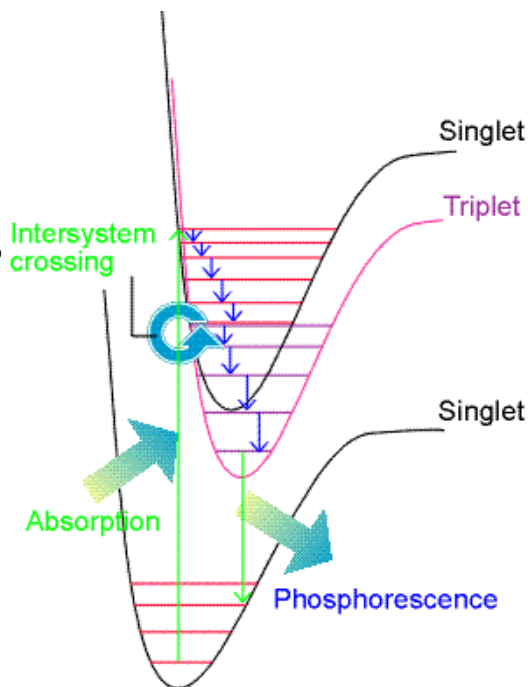
This aspect of the experiment is fairly routine since phosphorescence quenching of $\text{Ru}(\text{bpy})_3^{2+}$ obeys standard quenching kinetics, so-called Stern-Volmer kinetics. The Stern-Volmer model is the same for fluorescence and phosphorescence quenching. The experiment we will study has an added process, which is the combination of two ^3DPA molecules by triplet-triplet annihilation to make a higher energy singlet DPA.



When these reactions are combined they are given the name “upconversion” to refer to the fact that the output photon from the fluorescence of ^1DPA has a higher energy than the input photon used to excite $\text{Ru}(\text{bpy})_3^{2+}$. The issues surrounding the quenching of phosphorescence are the core of the lab. The observation of upconversion is mainly to show you one of the numerous applications of quenching processes.

In this experiment you will measure both the relative quantum yield and the photochemistry of electronically excited state of the tris(2,2'-bipyridine) ruthenium (II) ion $[\text{Ru}(\text{bpy})_3]^{2+}$ in which Ru(II) ion is surrounded by three bidentate chelating ligands of bipyridine (bpy) as shown in figure below:

Fluorescence vs. Phosphorescence. Excited states can be deactivated either by be **radiative** or **nonradiative** processes. Spin allowed radiative transitions are usually short-lived ($< 10^{-8}$ s) and give rise to luminescence, which is known as **fluorescence**. Spin forbidden radiative transitions can also be observed as a long-lived luminescence, which is called **phosphorescence**. Since singlet-triplet transitions are spin-forbidden, triplet excited states can be form only by means of a process known as **intersystem crossing**. The intersystem designation refers to the fact that the molecular system crosses from the singlet to the triplet state manifold. Although phosphorescence is often difficult to observe in many organic molecules, it is readily observed in $\text{Ru}(\text{bpy})_3^{2+}$.



Kinetics of luminescence and quenching. Ru(II) diimine complexes are relatively highly luminescent, even though observed emission is from a triplet $^3\text{MLCT}$ excited state. The reason for that is in a high spin-orbit coupling (Ru is a *heavy* metal) which couples singlet and triplet manifold of states in so called 'configurational interaction' and results in relatively short radiative lifetime. At room temperature and in aqueous solution, $^3\text{Ru}(\text{bpy})_3^{2+}$ shows strong luminescence at about 600 nm with lifetime around $\tau_0 \sim 600$ ns. There are two processes that compete with the phosphorescent deactivation. These are internal non-radiative process intrinsic to $^3\text{Ru}(\text{bpy})_3^{2+}$ and quenching processes. In this case we will focus on energy transfer quenching, which means that the triplet state of $^3\text{Ru}(\text{bpy})_3^{2+}$ is transferred to the energy transfer acceptor, which is 1,9-diphenylanthracene (DPA).

