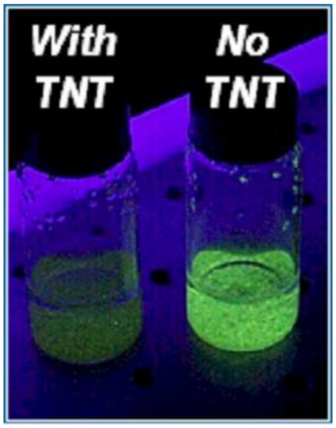
The Chemistry of Excited States

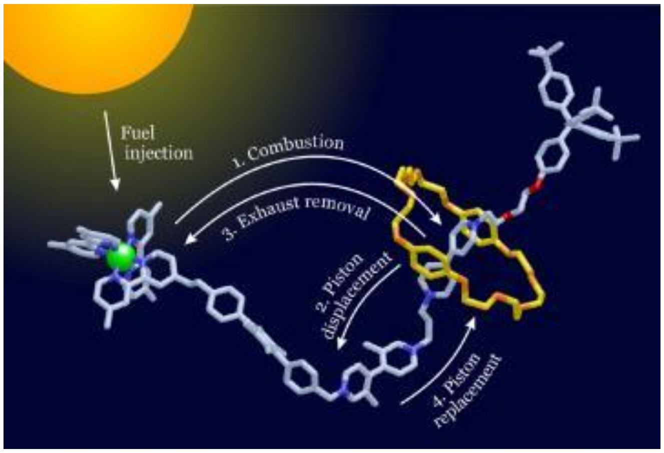
Introduction

How fast can an electron move along a strand of DNA? How might a plastic convert sunlight into electricity? How can a fluorescent polymer be used as a sensor to detect trace amounts of TNT explosives? How can the binding of a peptide to protein be monitored? How can new types of luminescent materials be developed for flat panel display technology? How can fluorescent dyes be used to image nitric oxide concentrations in a nerve cell? How could a molecular nano-car be fueled by light? How could light-harvesting molecules be used to produce hydrogen from water?

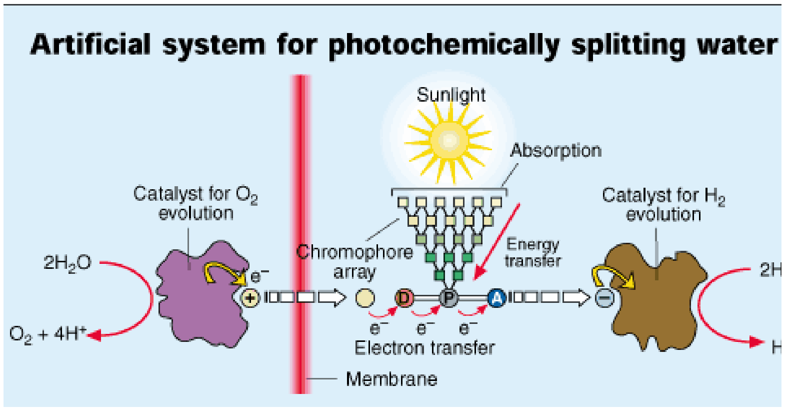
Research into questions like these often rely on understanding the excited-state properties of molecules: light absorption, light emission (luminescence) and excited-state reactions (electron transfer, energy transfer and bond breaking). Luminescence spectroscopy is an instrumental technique that has become one of the most valuable tools in chemistry for measuring ultra-fast chemical reactions and processes, learning about intermolecular interactions and imaging biochemical structures and processes.



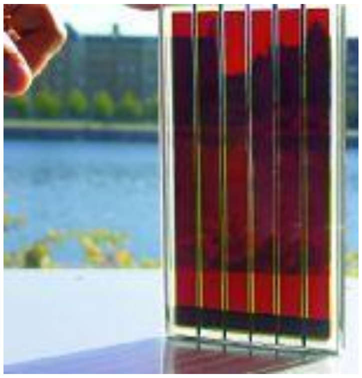
A TNT sensor based on luminescence quenching of a molecular wire; from Tim Swagar lab at M.I.T.



A "solar-powered nanomotor". from *C& E News*, Jan. 24, 2006.



A scheme for solar-energy conversion into hydrogen fuel. from *C& E News*, October 26, 1998 p. 37.



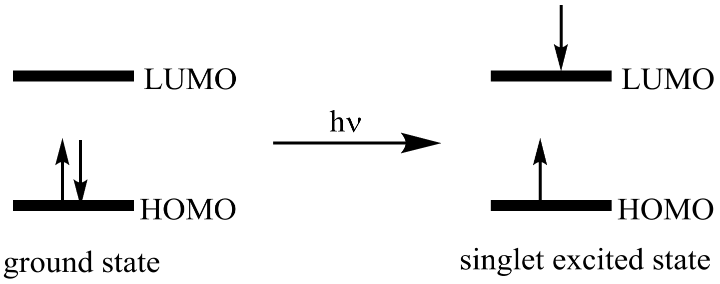
A dye-sensitized solar cell (DSSC) that uses a Ru(II) coordination compound light absorber; from *C&E News* June 21, 2004 p. 31.

A. absorption and molecular orbital energy diagrams

When a molecule absorbs light in the UV-vis region, an electron is promoted from a lower-energy occupied orbital to a higher-energy empty orbital resulting in an ***excited state*** molecule. One requirement for a molecule to absorb light is that the energy of the photon needs to match the energy difference between the orbitals ($\mathbf{\Delta E = E_{photon} = h\nu = hc/\lambda}$). Photons having insufficient energy will be transmitted. Therefore, the colors of light absorbed proved us with experimental information about the energy spacing between orbitals.

Because molecules can have *many* occupied and empty molecular orbitals, there can be many possible transitions to promote an electron from a low-energy occupied to higher-energy empty orbital. However, only a few of these molecular orbitals are involved in absorption of light and the formation of excited states: the ***frontier orbitals*** are the highest-energy orbitals "occupied" by electrons and the lowest-energy "unoccupied" orbitals having no electrons. Of these, the transition requiring the lowest-energy photon corresponds to a transition of an electron from the ***highest occupied molecular orbital*** (***HOMO***) to the ***lowest unoccupied molecular orbital*** (***LUMO***). The ***HOMO-LUMO energy gap*** (ΔE) typically determines the color of light we see transmitted through a solution. Transitions of an electron from lower-energy occupied orbitals or into higher-energy empty orbitals will necessarily require higher-energy photons.

A second requirement for absorption is that there no change in electron spin. Most molecules possess an even number of electrons, all of which are paired in the ground state (notable exceptions being O_2, radicals, and many transition metal ions). The highest energy electrons occupy the HOMO, and these electrons are paired with opposite spin (+½, -½) such that the total spin[*] of the electrons is $S = 0$ and the ***multiplicity*** of the ground state is "***singlet***". Excitation with a photon having energy that corresponds to the HOMO-LUMO energy gap would result in an excited state that is also "singlet".



The excited-state electron configuration involves an ***electron-hole pair***: a promoted high-energy electron and a low-energy "hole" it left behind. Recombination of the electron-hole pair causes the excited-state molecule to relax back to its ground state. This can be though of as a one-electron *intermolecular* redox reaction: the HOMO is oxidized and the LUMO is reduced.

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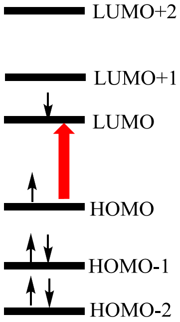
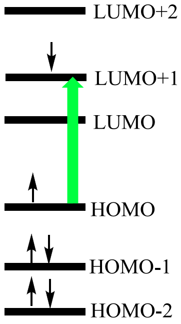
[*] Total spin is the vector sum of the individual electron spins. A molecule having equal numbers of + ½ and - ½ electrons has a total spin of $S = 0$. A molecule having two unpaired electrons, both with spin + ½, has a total spin of (+ ½) + (+ ½) = 1. The multiplicity is $2S+1$, called "singlet" when 2(0)+1 = 1, and "triplet" when 2(1)+1 = 3.

1. transitions and absorption spectra

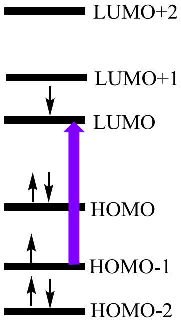
An ***absorption spectrum*** (a plot of absorbance vs. wavelength, obtained experimentally using a UV-vis spectrophotometer) of a solution will often display a series of ***absorption bands***. The ***wavelength maximum*** (***λ_{max}***) for each band can be used to approximate the energy difference (ΔE) between the orbitals involved in each type of transition. An example below shows three different transitions (A,B,C) corresponding to three different absorption bands. Transition A (HOMO → LUMO) is the lowest-energy transition, so it would correspond to the longest-wavelength absorption band. Transitions B and C would match the shorter-wavelength absorption bands.



