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MacMillan Group Meeting

February 12th, 2015

Part 1

**Photocatalyst Details
and Synthesis**

Part 2

**Mechanisms of
Operation**

Part 3

**Relevant Analytical
Methods**

this talk does not contain synthetic applications of photoredox catalysis

*instead it focuses on how and why the photocatalysts work
and why we use the ones we do*

Part 1

**Photocatalyst Details
and Synthesis**

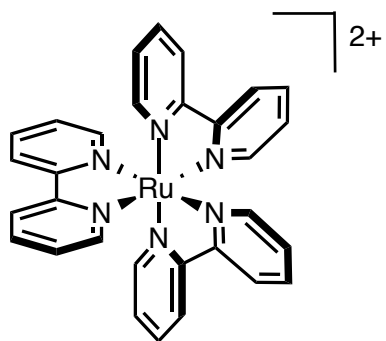
Part 2

**Mechanisms of
Operation**

Part 3

**Relevant Analytical
Methods**

Common Transition Metal Photocatalysts: the "Big 4"



$Ru(bpy)_3^{2+}$

$$E(M^+/M^*) = -0.81 \text{ V}$$

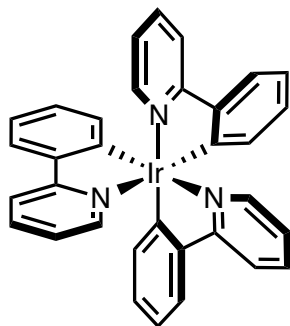
$$E(M^*/M^-) = +0.77 \text{ V}$$

$$\tau = 1.1 \mu\text{s}$$

$$\lambda_{abs} = 452 \text{ nm}$$

$$\lambda_{em} = 652 \text{ nm}$$

$$\Phi_{em} = 0.095$$



$Ir(ppy)_3$

$$E(M^+/M^*) = -1.73 \text{ V}$$

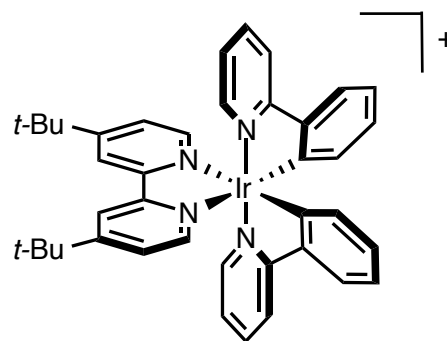
$$E(M^*/M^-) = +0.31 \text{ V}$$

$$\tau = 1.9 \mu\text{s}$$

$$\lambda_{abs} = 375 \text{ nm}$$

$$\lambda_{em} = 518 \text{ nm}$$

$$\Phi_{em} = 0.38$$



$Ir(ppy)_2(dtbbpy)^{2+}$

$$E(M^+/M^*) = -0.96 \text{ V}$$

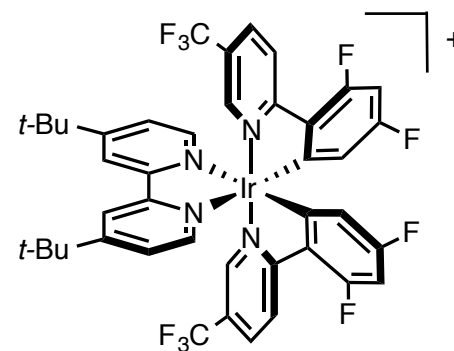
$$E(M^*/M^-) = +0.66 \text{ V}$$

$$\tau = 0.56 \mu\text{s}$$

$$\lambda_{abs} = 410 \text{ nm}$$

$$\lambda_{em} = 581 \text{ nm}$$

$$\Phi_{em} = 0.094$$



$Ir[dF(CF_3)ppy]_2(dtbbpy)^+$

$$E(M^+/M^*) = -0.89 \text{ V}$$

$$E(M^*/M^-) = +1.21 \text{ V}$$

$$\tau = 2.3 \mu\text{s}$$

$$\lambda_{abs} = 380 \text{ nm}$$

$$\lambda_{em} = 470 \text{ nm}$$

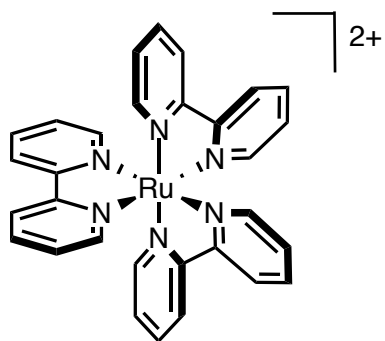
$$\Phi_{em} = 0.68$$

For very useful reviews see:

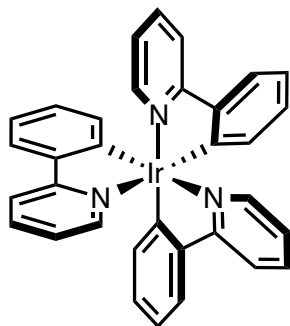
Tucker, J. W.; Stephenson, C. R. J. *J. Org. Chem.* **2012**, *77*, 1617

Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C. *Chem. Rev.* **2013**, *113*, 5322

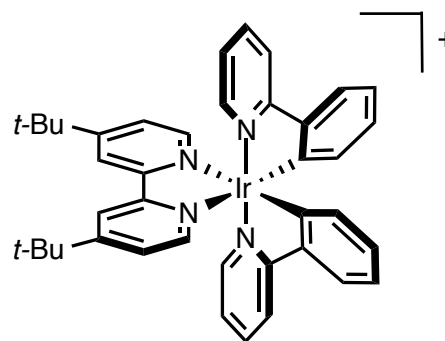
Common Transition Metal Photocatalysts: the "Big 4"



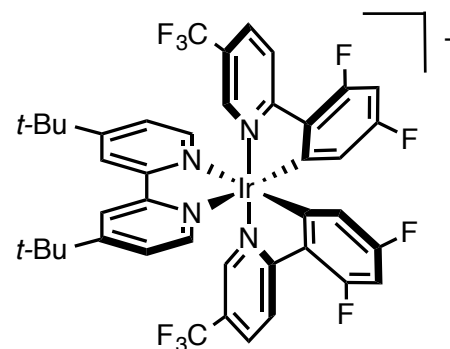
Ru(bpy)₃²⁺



Ir(ppy)₃



Ir(ppy)₂(dtbbpy)²⁺



Ir[dF(CF₃)ppy]₂(dtbbpy)⁺

these common photocatalysts can be divided 2 major ways

homoleptic (all ligands same) vs.
heteroleptic (different ligands)

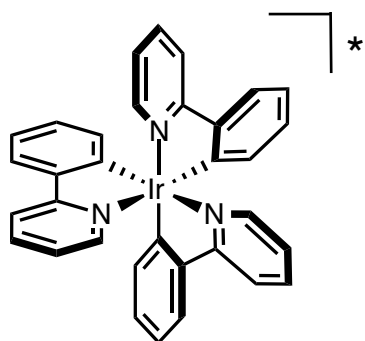
ruthenium vs. iridium

For very useful reviews see:

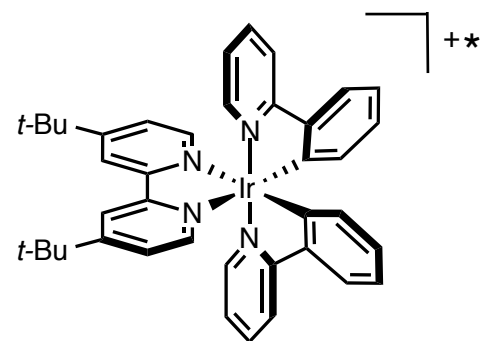
Tucker, J. W.; Stephenson, C. R. J. *J. Org. Chem.* **2012**, *77*, 1617
Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C. *Chem. Rev.* **2013**, *113*, 5322

Photocatalyst Comparison: Homoleptic vs. Heteroleptic

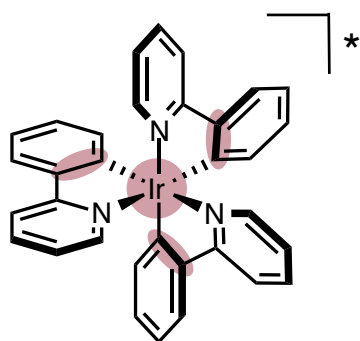
most significant difference is in the location of HOMO and LUMO of excited state



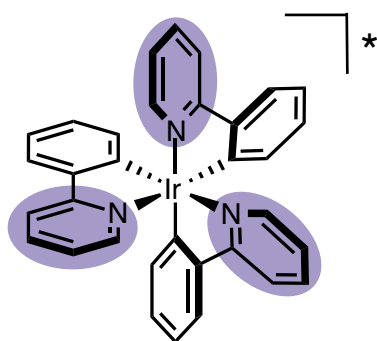
Ir(ppy)₃



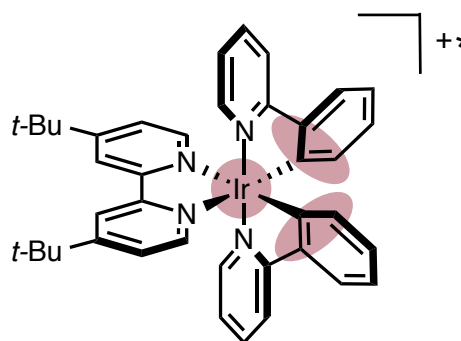
Ir(ppy)₂(dtbbpy)²⁺



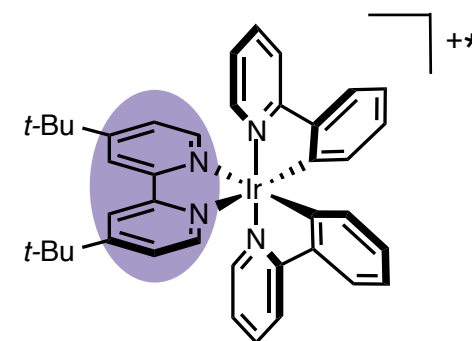
HOMO



LUMO



HOMO



LUMO

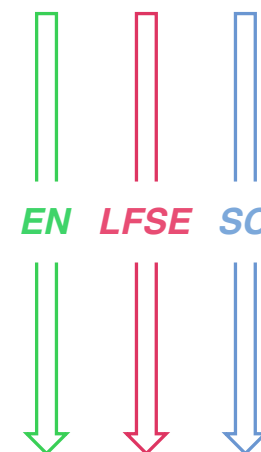
Thompson, M. E. *et al.* *J. Am. Chem. Soc.* **2003**, *125*, 7377