<i>Luminescence:</i>	$^3\text{Ru}(\text{bpy})_3^{2+} \rightarrow \text{Ru}(\text{bpy})_3^{2+} + h\nu$	(1)
<i>Nonradiative deactivation:</i>	$^3\text{Ru}(\text{bpy})_3^{2+} \rightarrow \text{Ru}(\text{bpy})_3^{2+} + \text{heat}$	(2)
<i>Quenching:</i>	$^3\text{Ru}(\text{bpy})_3^{2+} + \text{Q} \rightarrow \text{Ru}(\text{bpy})_3^{2+} + ^3\text{Q}$	(3)

We will use a nitrogen laser which provides excitation pulses of about 4 nsec half-width. A pulse excites a dilute solution of $[\text{Ru}(\text{bpy})_3]^{2+}$ and produces a population of excited states $^3[\text{Ru}(\text{bpy})_3]^{2+}$. Without a quencher, this population decays radiatively with an observed rate constant of $k_{obs} = k_r + k_{nr}$, where the radiative rate constant is k_r and the non-radiative rate constant is k_{nr} . If we assume that the laser pulse produces a population N_0 of $^3[\text{Ru}(\text{bpy})_3]^{2+}$ at time $t = 0$, the population can be shown to decay exponentially (first order kinetics), resulting in the following time dependence of the emission intensity I (photons/sec):

$$I = k_r [^3\text{Ru}(\text{bpy})_3^{2+}] = k_r N_0 \exp\{-t/\tau_0\} \quad (4)$$

where

$$\tau_0 = (k_r + k_{nr})^{-1} \quad (5)$$

The quenched emission decay will proceed with an accelerated speed. In other words, its lifetime will be shorter:

$$I = k_r N_0 \exp\{-t/\tau\} \quad (6)$$

Where

$$\tau = (k_r + k_{nr} + k_q[Q])^{-1} \quad (7)$$

Thus, the rate constant for the quenching reaction, k_q , can be obtained by analyzing the luminescence data. The quenching rate constant, k_q , is determined from the so-called **Stern-Volmer** relation:

$$\frac{\tau_0}{\tau} = 1 + \tau_0 k_q [Q] \quad (8)$$

which can be obtained from the rearrangement of Equations 5 and 7. The quantum yield of luminescence is proportional to the luminescence intensity, so that the Stern-Volmer relation may also be written as:

$$\frac{I_0}{I} = 1 + \tau_0 k_q [Q] \quad (9)$$

where I_0 and τ_0 are the luminescence intensity and the luminescence lifetime of ${}^3\text{Ru}(\text{bpy})_3^{2+}$ in the absence of quencher.

The equations above suggests that k_q may be obtained from an experiment where the luminescence lifetime or the luminescence intensity of $\text{Ru}(\text{bpy})_3^{2+}$ is measured at different quencher concentrations. A plot of τ_0/τ (or I_0/I) versus $[Q]$ is expected to be linear, with a slope:

$$K_{sv} = \tau_0 k_q \quad (10)$$

where K_{sv} is the Stern-Volmer rate constant.

Stern-Volmer quenching is derived with the assumption of dynamic quenching, which means that the quenching is free to diffuse in solution and that it interacts with the luminescent molecule by a second-order process. However, one must always be aware of the possibility that two molecules have formed a complex and therefore that the quenching is static, rather than dynamic. In order to be sure that a process is due to dynamic quenching it is necessary to determine both the yield and the lifetime.

Diffusion limited reactions. In a dynamic process the quenching rate constant k_q is a bimolecular rate constant (has units $\text{M}^{-1}\text{s}^{-1}$) and describes a process, in which the reactants first have to encounter and then react. Such reactions are often referred to as diffusion-assisted reactions. It is convenient to separate a reaction into two steps. First, there is a diffusion controlled formation of intermediate complex ($\text{A}^*\dots\text{Q}$) or transition state, with k_{diff} , and second the transition state can either react with the (first order) rate constant k_p or dissociate without reacting with the rate constant $k_{-\text{diff}}$ (also first order) :