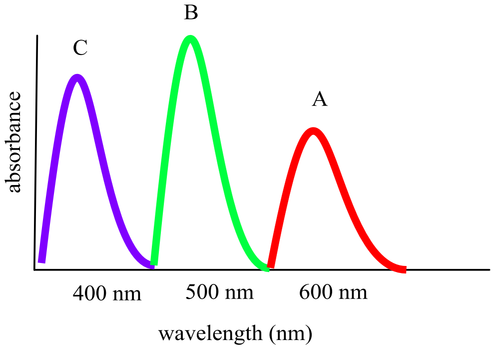
excited state A



excited state B

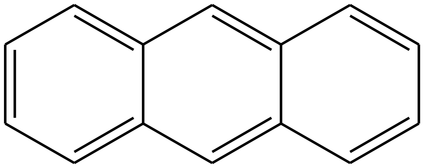


excited state C

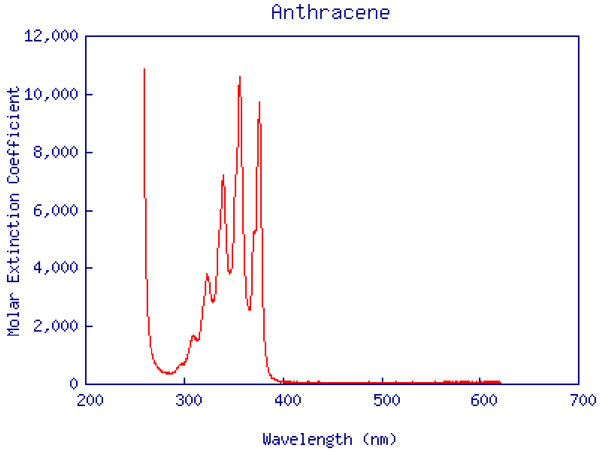


2. names of electronic transitions

From molecular orbital (MO) calculations, we can often determine the nature of the frontier molecular orbitals. For example, the molecule ***anthracene*** ($C_{14}H_{10}$) is a widely-used light absorbing compound. All 14 C atoms are involved in π-bonding, so that we can predict that there are 14 π MOs having 14 electrons; π MO #7 is the HOMO and π MO #8 is the LUMO.[†] This electronic transition is commonly called a ***π - π* transition***, indicating that excitation is promoting an electron from a π orbital (the HOMO) into a π* orbital (the LUMO)



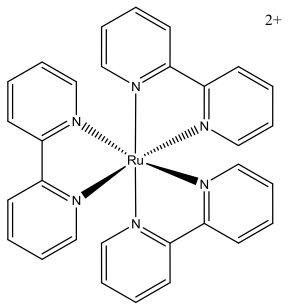
anthracene



The experimental absorption spectrum displays an absorption band in the 300-400 nm range, with the longest-wavelength maximum at ~370 nm.[‡] Higher-energy absorption bands (λ_{max} < 250 nm) correspond to other π - π* transitions.

[†] Overall, there are 66 molecular orbitals for anthracene constructed from the valence atomic orbitals of the C and H atoms, and 66 electrons.

[‡] The series of bands observed between 300-400 nm all belong to the same electronic transition. They are transitions to different *vibrational* energy levels of the excited state.

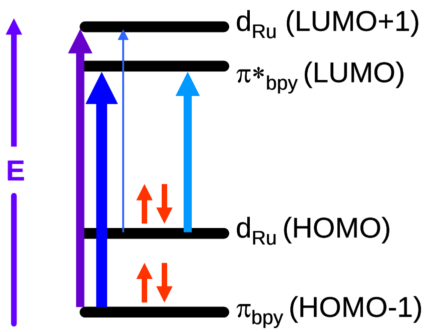


$[Ru(bpy)_3]^{2+}$ complex cation

The coordination compound ruthenium (II) *tris*(bipyridine) chloride, $[Ru(bpy)_3]Cl_2$, also has a rich amount of excited-state chemistry and is frequently employed for its light absorption, luminescence and excited-state electron transfer and energy transfer properties. This octahedral dicationic complex forms from the coordination of three "bpy" (2,2'-bipyridine) ligands with a Ru^{2+} metal ion center; two chloride (or other anions) serve as counter-ions for the salt.

Molecular orbital calculations, along with much experimental evidence, have been used to determine the frontier molecular orbitals for $[Ru(bpy)_3]^{2+}$. The HOMO is a filled d orbital on the Ru(II) ion and the LUMO is a π* orbital localized on bpy ligand. At slightly lower energy is a π orbital localized on bpy ligand (HOMO-1), and at slightly higher energy is an empty d orbital on the Ru(II) ion (LUMO +1).

This MO energy level diagram can be used to predict four different types of electronic transitions:

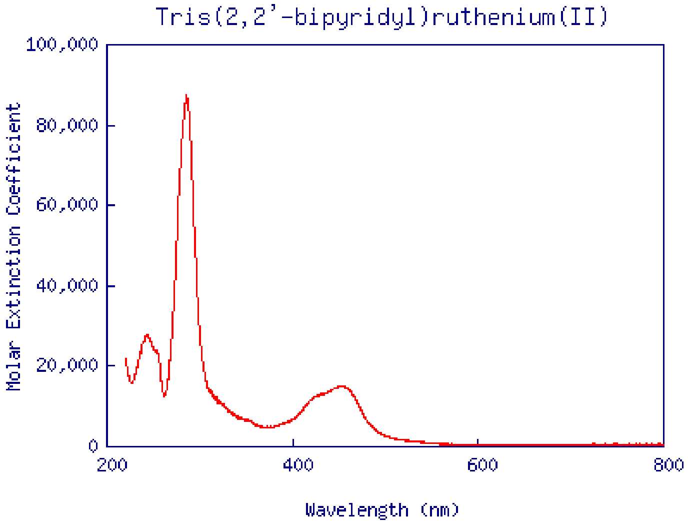


Frontier MOs for $[Ru(bpy)_3]^{2+}$, showing four electronic transition: MLCT, MC, IL and LMCT.

- "metal-to-ligand charge transfer" (***MLCT***): transition from HOMO to LUMO (d- π*)
- "metal-centered" (***MC***): transition from HOMO to LUMO+1 (d-d)
- "intraligand" (***IL***): transition from HOMO-1 to LUMO (π-π*)
- "ligand-to-metal charge transfer" (***LMCT***): transition from HOMO-1 to LUMO+1 (π-d)

Of these, the MLCT transition would be expected to be the lowest-energy (longest-wavelength) absorption.

The experimental absorption spectrum displays a long-wavelength band of moderate intensity centered at ~450 nm, assigned to a MLCT transition, and an intense band at ~380 nm assigned to a IL (π-π*) localized on the bpy ligand. The highest-energy band is a LMCT transition. The metal-centered d-d transition is too weak to be observed under the more intense bands.



3. intensity of absorption

Recall that the intensity of an absorption band relates to the ***molar absorptivity (ε)*** at that wavelength, which can be obtained experimentally from a Beer's Law plot (absorbance vs. concentration of the solute). Several factors affect the intensity of an absorption band. For efficient light absorption, the orbitals involved in the transition need to have significant overlap. Overlap in space occurs when these orbitals are close to each other, but ***orbital symmetry*** is also important.

For example, the bright colors of many organic dyes originates from a highly-allowed transition from an occupied π orbital into an empty π* orbital; the orbital overlap is large and the symmetry is "allowed",[§] leading to intense (large ε) π-π * transitions. Conversely, the pale colors of most transition metal ions in solution, result from transition between an occupied and an empty d orbital of the metal ion. This electronic transition is "forbidden" by the selection rules: any two metal d orbitals have no <u>net</u> orbital overlap with each other because they point in different directions. Metal-centered d-d transitions are very weak (small ε).

B. excited states and excited-state energy diagrams

1. orbitals vs. states

An electronic "state" is a particular electron configuration: the lowest-energy electron configuration (electrons occupying the lowest-energy orbitals, two at a time) is the ***ground state***. All other possible electron configurations are ***excited states***. For this reason, different states can be thought of as "electronic isomers" of each other. As our discussion moves to energy level diagrams, it is important to keep the distinction clear. <u>Orbitals</u> describe the location and energy of individual <u>electrons</u>; <u>states</u> describe the total energy and overall electron configuration of the whole <u>molecule</u>.

2. state diagrams

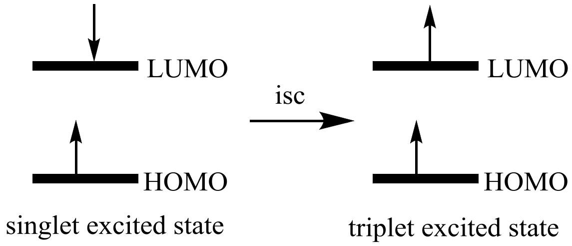
As described above, several different transitions can be identified for $[Ru(bpy)_3]^{2+}$. Each transition results in a different excited state being formed, which we give the same names. A plot of the relative energies of these states is shown below.

3. internal conversion

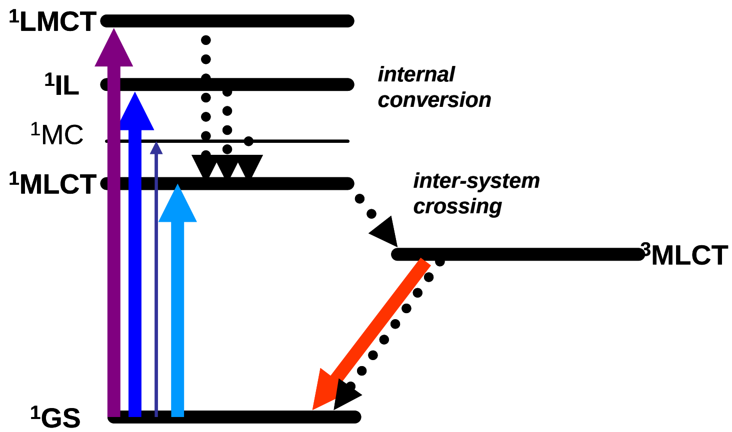
Most often, higher-energy excited states relax very rapidly to the lowest-energy excited state (known as ***Kasha's Rule***). This relaxation, known as ***internal conversion***, involves the dissipation of energy through intra-molecular vibrations and inter-molecular collisions with solvent molecules. For example, absorption of light having $\lambda < 400$ nm by $[Ru(bpy)_3]^{2+}$ results in the formation of LMCT, IL or MC excited-states which relax quickly to the lowest-energy MLCT state.

4. inter-system crossing and triplet excited states

[§] Not *all* π–π* transitions are symmetry-allowed, however. The symmetry of the donor and acceptor orbital must be considered.