Malliaras, G. G. and Bernhard, S. *et al.* *Chem. Mater.* **2005**, *17*, 5712

Photocatalyst Comparison: Choice of Metal Center

moving from ruthenium to iridium has a profound effect on photophysical properties

21 Sc Scandium 44.956	22 Ti Titanium 47.867	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.38
39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.95	43 Tc Technetium 98.907	44 Ru	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.414
57-71	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir	78 Pt Platinum 195.085	79 Au Gold 196.967	80 Hg Mercury 200.592



Ir complexes are less electron-rich than the corresponding Ru ones

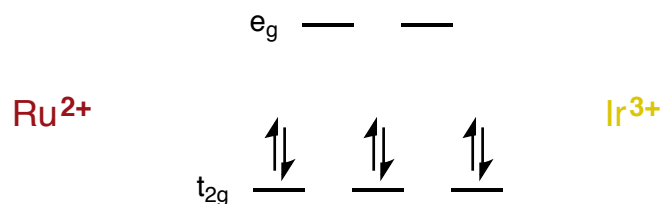
increased LFSE leads to larger HOMO-LUMO gap: more photonic input

large SO coupling improves MLCT efficiency: allows use of heteroleptic complexes

Photocatalyst Comparison: Choice of Metal Center

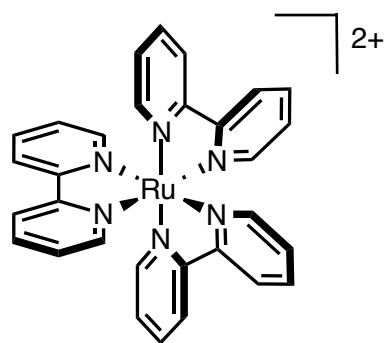
enhanced electrophilicity, LFSE and SO coupling manifest in a variety of ways

- location on periodic table affects d-electron count



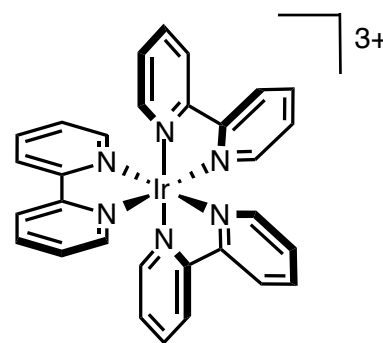
while Ru is in the +2 state, Ir must be more oxidized to reach the low-spin d^6 state characterized as substitutionally inert

- increased charge and electronegativity affects redox potentials:



$$E(M^+/M^*) = -0.81 \text{ V}$$

$$E(M^*/M^-) = +0.77 \text{ V}$$



$$E(M^+/M^*) = -0.88 \text{ V}$$

$$E(M^*/M^-) = +1.81 \text{ V}$$

$Ru(bpy)_3^{2+}$ – weaker oxidant, stronger reductant

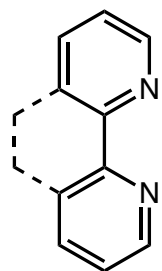
$Ir(bpy)_3^{3+}$ – similar reductant, much stronger oxidant

Flynn Jr., C. M.; Demas, J. N. *J. Am. Chem. Soc.* **1974**, *96*, 1979

Dixon, I. M.; Collin, J. P.; Sauvage, J.-P.; Flamigni, L.; Encinas, S.; Barigelletti, F. *Chem. Soc. Rev.* **2000**, *29*, 385

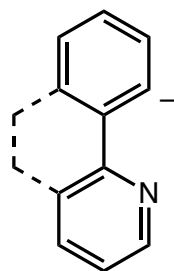
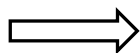
Photocatalyst Comparison: Choice of Metal Center

biggest difference: ability to support orthometalated (ppy-type) ligands



bpy, phen

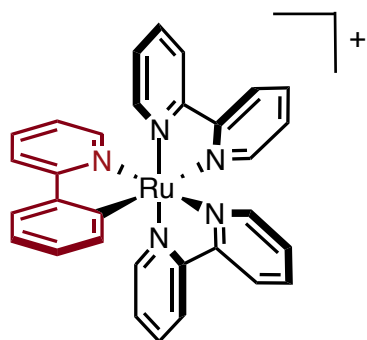
neutral, LL type



ppy, bzq

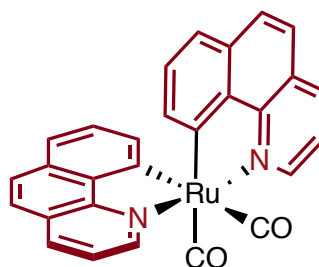
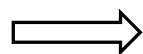
anionic, LX type

- moving from bpy to ppy increases e^- density enormously
- extreme donation necessitates e^- deficiency to stabilize
- additionally, asymmetric ligand field disrupts SO coupling, making MLCT less efficient with Ru (low quantum yield, Φ)



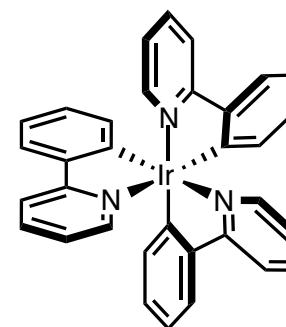
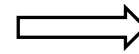
1 LX, **little stabilization**

$$\Phi_{em} \sim 0$$



2 LX, **2x CO stabilization**

$$\Phi_{em} < 10^{-4}$$



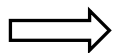
3 LX, **Ir³⁺ stabilization**

$$\Phi_{em} = 0.38$$

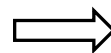
Photocatalyst Comparison: Choice of Metal Center

unlike Ru, Ir can support multiple LX ligands and promote efficient MLCT

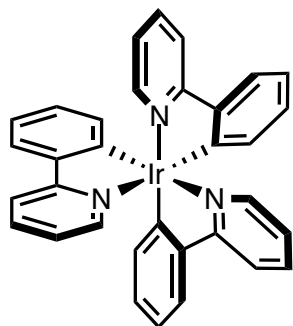
ability to support
multiple ligands without
loss of photocat. efficacy



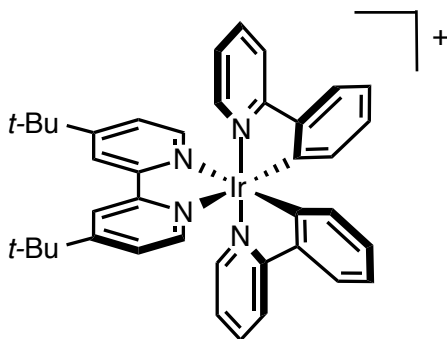
heteroleptic photocats.
can spatially separate
HOMO from LUMO



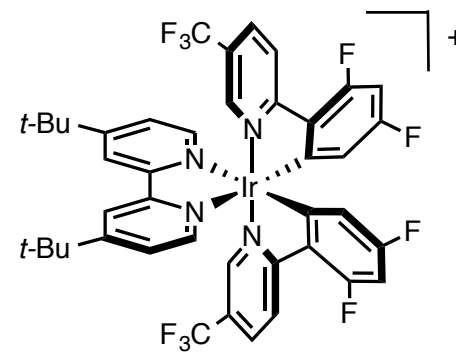
separation allows variation
of one potential with only
small change in the other



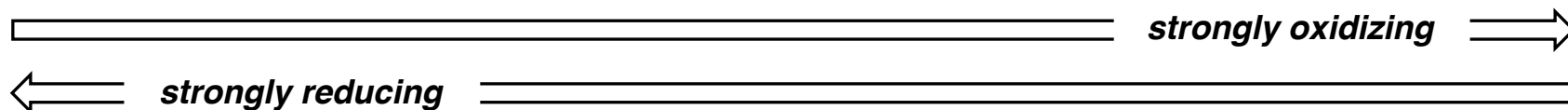
Ir(ppy)₃



Ir(ppy)₂(dtbbpy)₂²⁺

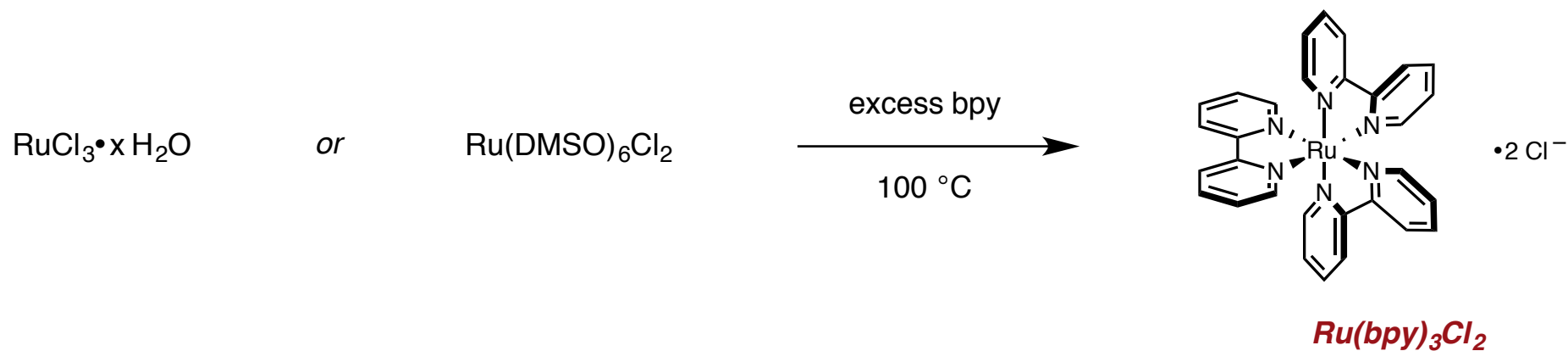


Ir[dF(CF₃)ppy]₂(dtbbpy)⁺

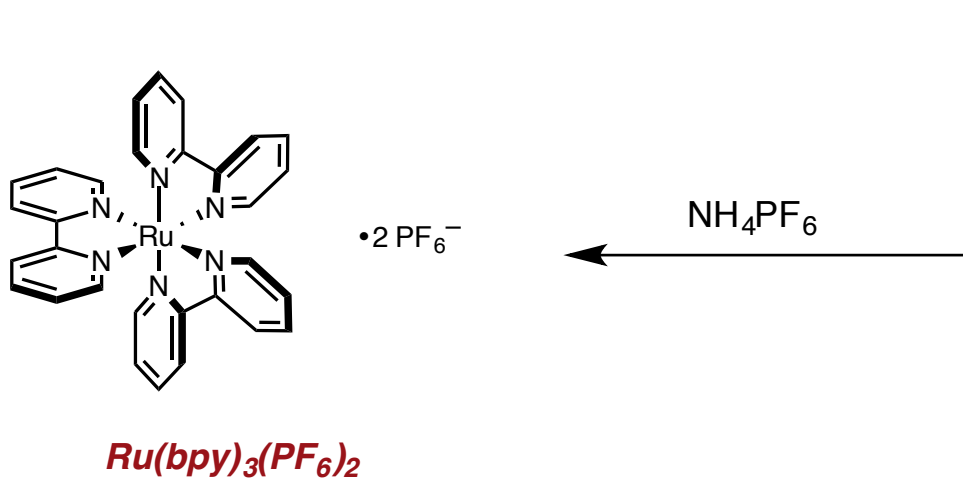


Ir photocatalysts are highly versatile and predictable allows rational catalyst design