Then the overall rate constant k' can be written as:

$$k' = \frac{k_{diff}k_p}{k_{diff} + k_p} \quad (12)$$

which in the limit of fast reaction rate $k_p \gg k_{diff}$ simplifies to:

$$k' = k_{diff} \quad (13)$$

when the diffusion becomes a limiting step. This case would correspond to the diffusion controlled (or diffusion limited) regime, when no matter how fast k_p is, the observed k' would be defined by how fast molecules encounter due to diffusion. The value of k_{diff} obviously depends on the diffusion coefficients of both reactants:

$$D = D_A + D_Q \quad (14)$$

According to the rate equation:

$$k_{diff} = 4\pi N_a D R_q \quad (15)$$

where N_a is the Avogadro's number $6.022 \times 10^{23} \text{ mol}^{-1}$, and R_q is the separation at which the quenching takes place, also called the quenching radius. For neutral molecules, the quenching radius equals the sum of molecular radii:

$$R_q = R_A + R_Q \quad (16)$$

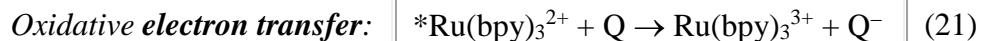
but the situation can differ dramatically if both species are charged. The Coulombic interaction leads to the following condition:

$$R_q > R_A + R_Q \text{ - for oppositely charged ions} \quad (17)$$

$$R_q < R_A + R_Q \text{ - for ions of the same charge} \quad (18)$$

Mechanisms of quenching. A variety of inorganic and organic species may act as quenchers. Determining k_q does not give any insight into the mechanism of quenching. For a given system, k_q may reflect a combination of energy and electron transfer processes. Energy transfer could occur in either the singlet or the triplet manifold. By detailed study of the system and application of control experiments one can determine whether the mechanism involves energy transfer or electron transfer. Triplet energy transfer can be established in part using the sensitivity of the process to O_2 . Since O_2 has a triplet ground state it is an effective triplet quencher (see below). When applied to simple systems, these criteria help determine the predominant mechanism of quenching.

<i>Energy transfer:</i>	$*Ru(bpy)_3^{2+} + Q \rightarrow Ru(bpy)_3^{2+} + Q^*$	(19)
<i>Reductive electron transfer:</i>	$*Ru(bpy)_3^{2+} + Q \rightarrow Ru(bpy)_3^+ + Q^+$	(20)



This laboratory experiment will provide an example of energy transfer quenching. When energy transfer takes place according to a transition dipole-transition dipole mechanism it is known as Förster energy transfer. Efficient energy transfer depends on a number of factors. There is a $1/R^6$ distance dependence for Förster energy transfer. This distance dependence arises from the dipolar nature of the process since the electric field that results from a dipole decays at $1/R^3$. A pair of dipoles that interact mutually has a distance dependence of $(1/R^3)^2 = 1/R^6$. There is also an orientation dependence for Förster energy transfer since the probability of energy transferring from one dipole to another depends on the square of the cosine of the angle between the two transition dipole moments. Clearly, there are many orientations in solution and one must carry out an orientation average. For a given distance, energy transfer depends on the Franck-Condon factors of the two molecules. The luminescence of the donor must have overlap with the absorption of acceptor. This condition does not mean that light is emitted by the donor and then absorbed by the acceptor. Indeed, energy transfer is NOT such a process, but it is a coherent oscillation of the two transition dipole moments subject to the correction conditions of orientation and energetics. One of your tasks in this laboratory will be to compare the emission of the donor ($^3\text{Ru}(\text{bipy})_3^{2+}$) with the absorption spectrum of the acceptor (DPA).

Degassing of samples. Given the role played by O_2 as a triplet quencher it is important to degas the solution of any sample, in which one wishes to measure the triplet energy transfer yield or rate constant. Degassing can be accomplished by two methods. First, one can use freeze-pump-thaw as a method. Second, one can bubble a gas such as N_2 or Ar through the sample for a period of time (usually about 20 minutes). Freeze-pump-thaw is considered the best way to degas a sample. However, it is quite time consuming. One usually freezes the sample in liquid N_2 or some other cryogen, then pumps on the sample by attaching it to a vacuum manifold and finally permits the sample to thaw after it is sealed so it has no contact with the atmosphere. Usually this process is repeated three times to ensure that all of the residual O_2 gas is removed from the sample. Degassing by bubbling a solvent is much faster, but is not as well controlled and has the disadvantage that one will often lose a fair amount of volatile solvent due to evaporation. One can control for evaporation by weighing the sample and either recording the new concentration or adding a small amount of (degassed!) solvent to the sample using a gas tight syringe. In general, all transfers in such experiments can be carried out using so-called Hamilton syringes. Hamilton has been the leading company that makes gas tight syringes for many years. Standard Hamilton syringes range in volume from 10 μL to 1000 μL .