Upon excitation, a ***singlet excited state*** has two unpaired electrons having opposite spin (see above). For some molecules, a process known as "***intersystem crossing***" (isc) occurs, and one of the electrons flips spin so that the two unpaired electrons have the same spin (+½, +½ or -½, -½). Although the same molecular orbitals are involved, this is a different excited state having a "***triplet***" multiplicity (because the total spin *S* = 1). This triplet excited state is always lower energy than the corresponding singlet excited state, as predicted by "***Hund's Rule***" which states that an electron configuration of higher multiplicity is more stable. The requirement that there no change in electron spin upon absorption means that molecule can not normally be excited from a singlet ground state directly to a triplet excited state. This transition is formally "forbidden". Superscripts 1 or 3 are used to distinguish the singlet and triplet states. Kasha's Rule also applies to triplet states: higher-energy triplet excited states relax very rapidly to the lowest-energy triplet excited state. Anthracene has a lower-energy $^3(\pi-\pi^*)$ excited state that can form from inter-system crossing from its higher-energy $^1(\pi-\pi^*)$ state.



State Diagram for [Ru(bpy)$_3$]$^{2+}$, showing four singlet excited states (and transitions): ^{1}MLCT, ^{1}MC, ^{1}IL and ^{1}LMCT, and one triplet excited state: ^{3}MLCT.

C. Luminescence and Non-radiative Decay of an Excited State

Following absorption by a molecule (M), **M + light → M***

the excited-state molecule (M*) formed is highly reactive and has many pathways by which it can release this added energy and return to its ground-state electron configuration. These include (i) non-radiative decay, (ii) luminescence (radiative decay), (iii) excitation energy transfer, (iv) electron transfer, and (v) bond-breaking or forming chemical reactions.

1. Non-radiative decay **M* → M + heat**

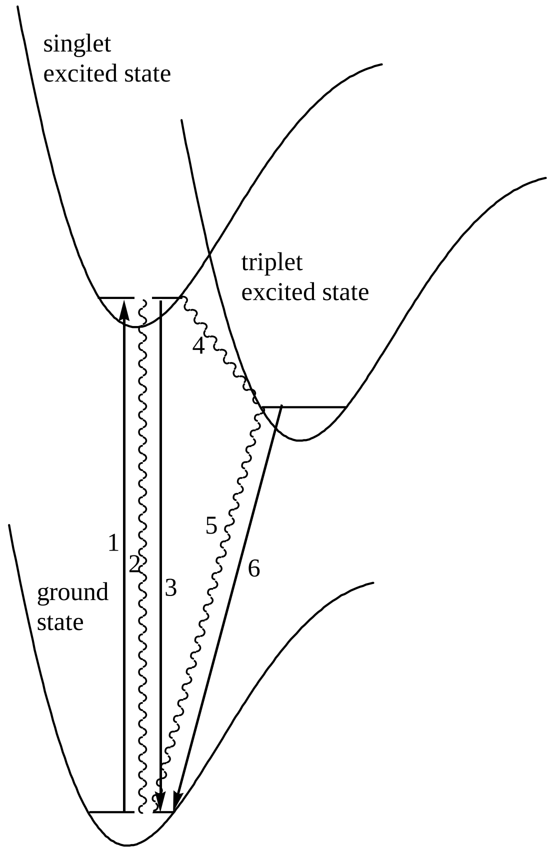
The most common pathway for molecules in fluid solution at room temperature is ***non-radiative decay***, a very fast set of processes that dissipate the excitation energy through molecular vibrations and collisions with solvent molecules. Alas, this process, which is simply the conversion of photonic energy to heat, is rarely useful. Because non-radiative decay involves intramolecular vibrations and solvent collisions, we can expect this set of processes to depend on temperature (i.e. – dissipation of energy through increased number of collisions) and flexibility of molecular structure (i.e. dissipation of energy through vibrations).

2. **Luminescence** **M* → M + light**

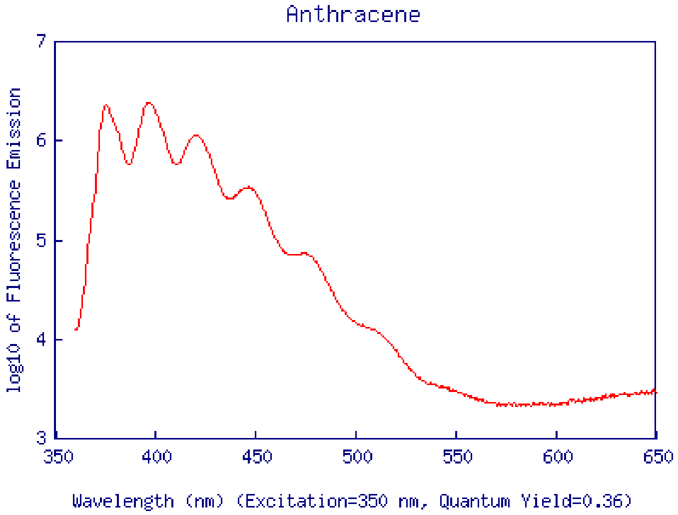
However, some molecules are capable of relaxing back to their ground state by also emitting a photon. ***Luminescence***, the emission of light from an excited-state molecule, is a most dramatic example of the fascinating colors of chemistry. The measurement of luminescence can be one of the most important methods for understanding excited states of molecules. Likewise, understanding the nature of excited states can be useful in making sense of luminescence measurements.

The luminescence (also known as ***radiative decay***) can be classified as ***fluorescence*** if the excited state and the ground state have the same spin (e.g. both are singlet) or ***phosphorescence*** if the excited state and the ground state have the different spin (e.g. triplet excited state and singlet ground state). These two types of light emission differ in two very important ways. First, the energy of fluorescence is only slightly lower than the energy of the photons used to excite the molecule, because both absorption and luminescence involve the same excited state. In contrast, the energy of phosphorescence is significantly lower than the excitation energy because the luminescence originates from the lower-energy triplet state. The difference is energy between the excitation and luminescence is released as heat. (Recall that direct excitation of a molecule from its singlet ground state to a triplet excited state is usually not possible). Second, the fluorescence rate is much faster (with a corresponding shorter excited state ***lifetime, τ***) than the phosphorescence rate (with a corresponding longer excited state lifetime), because there is no "spin flip" required for fluorescence. Whether a molecule fluoresces or phosphoresces depends on the rate of intersystem crossing from the singlet excited state to the triplet excited state. Typically, fluorescence is observed for organic molecules while phosphorescence is observed for transition metal complexes, a reflection of how heavy elements such as transition metals can enhance the rate of intersystem crossing.

These two differences give us a means to distinguish each type of luminescence experimentally: fluorescence is typically detected at wavelengths slightly longer than the longest-wavelength absorption and decays very rapidly (a few nanoseconds) after excitation; phosphorescence is typically detected at wavelengths much longer than the longest-wavelength absorption and decays more slowly (from hundreds of nanoseconds up to milliseconds) after excitation.

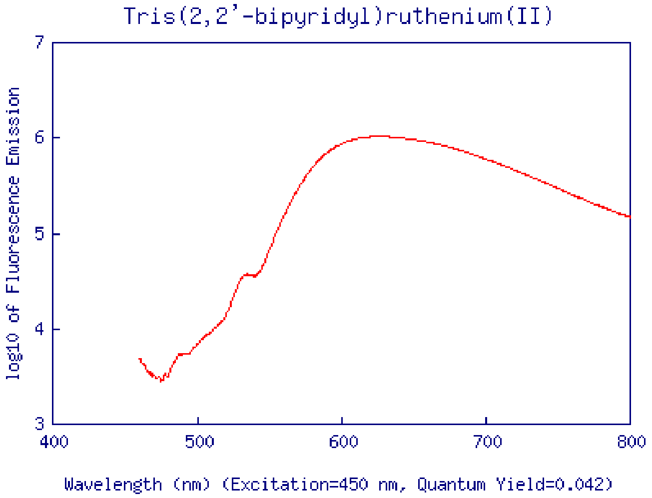


State Diagram of a general molecule, showing two excited states of different multiplicity and the processes of (1) absorption, (2) non-radiative decay from the singlet excited state, (3) fluorescence from the singlet excited state, (4) intersystem crossing, (5) non-radiative decay from the triplet excited state, and (6) phosphorescence from the triplet excited state.



The luminescence emission spectra of anthracene and $[Ru(bpy)_3]^{2+}$ are shown here.

Excitation of an anthracene solution using λ_{ex} = 350 nm results in bright blue fluorescence centered at ~400 nm, originating from the $^1(\pi\text{–}\pi^*)$ excited state. Experimental confirmation of Kasha's Rule comes from the observation that absorption of $\lambda < 250$ nm UV light by anthracene result in the same blue fluorescence as absorption of $\lambda > 250$ nm light; higher-energy $^1(\pi\text{–}\pi^*)$ excited states rapidly relax by non-radiative decay (internal conversion) to the lowest-energy π - π^* state, which is the only state that results in fluorescence. Phosphorescence from the lower-energy $^3(\pi\text{–}\pi^*)$ state of the anthracene is not usually observed in room-temperature fluid solution, but can be observed (at λ = 670 nm) in the solid-state or when the compound is dissolved in a solid-state host medium.



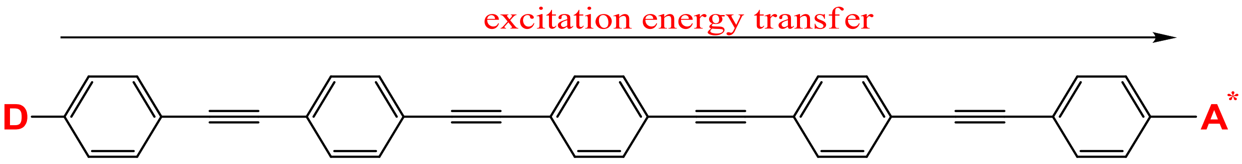
Excitation of an $[Ru(bpy)_3]^{2+}$ solution using λ_{ex} = 450 nm results in intense red phosphorescence centered at ~610 nm, originating from the ^{3}MLCT excited state. $[Ru(bpy)_3]^{2+}$ does not display fluorescence from any of its singlet excited states because internal conversion *and* inter-system crossing are very rapid for this transition metal complex.