Photocatalyst Synthesis: Ruthenium



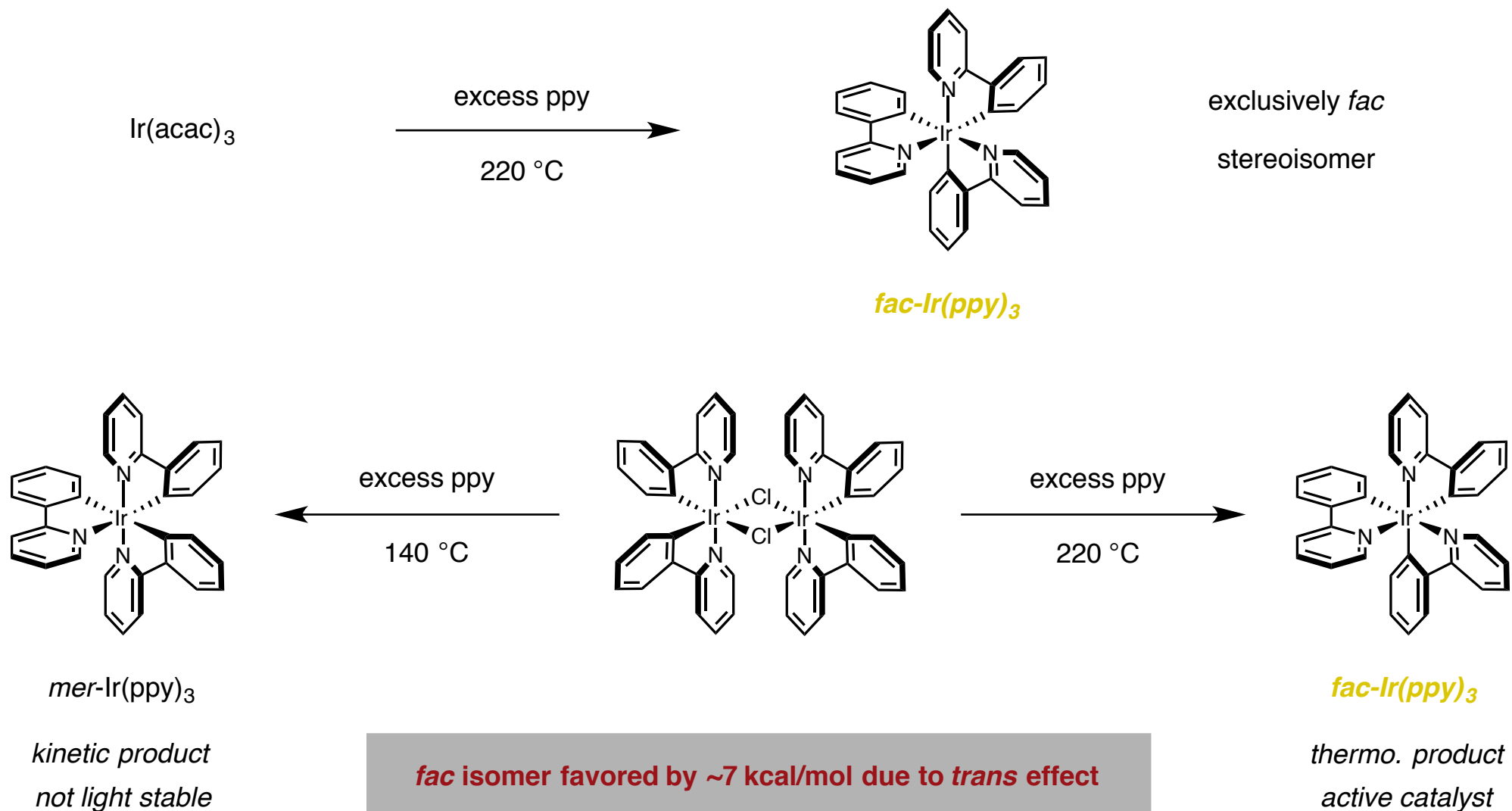
- both salts are active catalysts
- PF_6 shows greater solubility and stability towards deactivation



Evans, I. P.; Spencer, A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1973**, 204

Campagna, S.; Puntoriero, F.; Nastasi, F.; Bergamini, G.; Balzani, V. *Top. Curr. Chem.* **2007**, 280, 117

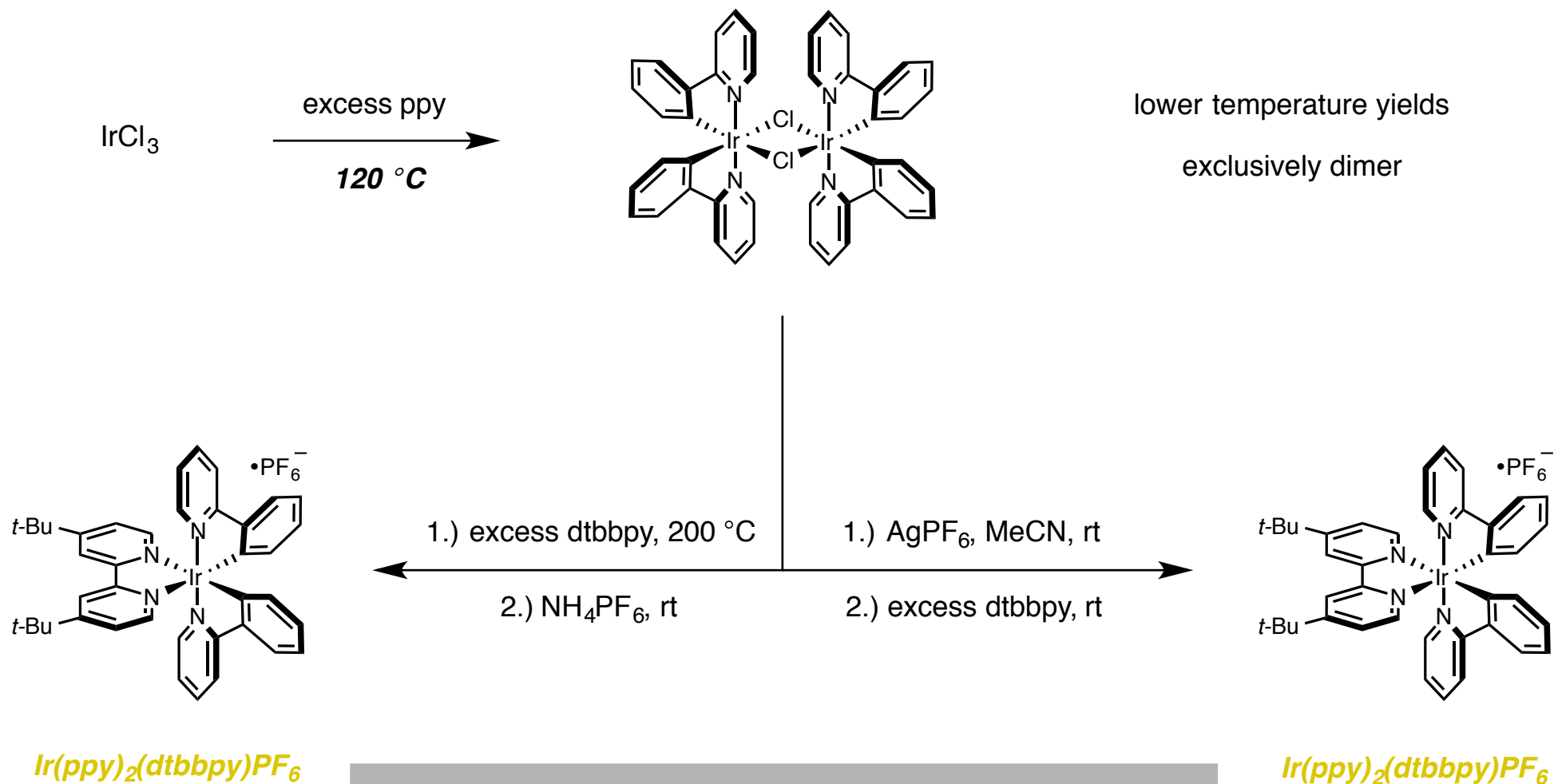
Photocatalyst Synthesis: Iridium Homoleptic



Thompson, M. E. *et al.* *J. Am. Chem. Soc.* **2003**, *125*, 7377

Dedeian, K.; Djurovich, P. I.; Garces, F. O.; Carlson, G.; Watts, R. J. *Inorg. Chem.* **1991**, *30*, 1685

Photocatalyst Synthesis: Iridium Heteroleptic



AgPF6 cracks dimer; increases yields (good for small scale)