CAUTION: When degassing using N_2 or Ar gas bubbled through the sample always ensure that there are two syringe needles, an input and output to prevent a pressure build-up in the sample.

Experimental

This laboratory experiment consists of two parts, 1. The measurement of the emission spectrum and 2. The measurement of the emission lifetime of $\text{Ru}(\text{bipy})_3^{2+}$ in solution with added DPA quencher molecules. You need to make solutions of both $\text{Ru}(\text{bipy})_3^{2+}$ and DPA in dichloromethane (DCM). The ideal solution for measurement of the phosphorescence quenching

will have an absorbance of ~ 0.2 in the MLCT band of $\text{Ru}(\text{bipy})_3^{2+}$ at ~ 452 nm. However, for observation of upconversion a higher concentration is desirable such that the $A \sim 1.0$ at 452 nm. Thus, the experiment should be run at two different concentrations of $\text{Ru}(\text{bipy})_3^{2+}$. To determine the appropriate concentrations you may use the extinction coefficient of $14,600 \text{ M}^{-1} \text{ cm}^{-1}$ at $\lambda_{\text{max}} = 452$ nm. Note that we will use the PF_6^- salt with the chemical formula $(\text{PF}_6)_2\text{Ru}(\text{bipy})_3$ with a formula weight of 859.6 a.m.u. The solutions of DPA will need to be much more concentrated since you will need to inject small volumes of this solution into the solution of $(\text{PF}_6)_2\text{Ru}(\text{bipy})_3$ in order to study a series of different concentrations of the quencher DPA (formula weight 330.4 a.m.u.). Using this background you may prepare the sample using the following step-by-step procedure:

1. The volume required in the quartz cuvette for phosphorescence and time-resolved measurements is ~ 3 mL.
2. This solution must be degassed. This is done by bubbling N_2 gas through the cuvette for 20 minutes. The cuvette has a septum cap so that it should be air tight. When bubbling N_2 always make sure to place a second needle in the septum as an outlet so that pressure does not build up inside.
3. You will need to add aliquots of DPA of volumes ranging from 10-100 μL to this solution. The stock solution of DPA should be approximately 20 mM. Add aliquots of this solution successively to the cuvette and acquire an emission spectrum and a time-resolved kinetics trace for each concentration. Use at least 5 concentrations of DPA (in addition to the pure $\text{Ru}(\text{bipy})_3^{2+}$ sample) ranging from 0 – 500 nM.
4. It is important to obtain the absorption spectrum of each solution since the absorption spectrum can be used to correct for any change in concentration in $\text{Ru}(\text{bipy})_3^{2+}$ due to the addition of DPA.
5. Each sample will be studied by two experiments:
 - A. Fluorescence emission from 550 to 850 nm. You will use the Edinburgh Instruments fluorescence spectrometer. The instructions are given below.
 - B. Time-resolved kinetics using the nanosecond fluorescence spectrometer. The instructions are given below.
6. Save the data in each experiment in ACSII format. For example, on the Edinburgh Instruments spectrometer use the EXPORT selection on the menu to write the data to disk. The data on the time-resolved nanosecond kinetics apparatus are stored on a Tektronix fast oscilloscope. The data need to be saved to a thumb drive of $< 2\text{Gb}$.

CAUTION #1: Xe arc lamps output a high voltage spike when the initially powered on. It is a good idea to power on the Xe arc lamp before other more sensitive circuits. Computers are fortunately not sensitive to these spikes.

CAUTION #2: Photomultiplier tubes (PMT) are sensitive detectors that can be destroyed by high light levels. Please follow the guidelines of each instrument closely and never change settings without consulting with your instructor. **DO NOT CHANGE THE PMT VOLTAGE SETTINGS!**

Edinburgh Instruments Fluorometer

There are three power supplies that need to be switched on. These are on the rack above the laser table. These consist of the Xe-arc lamp (always turn this on first!), then the photomultiplier tube (PMT) power supply and the temperature controller (in any order after the lamp). There is also a power switch on other side for the internal controls of the fluorometer. This switch is sometimes left on.