The color of luminescence is a qualitative gauge of the energy of the emitting excited state. An estimate of the energy of an excited state can be made by converting the wavelength of maximum intensity (λ_{max}) of a luminescence band to an energy ($E_{photon} = hc/\lambda$). Keep in mind that this is an approximation, and is a *low estimate* of the excited state energy. For $[Ru(bpy)_3]^{2+}$, the high-energy side of the band ($\lambda_{em} \approx 585$ nm) can be used to estimate an excited state energy of $\Delta G^0 \approx -204.6$ kJ/mol.

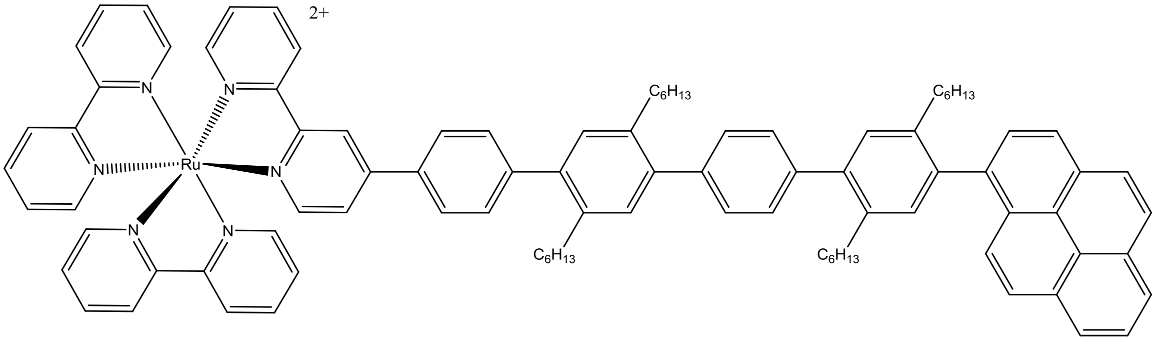
D. excited-state energy transfer

Energy transfer involves the transfer of excitation energy from an excited-state donor molecule to a ground-state acceptor molecule. This results in the donor molecule returning to its ground state and the formation of an excited state of the acceptor molecule. $\mathbf{M^* + Q \rightarrow M + Q^*}$

Energy transfer is an essential component of the light-harvesting array in natural photosynthesis, and plays a central role in photodynamic therapy and the operation of some types of luminescent sensors. Excitation energy transfer can take place “through space” (i.e. during a collision between donor and acceptor molecules in solution) or it can take place “through bond” and be facilitated by molecules that may connect the donor and acceptor. Molecular photonic wires can be build having photo-active (absorbing and/or luminescing) donor and acceptor molecules covalently linked by a conjugated bridge. In this type of system, selective excitation of the donor results energy transfer through the wire and luminescence by the acceptor.



As an example, consider the absorption and luminescence spectra for anthracene and for $[Ru(bpy)_3]^{2+}$. If these two photo-active molecules are connected by a conjugated π bridge such as poly(paraphenylene) (PPP), a molecular wire is constructed:

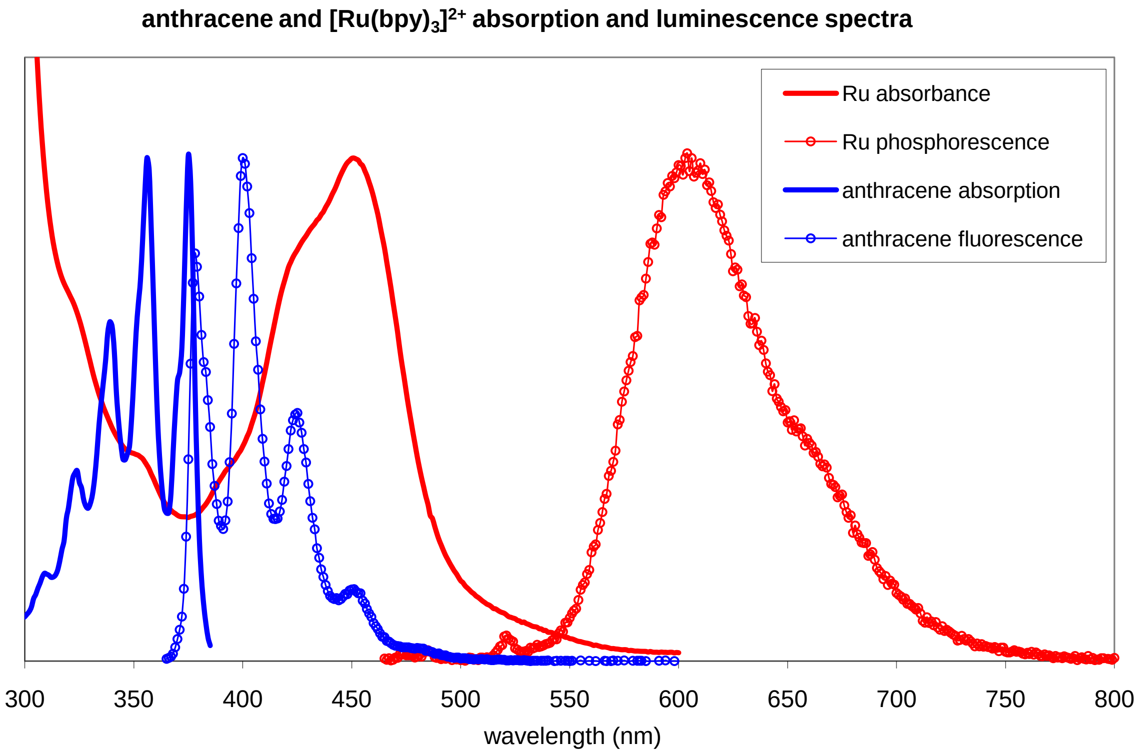


A “molecular wire” containing photo-active $[Ru(bpy)_3]^{2+}$ and anthracene termini connected by a poly(paraphenylene) bridge.

Considering the absorption and luminescence spectra of the two “termini” molecules (see overlaid spectra, below), we can find an excitation wavelength that would result in absorption by only one of the two molecules. Exciting this molecular wire using λ_{ex} = 450 nm would lead to absorption only by the $[Ru(bpy)_3]^{2+}$ unit, as anthracene has no absorption beyond $\lambda > 400$ nm. As described above, 450-nm excitation of a solution of just $[Ru(bpy)_3]^{2+}$ results in intense red phosphorescence centered at ~610 nm. But, that emission is not observed in this molecular wire. Energy transfer from the ^{3}MLCT excited state of $[Ru(bpy)_3]^{2+}$ (energy donor) into the

$^3(\pi-\pi^*)$ state of anthracene (energy acceptor) results in ***quenching*** of the $[Ru(bpy)_3]^{2+}$ phosphorescence. Phosphorescence from anthracene is usually not detected in fluid solution.

A different energy-transfer process can occur if the same molecular wire is excited using λ_{ex} = 350 nm light. This wavelength of light is preferentially absorbed by the anthracene, which has a much larger ε value at 350 nm than does $[Ru(bpy)_3]^{2+}$. As described above, 350-nm excitation of a solution of just anthracene results in bright blue fluorescence centered at ~400 nm, originating from the $^1(\pi-\pi^*)$ excited state. But, in this molecular wire, only weak blue fluorescence is observed. Energy transfer from the $^1(\pi-\pi^*)$ excited state of anthracene (energy donor) into the ^{1}MLCT state of $[Ru(bpy)_3]^{2+}$ (energy acceptor) and results in quenched anthracene fluorescence. Subsequent and rapid inter-system crossing into the ^{3}MLCT state of $[Ru(bpy)_3]^{2+}$ and energy transfer into the $^3(\pi-\pi^*)$ state of anthracene results in quenching of the $[Ru(bpy)_3]^{2+}$ phosphorescence. . Through selection of an excitation wavelength input, we can use the molecular photonic wire to transfer energy in one direction or the other.