Part 1

**Photocatalyst Details
and Synthesis**

Part 2

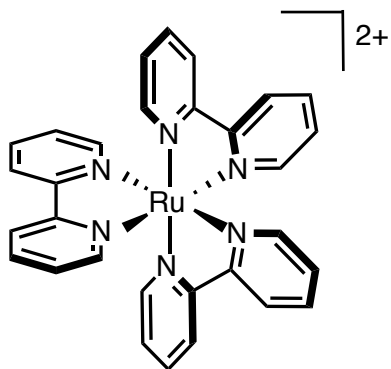
**Mechanisms of
Operation**

Part 3

**Relevant Analytical
Methods**

Photon Absorption and Generation of Excited State

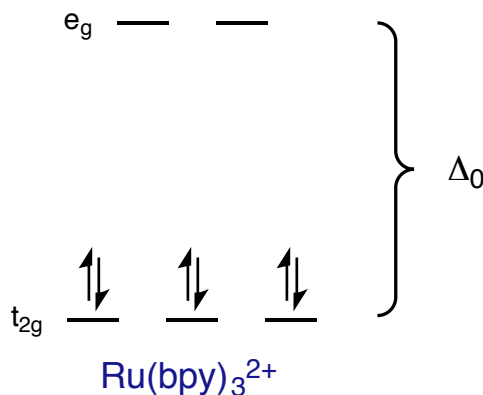
a short-lived singlet excited state rapidly converts to a long-lived triplet



6 d electrons in the octahedral,
low-spin configuration
(ie no electrons in e_g orbital)



this configuration is called
"substitutionally inert"
because e_g is antibonding

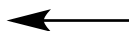


$\Delta_0 \equiv$ distance between t_{2g} and e_g – increases down the table
and with more highly charged ions

■ the bigger Δ_0 , the more LFSE and the more overall stability

■ Ir^{3+} photocats. are more stable than Ru^{2+}

ground state - singlet
" S_0 "

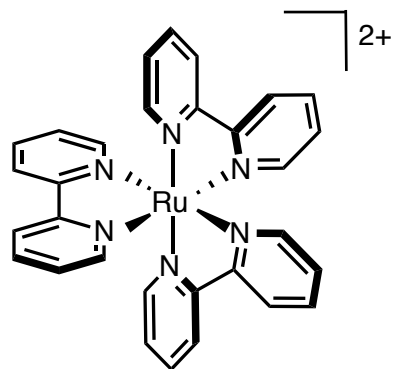


singlet \equiv 0 "un-spin-paired" electrons

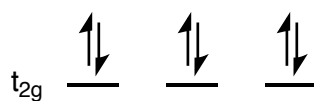
triplet \equiv 2 "un-spin-paired" electrons

Photon Absorption and Generation of Excited State

a short-lived singlet excited state rapidly converts to a long-lived triplet



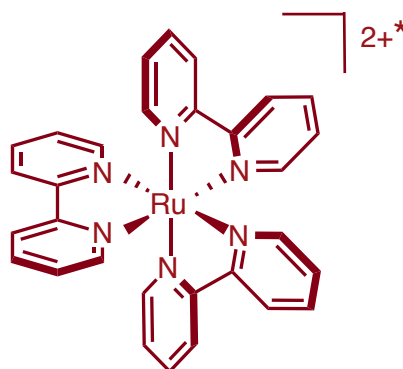
e_g — —



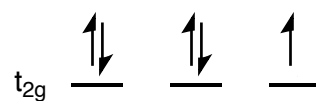
$Ru(bpy)_3^{2+}$

ground state - singlet
" S_0 "

452 nm
→



e_g — —



$*Ru(bpy)_3^{2+}$

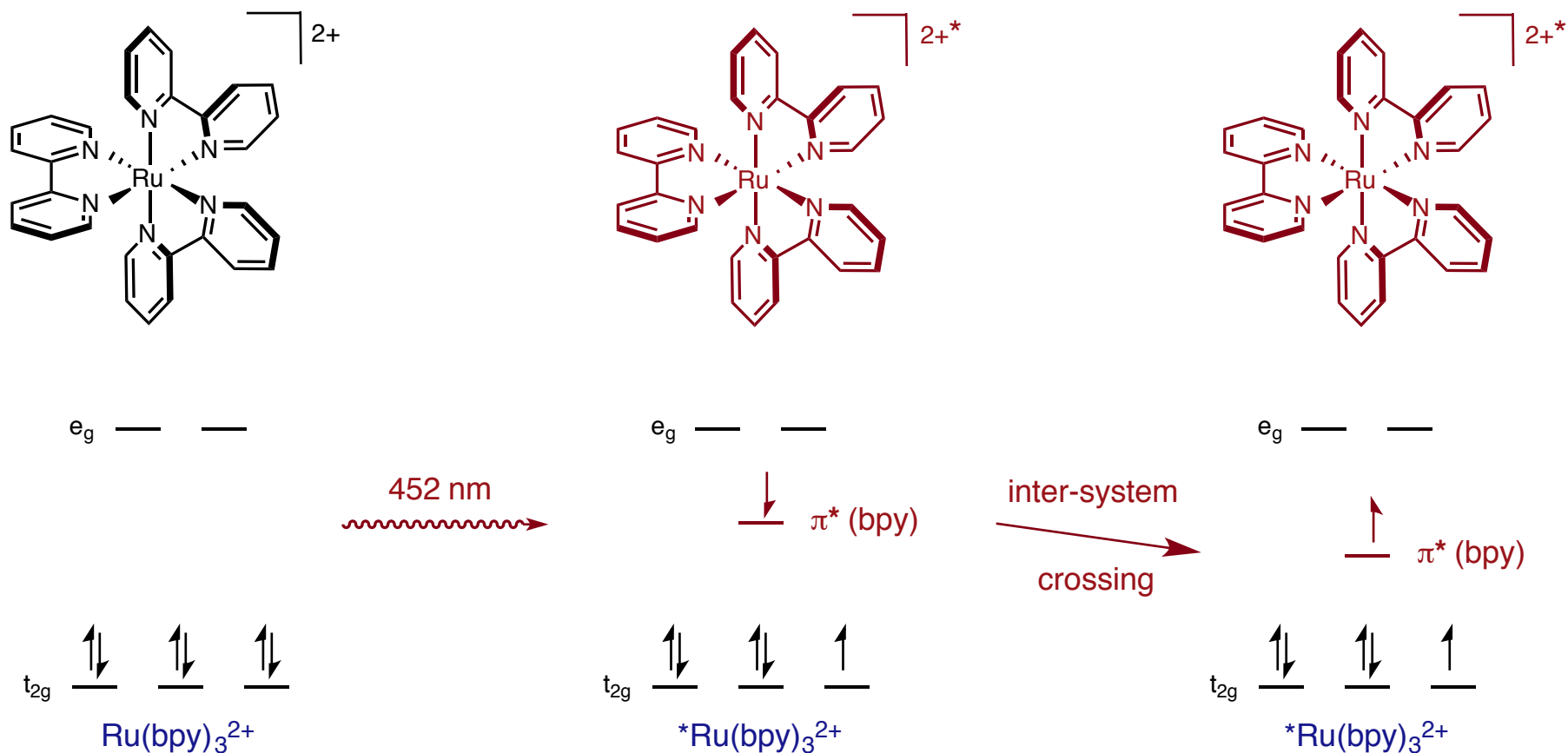
excited state - singlet
" S_1 ", $\tau = 100\text{-}300$ fs (10^{-15})

- the excited electron goes into LUMO (ligand π^*) – important because e_g is antibonding in character
- it retains its spin, as required by quantum mechanical selection rules (therefore this is still a singlet!)



Photon Absorption and Generation of Excited State

a short-lived singlet excited state rapidly converts to a long-lived triplet



ground state - singlet
" S_0 "

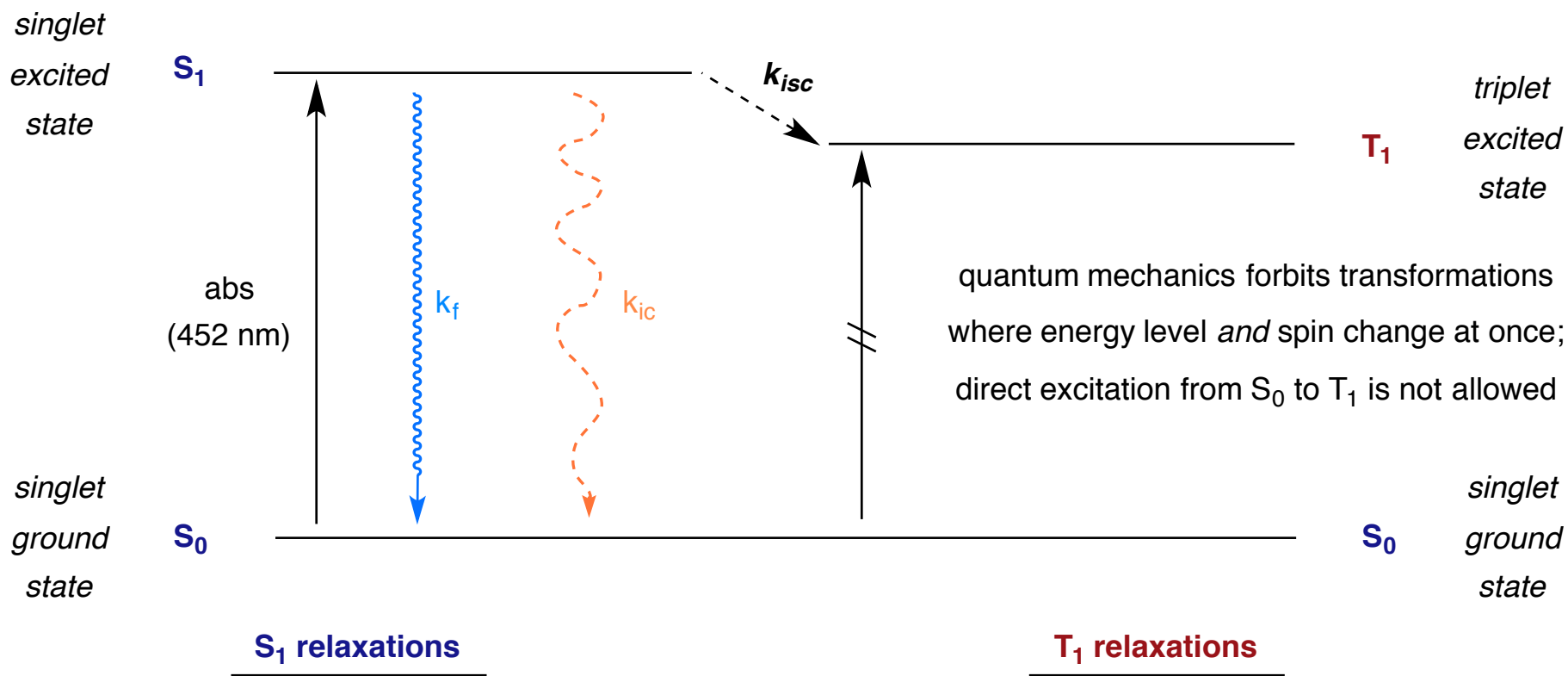
excited state - singlet
" S_1 ", $\tau = 100\text{-}300 \text{ fs}$ (10^{-15})

excited state - triplet
" T_1 ", $\tau = 1100 \text{ ns}$ (10^{-9})