The software on the computer is FL900. Open the software and check the signal at the initial wavelength settings. There are two digital meters, one of the reference and one for the sample PMT. Monitor the number of counts per second recorded by the PMT. The bandwidth (DI) will mostly be set to 4.00 nm for both the excitation and the emission. However, it is a good idea to set it to a smaller value (for example, 1.00 nm) when you first make a measurement. The idea is to limit the number of photons striking the PMT. This number should be less than 8×10^6 .

Set the excitation wavelength to 470 nm. Set the emission scan from 550 – 850 nm. The dwell time should be 0.1 seconds and the increment 1 nm. Set the number of scans to 3. The data will be written to a binary data file on the hard drive. In order to be able to use the data for analysis you will need to export it. In scientific software the export function is the usual way to write data in ASCII format as columns of numbers separate by either a comma or tab. This format can be read by programs such as Excel, Origin, Igor, etc. that are used for data fitting and analysis.

Time-Resolved Emission Apparatus

There is a black notebook on the table describing the steps to setup a time-resolved scan. You will work with your instructor to turn on the instrument and set up to take data. You may take data on your own by switching out samples and recording data, but do not change settings for the PMT or laser. You may examine the settings on the digital oscilloscope and your instructor will show you how to check for the trigger level, the settings in terms of time scale, voltage scale and so on. These are described in the book as well.

The Upconversion Measurement

Upconversion is an idea that has been developed and demonstrated in the Castellano research group. We have chosen a quenching experiment that added functionality. We can attempt to estimate the yield of upconversion by measuring the fluorescence emission of 1DPA created by triplet-triplet annihilation. You measure that emission between 250 and 400 nm. However, may need a concentrated sample to see the effect.

Report

You will acquire three kinds of data in this laboratory experiment, 1. UV-vis absorption spectra (on the HP8453 photodiode array), 2. Phosphorescence spectra from 550 – 850 nm on the EI fluorometer and 3. Time-resolved emission kinetics. You will use the Stern-Volmer relation to make a linear plot of the relative integrated phosphorescence yield as a function of $[Q]$, the quenching concentration. From a straight-line fit of these data (using linear least squares) you will obtain a slope. However, to further analyze that slope you need an independent measure of

the observed phosphorescence decay time from the time-resolved setup. If the quenching is dynamic quenching then you should also see a change in the lifetime as you increase the quencher concentration. Thus, the time-resolved experiment is a check on the assumptions of the Stern-Volmer derivation (dynamic quenching).

In the analysis you will first need to normalize the data to the initial $\text{Ru}(\text{bipy})_3^{2+}$ concentration using the UV-vis spectra. As you add aliquots of DPA the absorbance at 452 nm should decrease slightly. Thus, you can multiply the fluorescence by the value $A_{\text{initial}}/A_{\text{sample}}$ for each sample you study (A_{initial} means the absorbance of pure $\text{Ru}(\text{bipy})_3^{2+}$ at 452 nm and A_{sample} refers to the same measurement on each sample studied. Keep careful notes and a simple consistent nomenclature to avoid confusion in the interpretation of the files.

Integrate each phosphorescence signal in a software package such as Excel, Origin or Igor. Fit each decay to an exponential model in a software package. Examine the residuals to ensure that the fit to a single exponential is adequate. Use the integrated values obtained from the experiment to determine the Stern-Volmer rate constant (Eqn. 9). You will then need to use the measured lifetime, τ_0 , to determine the quenching rate constant (Eqn. 10).

Try to estimate the quantum yield for production of the upconversion signal in one sample. Clearly you will need to add enough DPA to completely quench the $^3\text{Ru}(\text{bipy})_3^{2+}$ emission.

Points for discussion

Look in the chemical literature and find diffusion coefficients for the molecules studied here or similar molecules. Using an estimate of the diffusion coefficient calculate the quenching radius. Discuss the assumptions that go into this calculation (as discussed above).

Compare the $\text{Ru}(\text{bipy})_3^{2+}$ emission spectrum to the DPA absorption spectrum. Keep in mind the criteria for energy transfer and discuss the features and relationship of these two spectra. Discuss the appropriateness of this pair of molecules for triplet energy transfer.

What are the consequences of incomplete deoxygenation of the sample. Which observables are the most sensitive to O_2 quenching. Include the production of $^1\text{O}_2$ in your discussion.