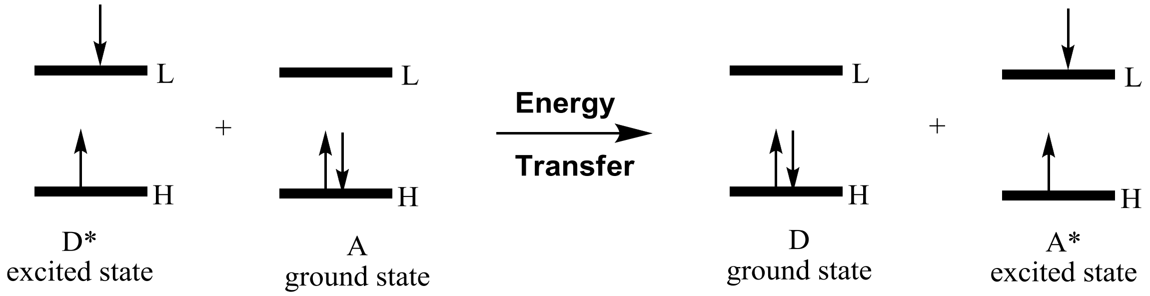
1. **Energy requirement for excitation energy transfer**

With a large number of photo-active molecules at our disposal, we could choose many combinations of molecules to serve as the termini in a molecular wire. However, only certain combinations will result in energy transfer. The thermodynamic requirement for energy transfer is that the energy of the donor molecule excited state is equal to or greater than the energy of the acceptor molecule excited state: $E_{donor} > E_{acceptor}$

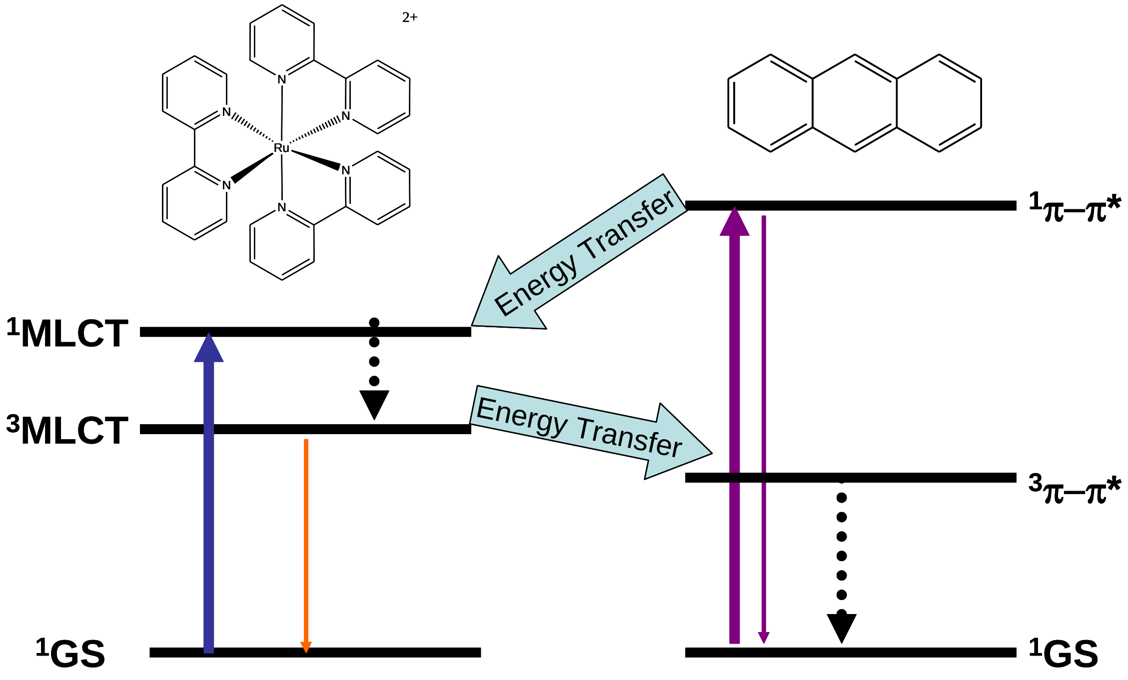
For example, energy transfer from the ^{3}MLCT excited state of $[Ru(bpy)_3]^{2+}$ to the $^1(\pi-\pi^*)$ excited state of anthracene is not thermodynamically favorable.

2. **orbital and state energy diagrams for Energy Transfer**

A ***molecular orbital energy diagram*** describing excitation energy transfer between a generic excited-state donor and ground-state acceptor molecule is shown below The transfer of excitation energy can be thought of as occurring by one of two mechanisms: (1) a double electron-transfer reaction, in which the electron in the LUMO of the excited donor moves into the LUMO of the acceptor while an electron in the HOMO of the acceptor moves into the "hole" on the HOMO of the donor, or (2) the relaxation of the electron-hole pair in the donor induces excitation of the electron in the acceptor. The net result is the same for both mechanisms.[**]



A ***state energy diagram*** for the excitation energy transfer reactions between $[Ru(bpy)_3]^{2+}$ and anthracene shows the flow of energy between the various excited states of these two molecules:



[**] Although the distance-dependence of these two mechanisms is different, and can sometimes be distinguished experimentally.

3. **distance-dependence of energy transfer rate**

The rate of energy transfer from an excited donor to an acceptor depends on the distance between the molecules. In a molecular wire system, this distance may be controlled precisely using a spacer group of varying length. The energy-transfer rate typically decreases with increasing donor-acceptor distance (r_{DA}).

These energy-transfer processes can also occur in homogeneous solution mixtures of $[Ru(bpy)_3]^{2+}$ and anthracene. Again, the rate of energy transfer depends on the distance between D and A. By manipulating the *concentration* of D and/or A, the average distance between D and A changes.

4. **Some additional examples of energy transfer**

- ***Cancer treatment using photodynamic therapy (PDT):***
  - photosensitizer (PS) dye administered to patient. In absence of light, PS is inactive.
  - upon irradiation of tumor using long-wavelength light, PS is excited:
    $$PS + h\nu \rightarrow PS^*$$
  - energy transfer from PS to oxygen ("dye-sensitization") produces ***singlet oxygen*** excited state
    $$PS^* + {}^3O_2 \rightarrow PS^* + {}^1O_2^*$$
  - singlet oxygen can react with and destroy tumor.

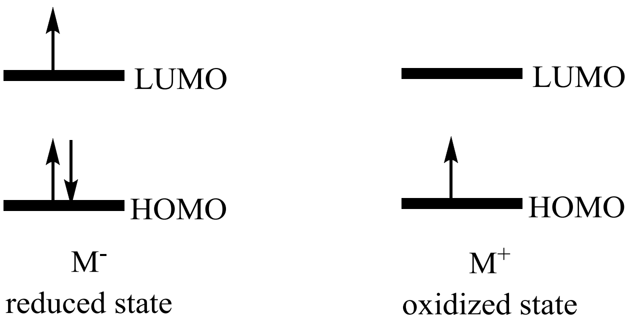
- ***natural and artificial photosynthesis***

- ***FRET assays***

E. excited-state electron transfer

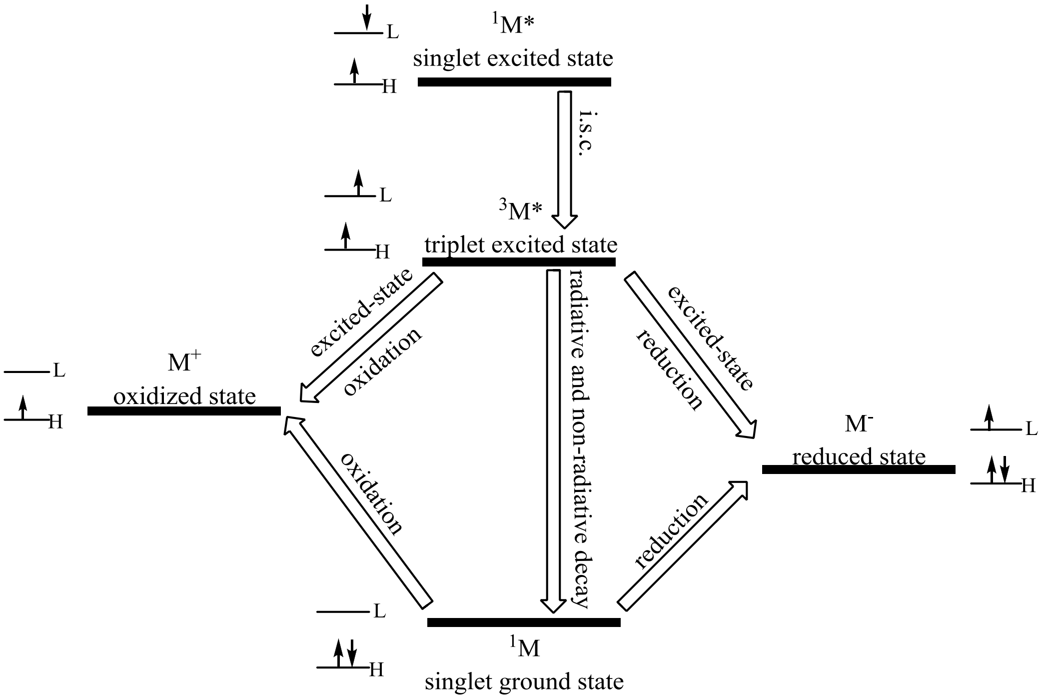
1. Redox orbitals

Oxidation of molecule involves loss of an electron, and the thermodynamically most favorable electron to remove is the one in the highest-energy occupied molecular orbital (HOMO). Likewise, reduction of molecule involves gaining an additional electron, and the lowest-energy empty orbital (LUMO) is the thermodynamically-favorable acceptor orbital. For this reason, the HOMO and LUMO can be considered "redox orbitals", and electrochemical redox potentials (voltages) give us information about the HOMO and LUMO energies. For example, a strong oxidant is a molecule that has a low-energy LUMO, capable of accepting an electron.



However, in the excited state, the electron-hole pair cause a switch in the orbitals involved in redox reactions. Oxidation of an excited-state molecule involves loss of an electron, and the thermodynamically most favorable electron to remove is the excited one in the LUMO. Likewise, reduction of an excited-state molecule involves gaining an additional electron, and the HOMO is the thermodynamically-favorable acceptor orbital.

2. Excited-state redox reactions: state energy diagram



3. **Excited-state redox potentials**

One important aspect of photochemistry is that an excited-state species is a stronger oxidant than the corresponding ground-state species. Therefore, the absorption of light can drive electron-transfer reactions that may be thermodynamically unfavorable in the ground state.

The driving force for electron transfer can be expressed as a change in Gibbs Energy (ΔG^0) or in terms of a redox potential (E^0). These two parameters are related by the number of electrons involved in the electron transfer process (n) and Faraday's constant (F): $\Delta G^0 = -nFE^0$

Just as we characterize ground-state redox half-reactions with reduction and oxidation potentials (E^0):

$M + e^- \rightarrow M^-$ $\quad E^0\ (M^0/M^-)$
$M^+ + e^- \rightarrow M$ $\quad E^0\ (M^+/M^0)$

the propensity of an excited-state molecule to gain or lose an electron can described by its excited-state reduction and oxidation potentials:

$M^* + e^- \rightarrow M^-$ $\quad E^0\ (M^*/M^-)$
$M^+ + e^- \rightarrow M^*$ $\quad E^0\ (M^+/M^*)$

How can these values be estimated?