Either Excited State can Relax through a Variety of Pathways

Jablonski diagram highlights enumerates relaxation pathways

Jablonski diagram \equiv similar to an MO diagram, except the levels refer to ground state and excited state energy, rather than HOMO and LUMO energy



k_f \rightarrow fluorescence (452 nm)

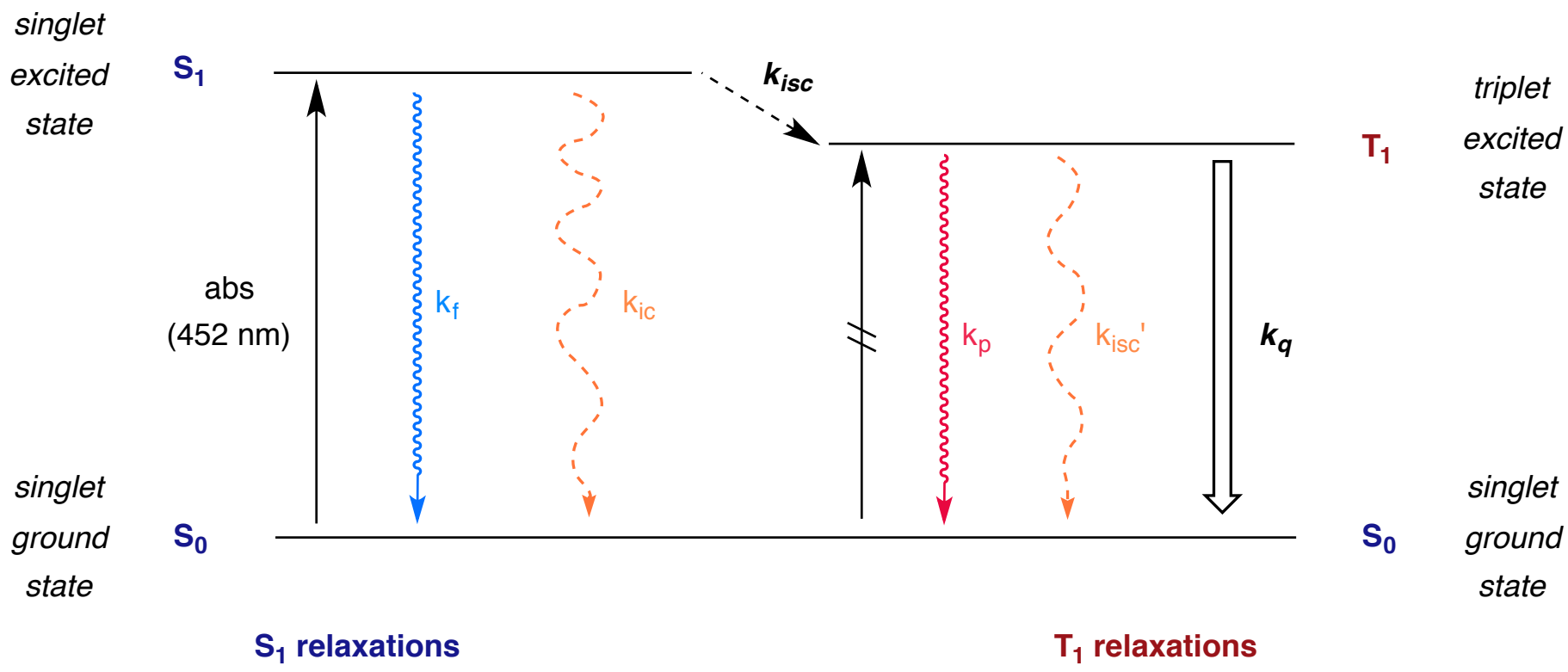
k_{ic} \rightarrow internal conversion

k_{isc} \rightarrow intersystem crossing to T_1

Either Excited State can Relax through a Variety of Pathways

Jablonski diagram highlights enumerates relaxation pathways

Jablonski diagram \equiv similar to an MO diagram, except the levels refer to ground state and excited state energy, rather than HOMO and LUMO energy



k_f \rightarrow fluorescence (452 nm)

k_{ic} \rightarrow internal conversion

k_{isc} \rightarrow intersystem crossing to T_1

k_p \rightarrow phosphorescence (652 nm)

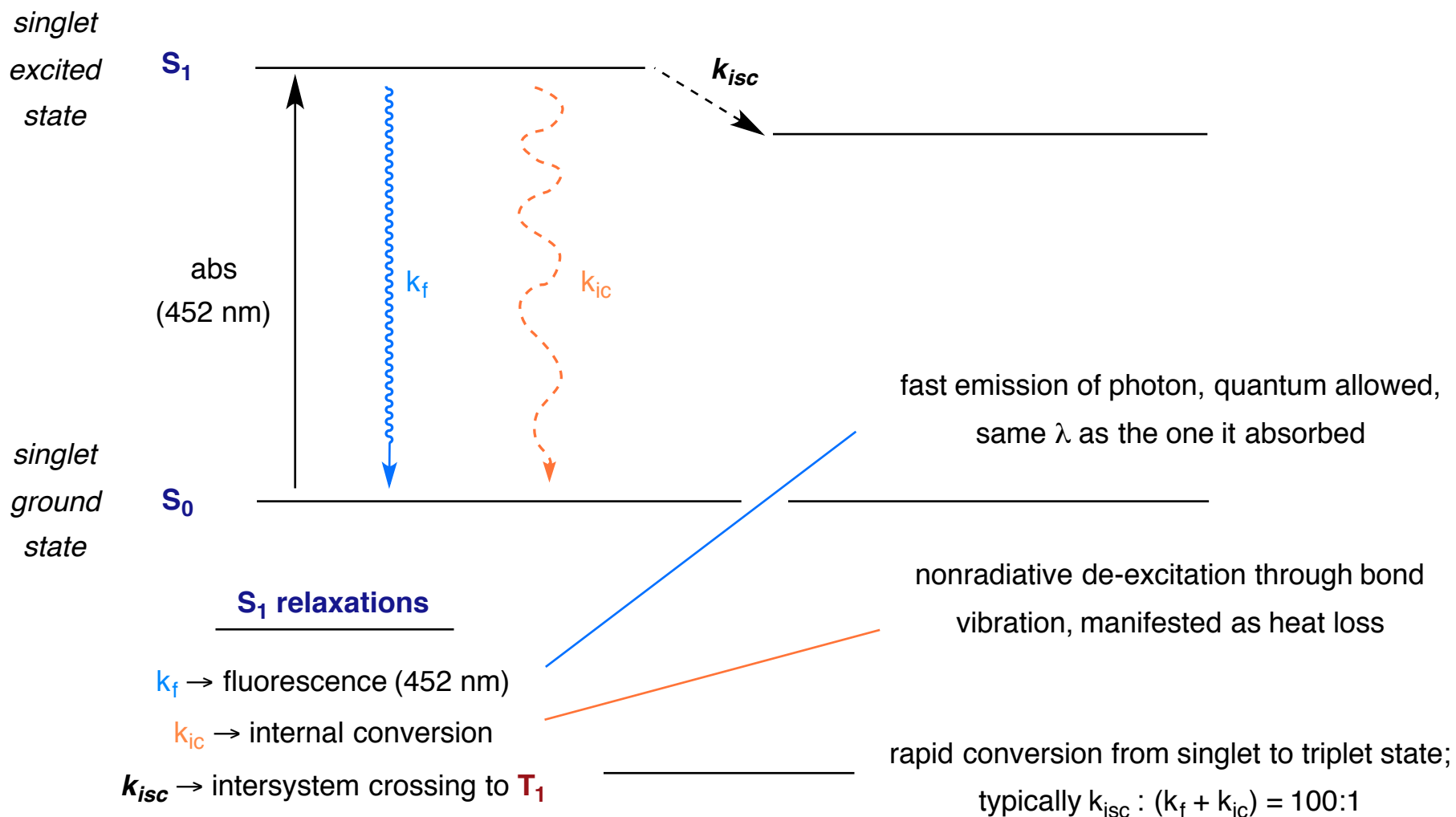
k_{isc}' \rightarrow alternate intersystem crossing