References

1. Wilke B.M. and Castellano, F.N. "Photochemical Upconversion: A Physical or Inorganic Chemistry Experiment for Undergraduates Using a Conventional Fluorimeter" J. Chem. Ed. 2013, 90, 786-789
2. Singh-Rachford, T.N.; Castellano, F. N. "Photon upconversion based on sensitized triplet-triplet annihilation" Coord Chem. Rev. 2010, 254, 2560-2573
3. Stern, O; Volmer, M "The Fading Time of Fluorescence" Phys. Zetischr. 1919, 20, 183-188

4. Wilkinson F.; Helman, W.R.; Ross A.B. "Quantum Yields for the Photosensitized Formation of the Lowest Electronically Excited Singlet State of Molecular Oxygen in Solution" J. Phys. Chem. Ref. Data 1993, 22, 113-150

Appendix. A discussion of electron transfer quenching of the Ru(bipy)₃²⁺ excited state.

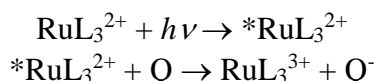
The electron transfer rate constant, k_{ET} , depends:

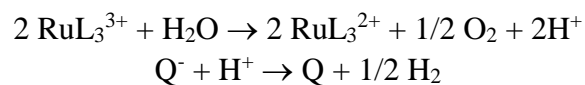
- (i) distance between the donor and acceptor,
- (ii) the degree of quantum mechanical coupling between the molecular orbitals of donor and acceptor, and
- (iii) the free energy change, ΔG°
- (iv) the reorganization energy, λ .

The latter parameter refers to the energy cost incurred by molecular rearrangements that must result from the transfer of charge along a finite distance. Generally, it is expected that rates of electron transfer will increase with decreasing donor-acceptor distances, and that the maximum rate will be observed when the reaction is activationless, i.e., when ΔG° is **negative**, preferably when $\Delta G^\circ = -\lambda$. In other words, the rate is optimized when the standard free energy change for the reaction is matched exactly by the energy required for reorganization of the donor, acceptor, and solvent molecules. In the table below you see the redox potentials for the species involved in this experiment. By analysing it you should conclude what quenching mechanisms are plausible for different quenchers. **NB**. The exact expression for

Species	Redox potential
$\text{Ru}(\text{bpy})_3^{3+} + e^- \rightarrow \text{Ru}(\text{bpy})_3^{2+}$	+ 1.26 V
$\text{Ru}(\text{bpy})_3^{2+} + e^- \rightarrow \text{Ru}(\text{bpy})_3^+$	+1.28 V
$*\text{Ru}(\text{bpy})_3^{2+} \rightarrow \text{Ru}(\text{bpy})_3^{3+} + e^-$	+ 0.84 V
$\text{Ru}(\text{bpy})_3^{2+} \rightarrow *\text{Ru}(\text{bpy})_3^{2+}$	(+ 2.1 V)
$\text{Fe}(\text{CN})_6^{3-} + e^- \rightarrow \text{Fe}(\text{CN})_6^{4-}$	+ 0.36 V
$\text{Fe}(\text{H}_2\text{O})_6^{3+} + e^- \rightarrow \text{Fe}(\text{H}_2\text{O})_6^{2+}$	+ 0.77 V
$\text{O}_2 + e^- \rightarrow \text{O}_2^-$	- 0.365 V

In principle, there is sufficient potential energy in a photo-generated redox pair that one devise a scheme to split water into H₂ and O₂. The goal of light-driven water splitting has been approached by hundreds of different research teams. The processes relevant to the process using Ru(bipy)₃²⁺ are summarized below, where L represents the diimine ligand and Q represents the oxidant:





In other words, solar energy can be used to make fuels from water. Although the chemistry of such a solar cell is straightforward, there are some technological barriers to be overcome before ruthenium (II) complexes can form the basis of a commercial photovoltaic device.

Other applications for photooxidation of ruthenium (II) complexes involves development of dye-sensitized photovoltaic devices, where $^*\text{RuL}_3^{2+}$ is oxidized by a network of TiO_2 nanoparticles and consequently RuL_3^{3+} is reduced with a help of I_3^-/I^- redox pair. Resulting charges recombine at the electrodes, thus, producing a photovoltage equal (without a load) to the overall redox potential through all the steps.