Recall Hess's Law of Heat Summation, an approach used to calculate the enthalpy changes for a sum of reactions. Similarly, ΔG associated with reduction of an excited state is related to ΔG for relaxation of excited state and ΔG for reduction of ground state.

As an example, we can estimate the ***excited-state reduction potential*** for $^*[Ru(bpy)_3]^{2+}$. The reduction potential for *ground-state* $[Ru(bpy)_3]^{2+}$ can be obtained from electrochemical experiments:

$$[Ru(bpy)_3]^{2+} + e^- \rightarrow [Ru(bpy)_3]^+ \qquad E^0 = -1.33\ V$$

$$\text{and}\ \ \Delta G^0 = -nFE^0 = -(1)(96.50)(-1.33) = +128.3\ kJ/mol$$

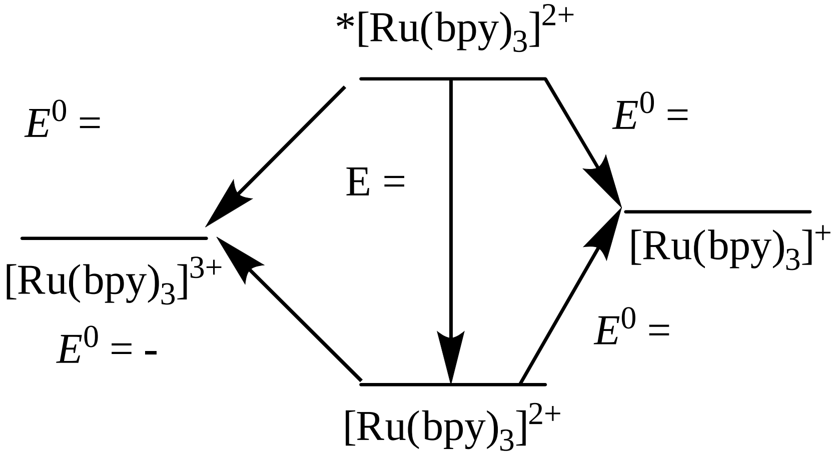
The Gibbs Energy change associated with relaxation of the ^{3}MLCT excited state can be estimated from the $[Ru(bpy)_3]^{2+}$ phosphorescence spectrum ($\Delta G \approx E = hc/\lambda$). Using the high-energy side of the phosphorescence band ($\lambda_{em} \approx 585$ nm), the excited-state energy can be estimated to be $\Delta G^0 \approx -204.6$ kJ/mol. Just as excitation can be thought of as a one-electron *intermolecular* redox reaction, so can luminescence. Therefore, we can calculate a voltage associated with relaxation of the ^{3}MLCT excited state:

$$E^0 = -\Delta G^0 / nF = -(-204.6\ kJ/mol)/(1)(96.50) = +2.12\ V$$

Combining these two potentials or ΔG values yields the excited-state reduction potential of +0.79 V vs. NHE and a corresponding change in Gibbs energy of $\Delta G = -76.3$ kJ/mol for the reduction of the excited state complex $^*[Ru(bpy)_3]^{2+}$ to $[Ru(bpy)_3]^+$:

$^*[Ru(bpy)_3]^{2+} \rightarrow [Ru(bpy)_3]^{2+}$	$\Delta G^0 \approx -204.6$ kJ/mol	$E^0 = +2.12$ V
$[Ru(bpy)_3]^{2+} \rightarrow [Ru(bpy)_3]^+ + e^-$	$\Delta G^0 = +128.3$ kJ/mol	$E^0 = -1.33$ V
$^*[Ru(bpy)_3]^{2+} + e^- \rightarrow [Ru(bpy)_3]^+$	$\Delta G^0 \approx -76.3$ kJ/mol	$\boldsymbol{E^0 = +0.79\ V}$

This calculation shows that the ^{3}MLCT excited-state of $[Ru(bpy)_3]^{2+}$ is more easily reduced (is a stronger oxidant) than is the ground state. Using a similar approach, the ***excited-state oxidation potential*** for the half-reaction $*[Ru(bpy)_3]^{2+} \rightarrow *[Ru(bpy)_3]^{3+} + e-$ can be calculated to be $E^0 = +0.83$ V. Again, the ^{3}MLCT excited-state of $[Ru(bpy)_3]^{2+}$ is more easily oxidized (is a stronger reductant) than is the ground state.



F. Experimental Luminescence Spectroscopy

A **fluorescence spectrophotometer** ("fluorimeter") is used to measure luminescence (either fluorescence or phosphorescence) intensity as a function of wavelength emitted, yielding a luminescence emission spectrum. To obtain an emission spectrum, a sample solution is placed in a cuvette placed in the instrument sample chamber. The cuvette is similar to that used in UV-vis spectroscopy, except that all four windows are optically transparent and the glass is a special type of quartz allowing for transmission of UV light. An excitation wavelength (λ_{ex}) is selected to irradiate the sample solution, and the intensity of the resulting luminescence is measured through a region of emission wavelengths.

The components of the fluorimeter include:

1. POWER SUPPLY: powers the lamp
2. LIGHT SOURCE: lamp providing light in the UV and visible wavelengths region for excitation of the sample.
3. EXCITATION MONOCHROMATOR: selects a particular wavelength of light from the lamp to excite the sample
4. SAMPLE CHAMBER: holds the solution in a cuvette; may be temperature controlled.
5. EMISSION MONOCHROMATOR: located at a right angle to the excitation, scans through the luminescence wavelength region.
6. DETECTOR: a photomultiplier tube "PMT" transforms photons into an electrical current signal to detect the number of photons emitted at each wavelength scanned.

Using a computer software program interfaced to the spectrophotometer, you can select:

- the wavelength of excitation (λ_{ex}),
- the wavelength range for scanning the emission,
- the increment of wavelengths to measure in this range,
- the amount of time spent measuring photons at each wavelength,
- the slit width of the excitation and emission monochromators (which adjusts how much light passes through each monochromator)

Within the fluorimeter software or using an external spreadsheet or plotting program, you can prepare a luminescence spectrum and calculate the area underneath an emission curve (integration) which is a measure of the luminescence intensity.

Several factors can affect luminescence intensity. They include:

- instrumental parameters such as the slit width, and signal averaging (integration time and averaging multiple scans),
- solution concentration & absorbance,
- solvent (or microenvironment)
- temperature
- the presence in solution of other molecules or ions that can act as quenchers

G. Excited-State Kinetics

***Absorption*:** **$M + h\nu \rightarrow M^*$**

An excited state molecule M* is formed by the absorption of UV -vis light; this process is almost instantaneous, and the rate can be given as "I_a", which is related to both the concentration of the absorbing ground-state molecule [M], the efficiency of absorption (related to the molar absorptivity, ε) and the intensity of light. Following absorption, excited-state molecule may relax to a different excited state (such as a triplet state). The *lowest energy* excited state is typically the state from which luminescence and excited-state reactivity occurs.

An excited-state molecule is highly reactive and typically only survives for a fraction of a second (often as short as a few nanoseconds), because several processes allow the excited state energy to be dissipated. The relative rates of luminescence and non-radiative decay determines the intensity and lifetime of luminescence (fluorescence or phosphorescence) that may be observed from a sample. Let's explore these rates and their corresponding rate laws for a generic molecule M that absorbs light and forms a excited state M* which can relax back to the ground state by luminescence (fluorescence or phosphorescence) or non-radiative decay.

***Luminescence*:** **$M^* \rightarrow M + h\nu$**

Also called "radiative decay", luminescence is a unimolecular process, so the ***rate of luminescence*** is dependent only on the concentration of the excited state molecule M* and therefore has a ***first-order rate law***:

$$\text{Rate of luminescence} = k_r[M^*] \qquad (1)$$

***Non-radiative decay*:** **$M^* \rightarrow M + \text{heat}$**

The ***rate of non-radiative decay*** also depends on the concentration of the excited state molecule M*. However, non-radiative decay is actually a group of processes by which the excitation energy is released as heat; some processes are unimolecular (such as dissipating the electronic excitation energy through molecular vibrations) and others are bimolecular (such as collisions with a solvent molecule). Although the actual rate law may be complex, it can be simplified. The sum of several first-order rates occurring in parallel is first order. Also, the rate law for a second order rate law having one reagent (such as a solvent) in large excess concentration can also be approximated as first order (often called "pseudo-first order"). So, the rate law for non-radiative decay can be expressed as a simple ***first-order kinetics***:

$$\text{Rate of non-radiative decay} = k_{nr}[M^*] \qquad (2)$$

SCHEME for excited-state kinetics

	process	rate	description
(i)	$M + h\nu \rightarrow M^*$	I_a	absorption
(ii)	$M^* \rightarrow M + h\nu$	$k_r[M^*]$	luminescence
(iii)	$M^* \rightarrow M + \text{heat}$	$k_{nr}[M^*]$	non-radiative decay

Quantum Efficiency of Luminescence. Experimentally, luminescence intensity can be measured using a fluorescence spectrometer and expressed as the **luminescence quantum efficiency** (ϕ), the ratio of the amount of light emitted (fluorescence or phosphorescence) to the amount of light absorbed. The luminescence quantum efficiency can also be expressed as the ratio of the *rate* of luminescence (eqn. 1) to the *rate* of absorption (I_a)[††]:

$$\phi = k_r[M^*] / I_a \qquad (4)$$

Under continuous excitation, the concentration of the highly reactive excited state molecule is essentially constant, so the rate of formation and the rates of disappearance are equal. This is an application of the **Steady State Approximation**:

$$\text{Rate of formation of } M^* = \text{Rate of disappearance of } M^* \qquad (5)$$