k_q \rightarrow intermolecular quenching

Either Excited State can Relax through a Variety of Pathways

Jablonski diagram highlights enumerates relaxation pathways

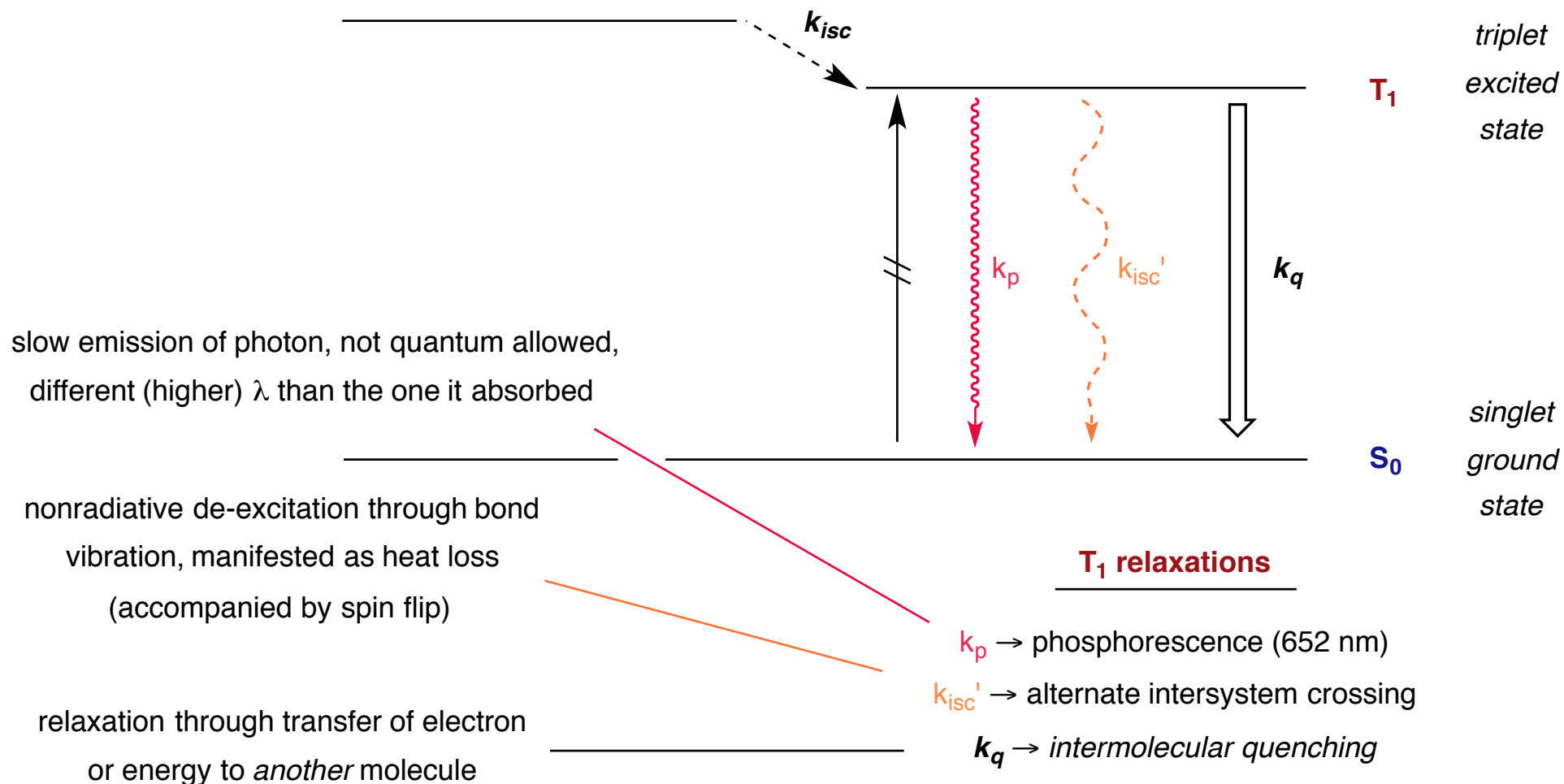
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Either Excited State can Relax through a Variety of Pathways

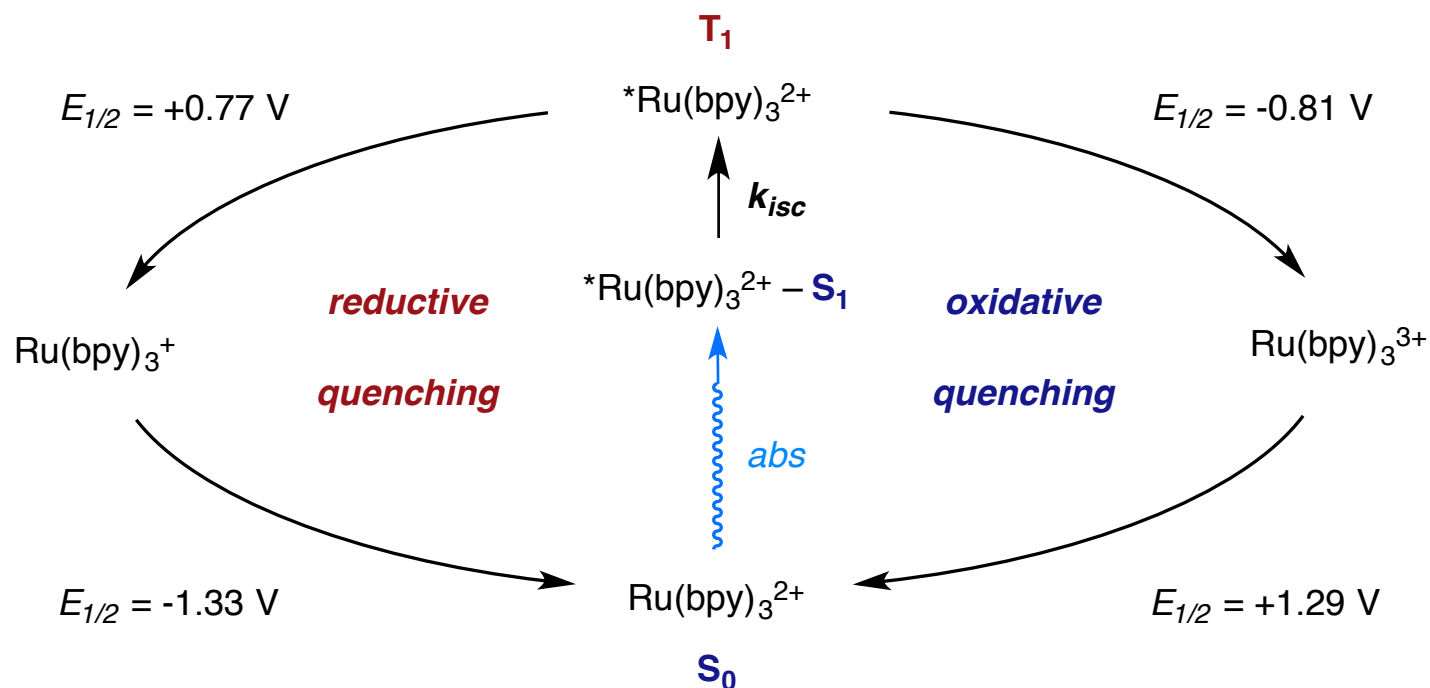
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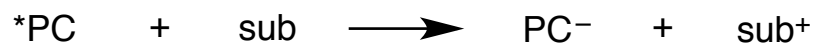


Intermolecular Quenching: Single Electron Transfer

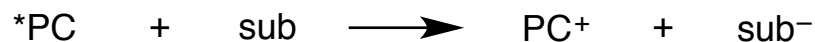
excited photocatalyst has extra energy (1.5 – 3 eV) and can do productive chemistry



in **reductive** quenching,
photocat. **oxidizes** substrate



in **oxidative** quenching,
photocat. **reduces** substrate

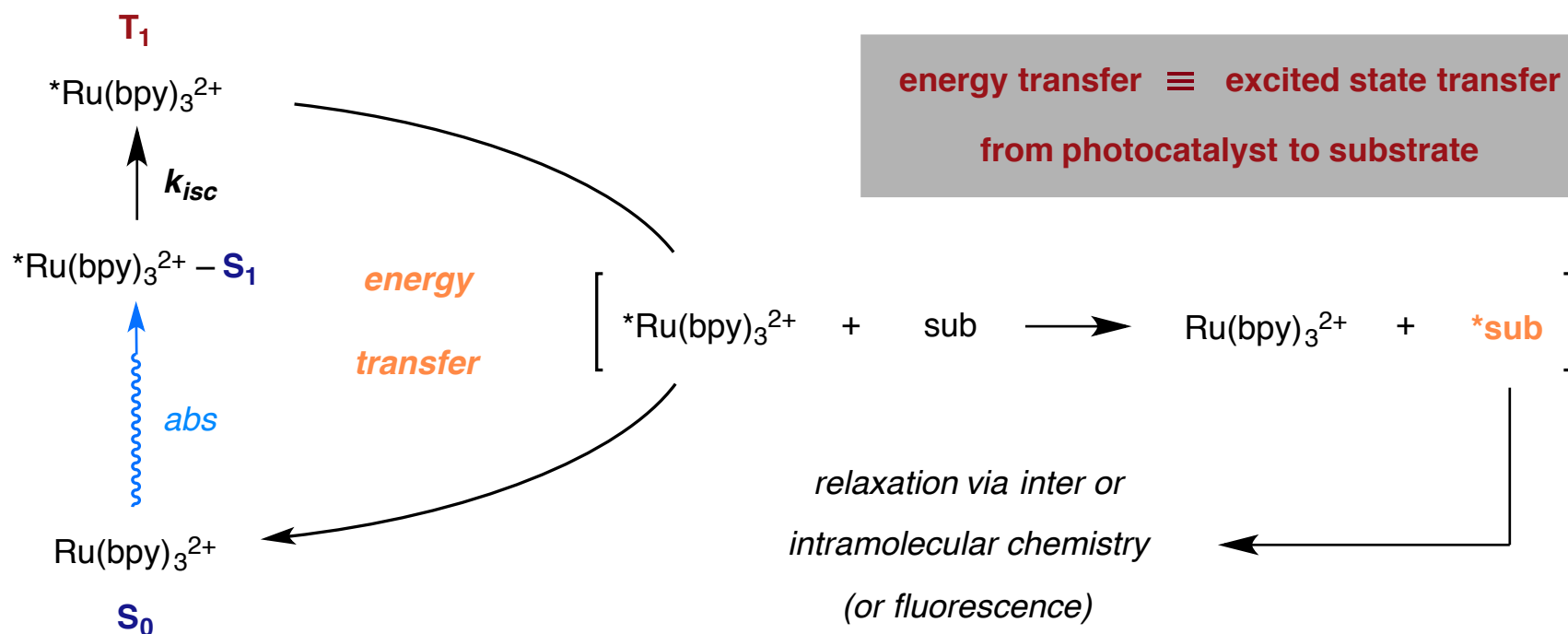


Tucker, J. W.; Stephenson, C. R. J. *J. Org. Chem.* **2012**, *77*, 1617

Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C. *Chem. Rev.* **2013**, *113*, 5322

Intermolecular Quenching: Energy Transfer

excited photocatalyst has extra energy (1.5 – 3 eV) and can do productive chemistry



- energy transfer allows excitation of molecules that do not have favorable redox potentials
- unlike electron transfer, relaxation of T_1 (excited state) to S_0 (ground state) occurs in a single step
- energy transfer can occur via 2 potential mechanisms (Förster transfer or Dexter transfer)

Tucker, J. W.; Stephenson, C. R. J. *J. Org. Chem.* **2012**, *77*, 1617

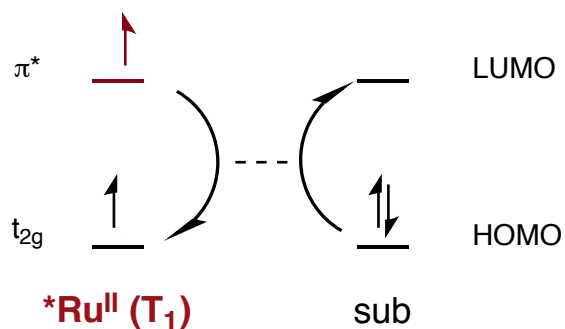
Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C. *Chem. Rev.* **2013**, *113*, 5322

Intermolecular Quenching: Energy Transfer

major differences are how substrates are engaged and distance from which transfer occurs

■ Förster Energy Transfer – vibrational relaxation/collision mechanism

■ occurs through space (1 – 10 nm)



■ T_1 and substrate form "encounter complex"

■ T_1 relaxes through vibrational motion; this energy is funneled into a vibrational mode of the substrate

■ electron is transferred from HOMO to LUMO

Intermolecular Quenching: Energy Transfer

major differences are how substrates are engaged and distance from which transfer occurs

■ Förster Energy Transfer – vibrational relaxation/collision mechanism

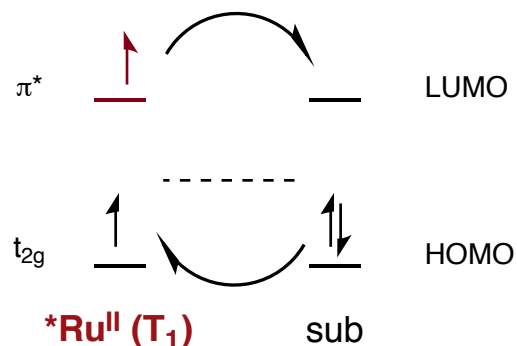
■ occurs through space (1 – 10 nm)



quantum mechanical laws
require overlap of *Ru's
emission spectrum and sub's
ground state UV-Vis spectrum

■ Dexter Energy Transfer – simultaneous, double electron transfer mechanism

■ occurs through physical contact (< 0.01 nm)



■ T₁ and substrate form "encounter complex"

■ electrons are simultaneously from HOMO to t_{2g} and π* to LUMO, generating excited substrate

Intermolecular Quenching: Energy Transfer

major differences are how substrates are engaged and distance from which transfer occurs

■ Förster Energy Transfer – vibrational relaxation/collision mechanism

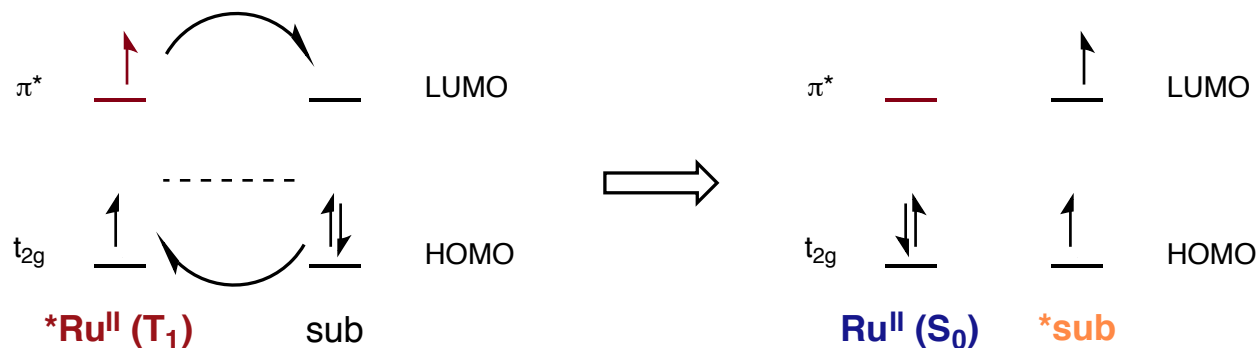
■ occurs through space (1 – 10 nm)



quantum mechanical laws
require overlap of $*Ru$'s
emission spectrum and sub's
ground state UV-Vis spectrum

■ Dexter Energy Transfer – simultaneous, double electron transfer mechanism

■ occurs through physical contact (< 0.01 nm)



subject to standard rules of
electron transfer (ie Marcus
Theory), but no spectral
overlap is required

Scholes, G. D. *Annu. Rev. Phys. Chem.* **2003**, 54, 57

Scandola, F.; Indelli, M. T.; Chiorboli, C.; Bignozzi, C. A. *Top. Curr. Chem.* **1990**, 158, 73

Part 1

**Photocatalyst Details
and Synthesis**

Part 2

**Mechanisms of
Operation**

Part 3

**Relevant Analytical
Methods**

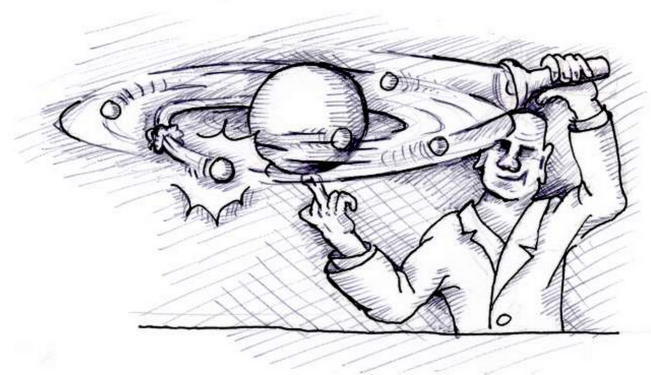
Studying the Photocatalysts through (Mostly) Spectroscopic Techniques

photocatalysts necessitate the use of visible light, making spectroscopy the principle form of analysis

- ground state studies – photocatalyst's physical properties

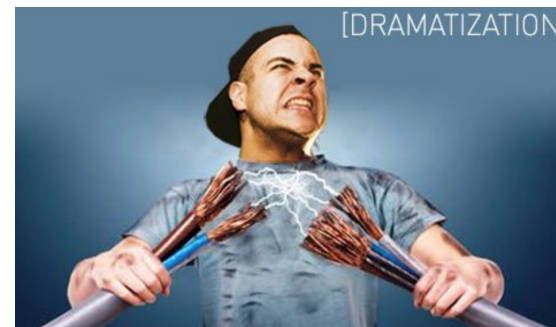
- UV-Vis spectroscopy

- Absorbance (measures HOMO-LUMO gap and other electronic transitions)
 - Emission (measured 90° from light source; measures phosphorescence and therefore energy of the triplet excited state T_1)



- Cyclic Voltammetry

- measures redox potentials of the photocatalyst's ground state
 - with emission data, can be converted to the excited state

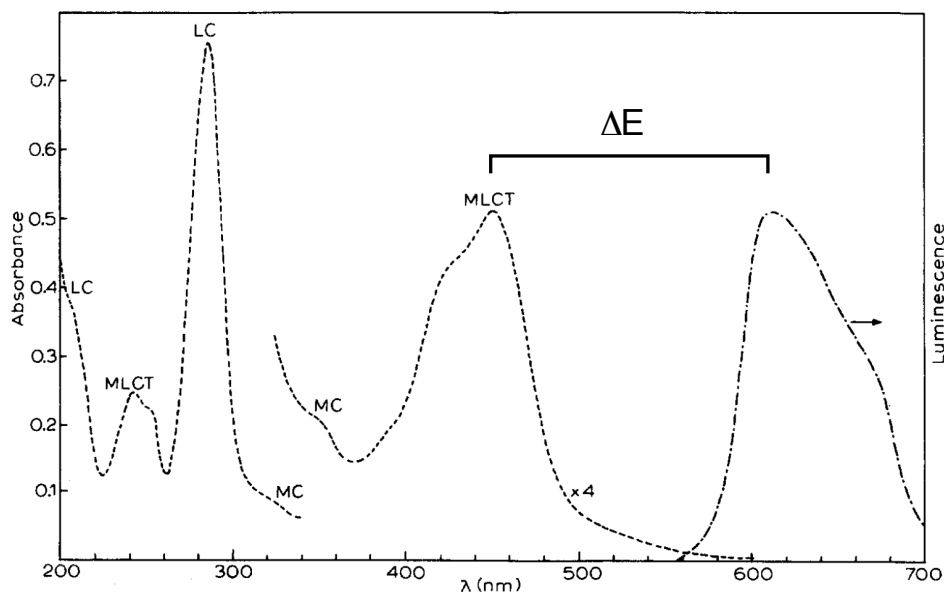


Studying the Photocatalysts through (Mostly) Spectroscopic Techniques

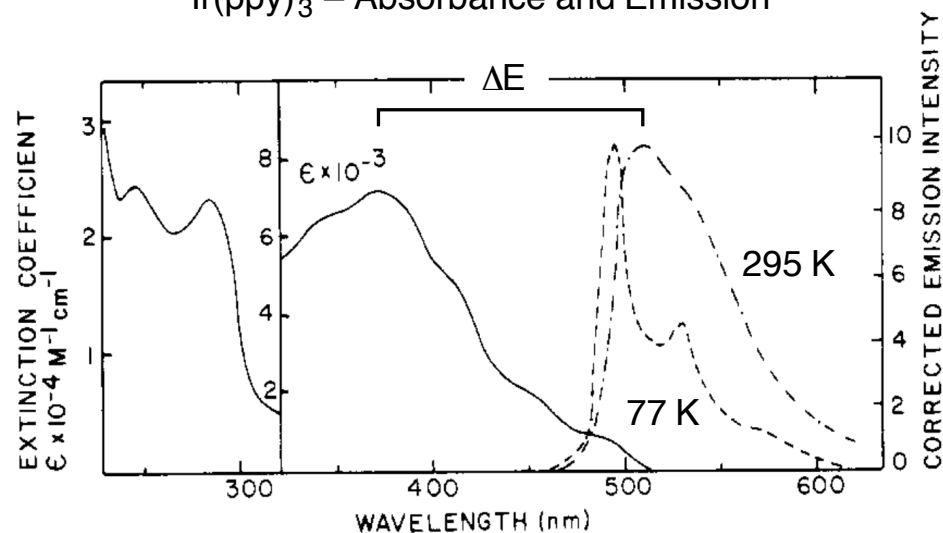
photocatalysts necessitate the use of visible light, making spectroscopy the principle form of analysis