With luminescence and non-radiative decay pathways competing with each other, the overall rate of decay of the excited state is simply the sum of these two rates:

$$I_a = k_r[M^*] + k_{nr}[M^*] \qquad (6)$$

Combining equations (4) and (6) yields an expression for the quantum efficiency (ϕ_0):

$$\phi_0 = k_r / (k_r + k_{nr}) \qquad (7)$$

Lifetime. The ***luminescence lifetime*** (τ_0) can be measured using a laser system and measuring the intensity of luminescence as a function of time following excitation by a very short "pulse" of light. Usually, the rate of decay of luminescence intensity is directly proportional to the concentration of the excited state molecule M* -- a unimolecular process that follows first-order kinetics.

$$\text{Rate of luminescence intensity decay} = k_{obs}[M^*] \qquad (X)$$

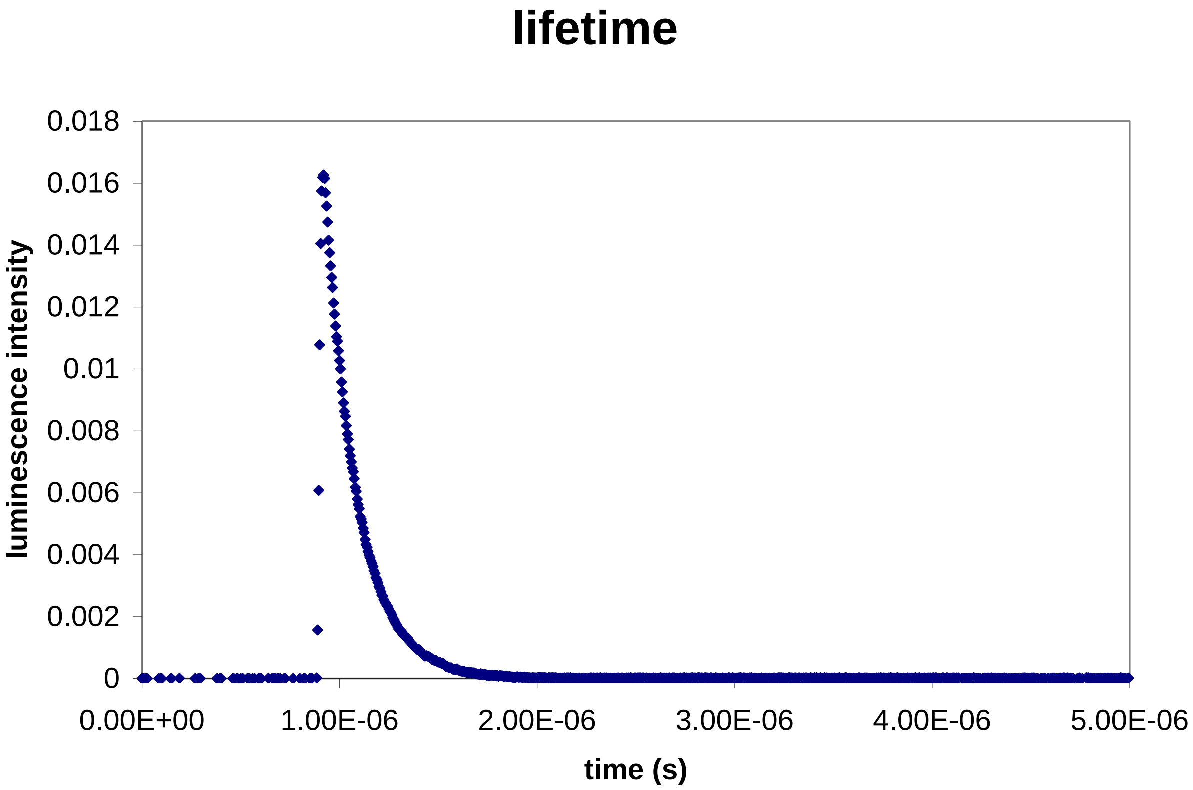
Comparing this experimental observation with the excited-state mechanism indicates that this observed rate constant k_{obs} is simply the sum of the luminescence and non-radiative decay rate constants ($k_r + k_{nr}$):

$$\text{Rate of luminescence intensity decay} = k_r[M^*] + k_{nr}[M^*] = (k_r + k_{nr})[M^*]$$

The lifetime is the inverse of this rate constant (faster decay rates result in a shorter lifetime). Therefore, the lifetime is expressed as the inverse of the sum of the decay rate constants:

$$\tau_0 = 1/(k_r + k_{nr}) \qquad (10)$$

[††] For phosphorescence, the quantum efficiency also depends on the rate of intersystem crossing, but this process is often very fast and does not have a significant influence on the rate equations presented here.



H. Luminescence Quenching

Luminescent molecules have been employed in several applications in materials chemistry due their excited-state properties. One commercially available device is based on a luminescent Ru(II) transition metal complex cation, $[Ru(bpy)_3]^{2+}$, embedded inside of a polymer host. A fiber optic cable is used as a light source to photo-excite the metal complex, and the resulting phosphorescence is "quenched" (reduced in intensity) in the presence of oxygen gas. This luminescence quenching is a result of a specific interaction between the $*[Ru(bpy)_3]^{2+}$ excited-state and molecular oxygen.

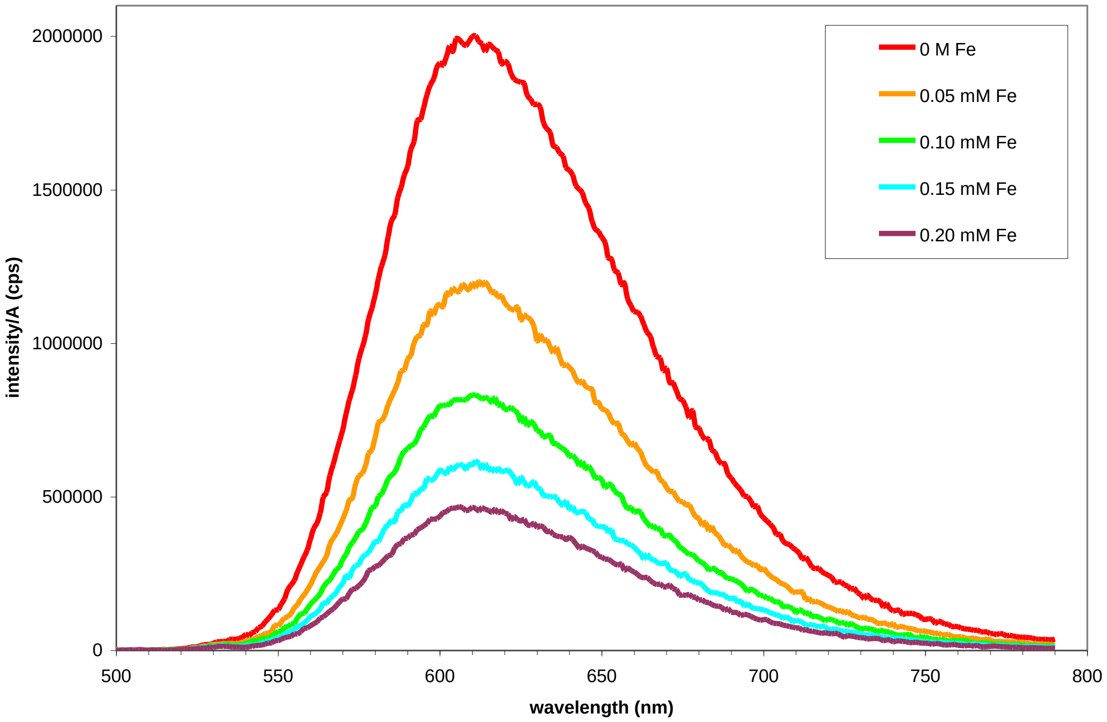
A landmine sensor has been built that relies on a mechanism by which TNT (trinitrotoluene) quenches the luminescence intensity of a molecular wire material known as PPV (poly-phenylene vinylene)

An excited-state molecule may react with a quencher molecule Q by several different mechanisms:

$M^* + Q \rightarrow M + Q^*$	energy transfer
$M^* + Q \rightarrow M^+ + Q^-$	electron transfer
$M^* + Q \rightarrow M^- + Q^+$	electron transfer
$M^* + Q \rightarrow M + Q + \text{heat}$	collisional quenching

Typically only <u>one</u> of these quenching mechanisms is occurring in a particular system, but determining <u>which</u> mechanism might be occurring may be difficult in practice. However, we can often understand which mechanism is *thermodynamically favored* by predicting the value of ΔG, and this will be discussed below for the cases of energy transfer and electron transfer. In terms of *kinetics*, each of this processes is bimolecular so their rates are dependent on both the concentration of the excited state molecule M* and on the concentration of the quencher.

luminescence spectra of $[Ru(bpy)_3]^{2+}$ (*aq*) with varying concentration of $[Fe(CN)_6]^{3-}$ (*aq*)

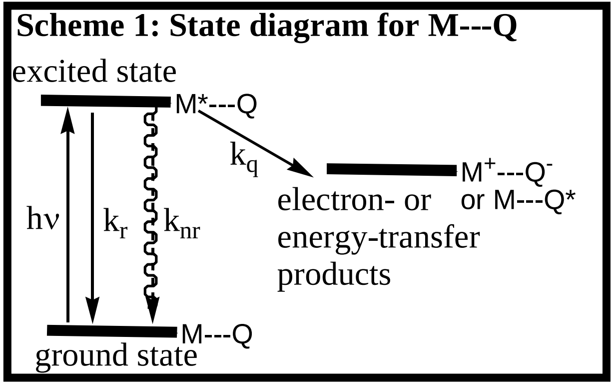


Excited-State Quenching $M^* + Q \rightarrow$ products

If a quencher is present in a mixture with a luminescent molecule, the quenching pathway introduces another rate (competing with radiative and non-radiative decay) for deactivating the excited state. The result is a decrease in the intensity and lifetime of the luminescence, so the process is termed **quenching** and the molecule Q is called a **quencher**. The rate law for bimolecular quenching follows a ***second order kinetics***:

Rate of quenching = $k_q[M^*][Q]$ (3)

In Scheme 1, we can see that the excited-state M* can have either two or three reaction pathways, depending whether or not a quencher Q is present in solution. <u>As the concentration of Q increases, the rate of the quenching increases</u>. We can take advantage of this to systematically


Scheme 1: State diagram for M---Q

control the rate of the quenching pathway. The Stern-Volmer method can be used to calculate k_q for these ultra-fast excited state quenching reactions.

SCHEME for excited-state kinetics *with quenching*

	process	rate	description
(i)	$M + h\nu \rightarrow M^*$	I_a	absorption
(ii)	$M^* \rightarrow M + h\nu$	$k_r[M^*]$	luminescence
(iii)	$M^* \rightarrow M$ + heat	$k_{nr}[M^*]$	non-radiative decay
(iv)	$M^* + Q \rightarrow$ products	$k_q[M^*][Q]$	dynamic quenching

Stern-Volmer Equation. By adding a known concentration of quencher to the solution, we can increase the rate of quenching (eqn. 3). Because there is now an additional deactivation pathway for the excited state complex, the steady-state expression and the quantum efficiency expression become:

$$I_a = k_r[M^*] + k_{nr}[M^*] + k_q[M^*][Q] \qquad (8)$$

and

$$\phi_q = k_r / (k_r + k_{nr} + k_q[Q]) \qquad (9)$$

The luminescence quantum efficiency when quencher is present is termed ϕ_q and the bimolecular quenching rate constant is termed k_q.

By combining equations (7), (9) and (10), we find that the ratio of quantum efficiencies for a solution without and with quencher depends linearly on the quencher concentration:

$$\boxed{\phi_0/\phi_q = 1 + k_q\tau_0[Q]} \qquad \textbf{Stern-Volmer Equation} \qquad (11)$$

Using a similar approach, one can show that the lifetime of luminescence decay should decrease with increased quencher concentration, and that the ratio of the luminescence lifetime without quencher (τ_0) and with quencher (τ_q) present yields the same equation as for quantum efficiency quenching:

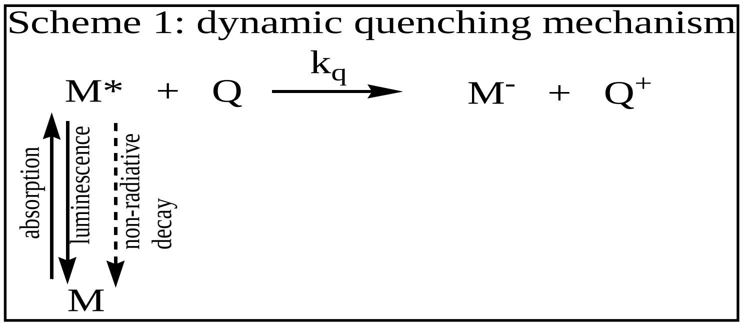
$$\tau_0/\tau_q = 1 + k_q\tau_0[Q] \qquad \textbf{Stern-Volmer Equation} \qquad (11)$$

These are two forms of the Stern-Volmer (SV) equation, and indicate that plots of ϕ_0/ϕ_q vs. [Q] and τ_0/τ_q vs. [Q] should be linear with a slope of $k_q\tau_0$ and an intercept of unity. The quenching rate constant k_q can be determined by measuring changes in luminescence quantum efficiency and/or lifetimes for solutions having varying quencher concentration.[‡‡]

[‡‡] *Principles of Fluorescence Spectroscopy* (2nd Ed.) by Joseph R. Lakowicz. Chapter 8.

I. (ALTERNATE) Thermodynamics of Excited-state Electron Transfer

A mechanism for the excited-state reactivity of $[Cr(phen)_3]^{3+}$ is given in Scheme 1. The ground-state d^3 Cr^{3+} complex is a quartet state (given the term symbol ^4A) due to the three unpaired electrons. Upon excitation with visible light (λ_{ex} < 440 nm), an electron is promoted from one of the partially-filled d orbitals (d_{xy}, d_{xz} or d_{yx}) to an empty d orbital ($d_{x^2-y^2}$ or d_{z^2}) yielding an "metal-centered" excited-state complex $*[Cr(phen)_3]^{3+}$ also having a quartet spin state (^4T). Detailed discussions of the nature of these orbitals and other transitions can found be found in the literature.[§§,***] This quartet state relaxes quickly to a set of lower-energy metal-centered doublet states (^2T and ^2E). These doublet excited states can relax back to the ground state by two major pathways: luminescence (also known as ***radiative decay***) or a set of non-radiative decay pathways that involve intramolecular vibrations and collisions with solvent that result in the formation of heat. For $[Cr(phen)_3]^{3+}$, the luminescence is long-lived phosphorescence (due to the required spin flip involved) consisting of two bands, one at 700 nm and one at 730 nm. The absorption and luminescence spectra of $[Cr(phen)_3]^{3+}$ in water are shown in Figure 1.


Scheme 1: dynamic quenching mechanism

In addition to relaxing back to the ground state, the energy-rich excited-state complex is capable of oxidizing a suitable substrate, if present, and being reduced to $[Cr(phen)_3]^{2+}$ through a redox reaction.

Thermodynamics of Electron-Transfer Quenching. One important aspect of photochemistry is that an excited-state species is a stronger oxidant than the corresponding ground-state species. Therefore, the absorption of light can drive electron-transfer reactions that may be thermodynamically unfavorable in the ground state. The driving force for electron transfer can be expressed as a change in Gibbs Energy (ΔG^0) or in terms of a redox potential (E^0). These two parameters are related (eqn. 1) by the number of electrons involved in the electron transfer process (n) and Faraday's constant (F).

$$\Delta G^0 = -nFE^0 \qquad (1)$$

The ground-state reduction potential of $[Cr(phen)_3]^{3+}$ can be determined using cyclic voltammetry (eqn. 2):

$$[Cr(phen)_3]^{3+} + e^- \rightarrow [Cr(phen)_3]^{2+} \quad E^0(Cr^{3+}/Cr^{2+}) = -0.28 \text{ V vs. NHE} \quad (2)$$

$$\Delta G^0 = +27 \text{ kJ/mol}$$

The excited-state reduction potential, $E^0(*Cr^{3+}/Cr^{2+})$, can be estimated using an analysis similar to Hess's Law of Heat Summation (Figure 2). Using the emission maximum (730 nm) in

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[§§] Bolletta, F.; Maestri, M.; Moggi, L.; Jamieson, M.A.; Serpone, N.; Henry, M.S.; Hoffman, M.Z. *Inorg. Chem.* **1983**, *22*, 2502-2509

[***] Jamieson, M.A. *Coord. Chem. Rev.* **1981**, *39*, 121-

the luminescence spectrum and converting units yields an excited-state energy of 164 kJ/mol for *$[Cr(phen)_3]^{3+}$. This can also be expressed as a one-electron electrochemical potential of the excited state, $E_{00} = +1.70$ V. Combining these two potentials or ΔG values (Figure 2) yields the excited-state reduction potential of +1.42 V vs. NHE and a corresponding change in Gibbs energy of ΔG = -137 kJ/mol for the reduction of the excited state complex *$[Cr(phen)_3]^{3+}$ to $[Cr(phen)_3]^{2+}$.

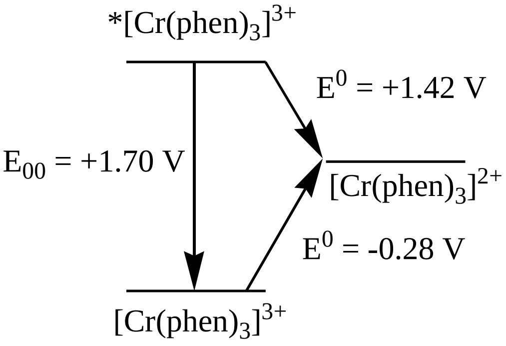

Figure 2: excited state reduction potential diagram

The excited-state and ground-state reduction potentials indicate that a substrate (Q) having an oxidation potential (for the process Q → $Q^+ + e^-$) of E^0 (Q/Q$^+$) = -1.29 V vs. NHE, for example, could be oxidized by the excited-state complex *$[Cr(phen)_3]^{3+}$ (equation 3) but not by the ground state complex $[Cr(phen)_3]^{3+}$ (equation 4):

$$^*[Cr(phen)_3]^{3+} + Q \rightarrow [Cr(phen)_3]^{2+} + Q^+$$
$$E^0 = (+1.42 \text{ V}) + (-1.29 \text{ V}) = +0.13 \text{ V} \tag{3}$$

$$[Cr(phen)_3]^{3+} + Q \rightarrow [Cr(phen)_3]^{2+} + Q^+$$
$$E^0 = (-0.28 \text{ V}) + (-1.29 \text{ V}) = -1.57 \text{ V} \tag{4}$$

The excited-state redox reaction (3) is thermodynamically favorable ($E^0 > 0$) while ground-state reaction (4) is not ($E^0 < 0$). Therefore, a mixture of $[Cr(phen)_3]^{3+}$ and such a substrate will only undergo a redox reaction after the chromium complex has been excited. This is the process of ***photo-induced electron transfer***: light initiates an electron-transfer reaction. This experiment will explore how substrates such as DNA may be oxidized by the excited-state *$[Cr(phen)_3]^{3+}$ complex.