■ UV-Visible absorbance spectra of 2 common photocatalysts

Ru(bpy)₃Cl₂ – Absorbance and Emission



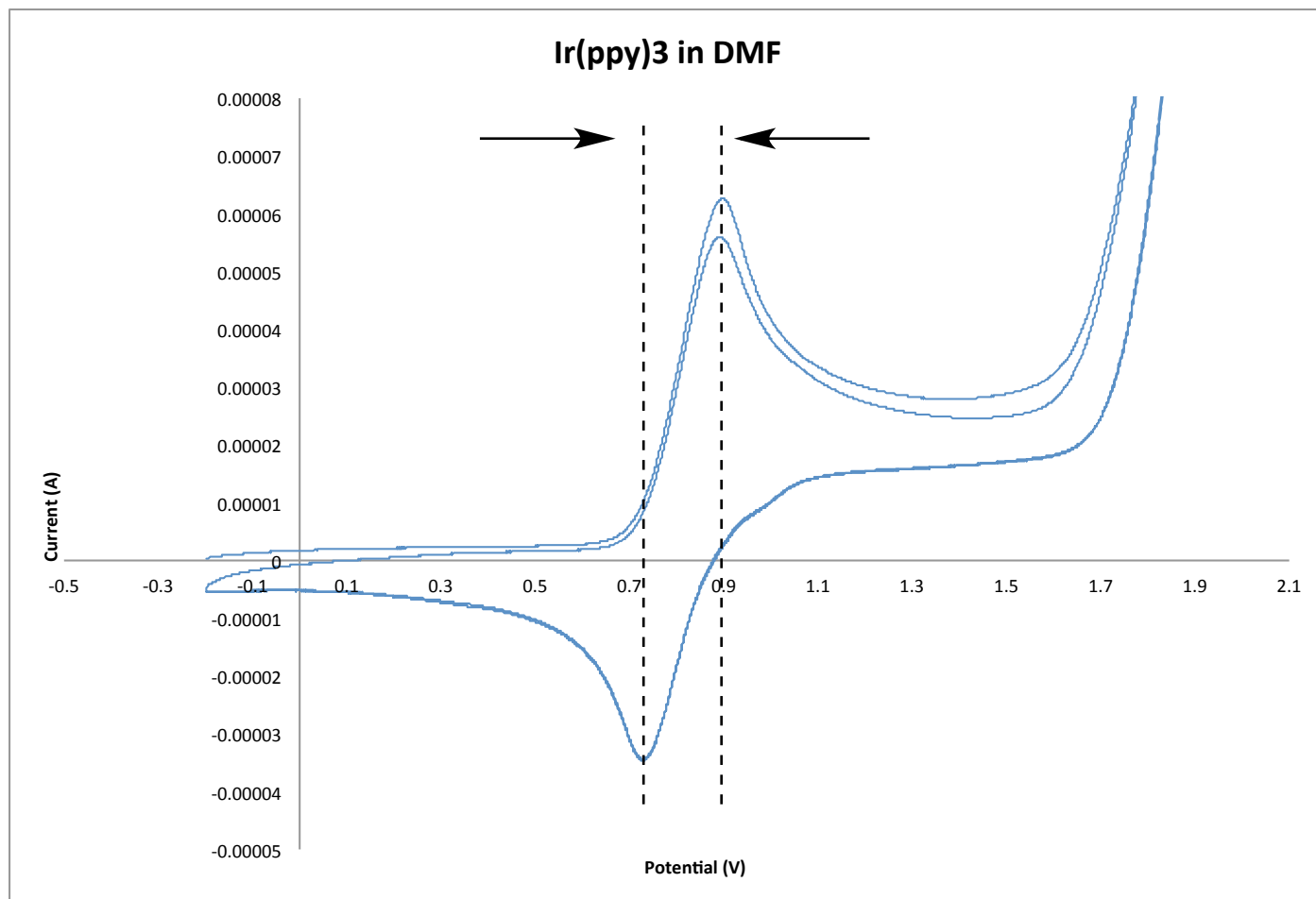
Ir(ppy)₃ – Absorbance and Emission



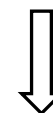
■ note the change in energy (ΔE) from absorbance to emission – stabilization energy from ISC

Studying the Photocatalysts through (Mostly) Spectroscopic Techniques

cyclic voltammetry of Ir(ppy)₃ provides redox values for ground state



$E_{1/2} (M^+/M) \approx$ average
of the two peaks for ground
state potential = +0.81 V



to convert to excited state
reduction, subtract E_{em} (in eV!)
(for oxidation potentials, add E_m)

$\lambda_{em} = 518 \text{ nm}; E_{em} = 2.44 \text{ eV}$

$E_{1/2} (M^+/*M) = -1.58 \text{ V}$

strong reductants have $E_{1/2} (M^+/*M) < -1.5$, strong oxidants have $E_{1/2} (*M/M^-) > +1.2$

Tucker, J. W.; Stephenson, C. R. J. *J. Org. Chem.* **2012**, *77*, 1617

Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C. *Chem. Rev.* **2013**, *113*, 5322

Studying the Photocatalysts through (Mostly) Spectroscopic Techniques

photocatalysts necessitate the use of visible light, making spectroscopy the principle form of analysis

- excited state studies – what the photocatalyst is reacting with, and how

■ Stern-Volmer Analysis

- measures quantity of emitted photons in presence and absence of a possible quencher
- determines what the excited photocatalyst is reacting with, and to what degree



■ Transient Absorption Spectroscopy

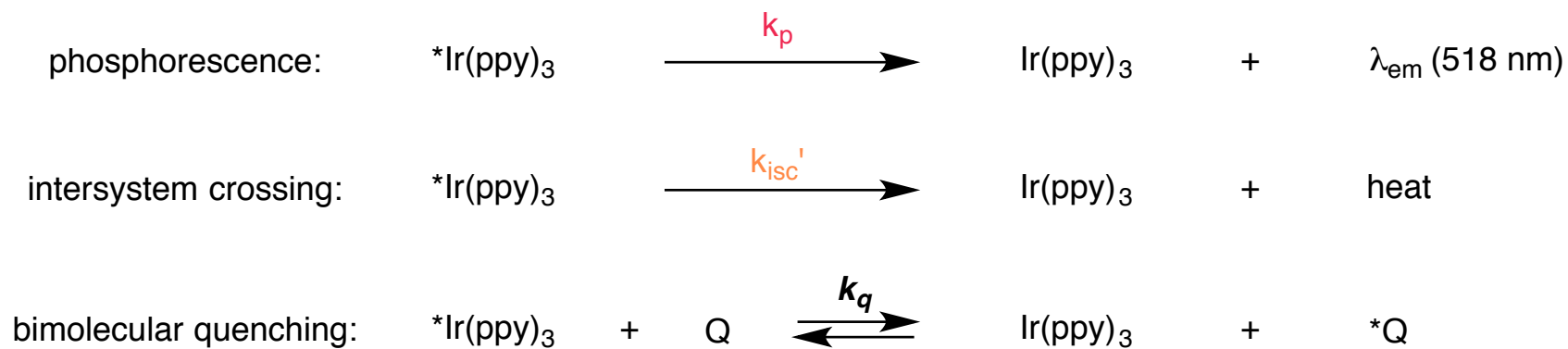
- uses time-resolved laser pulses to measure the lifetime of each unpaired electron in T_1 excited state
- in the presence of a quencher, electron transfer can be distinguished from energy transfer



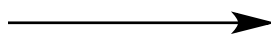
Studying the Photocatalysts through (Mostly) Spectroscopic Techniques

Stern-Volmer phosphorescence quenching identifies quencher

- because ISC is so favorable after the MLCT, there are 3 major decay pathways (from Jablonski diagram)



k_p and k_{isc}' represent
unimolecular reactions



varying $[Q]$ does not
affect their rate laws

however:

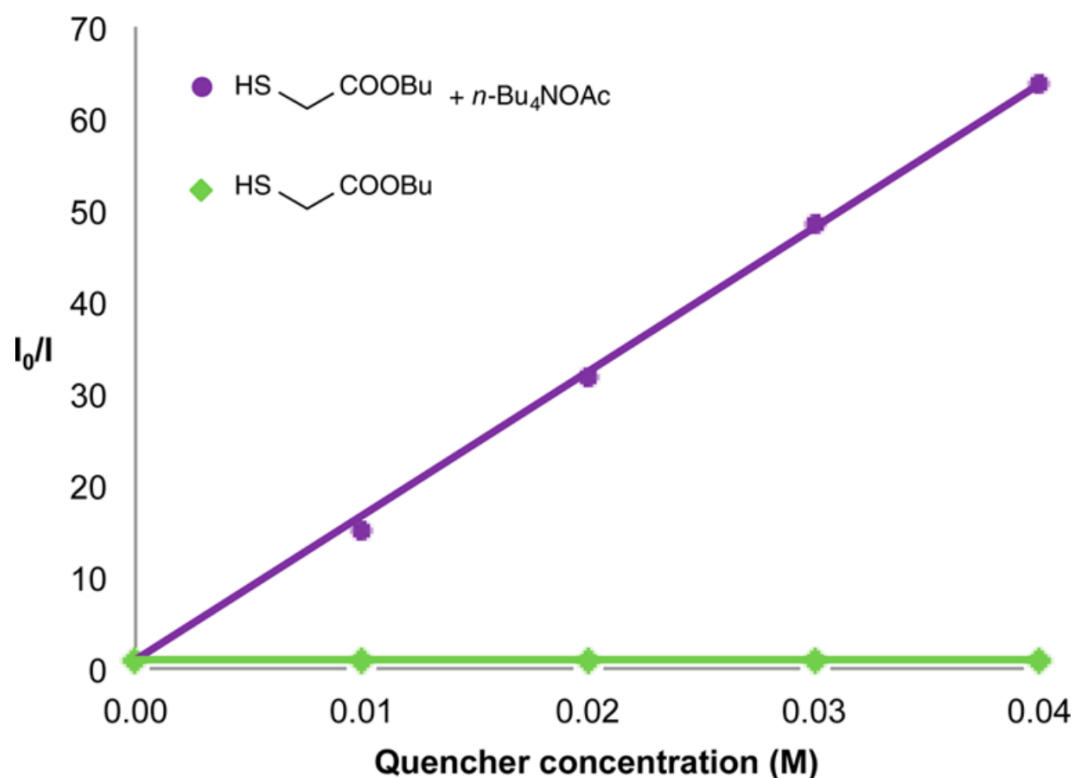
increasing $[Q]$ decreases $[^*Ir(ppy)_3]$
by Le Châtelier's principle



**increasing $[Q]$ decreases
intensity I of phosphorescence**

Studying the Photocatalysts through (Mostly) Spectroscopic Techniques

Stern-Volmer phosphorescence quenching identifies quencher



I_0 ≡ phosphorescence intensity in the absence of quencher

I ≡ phosphorescence intensity in the *presence* of quencher

slope of I_0/I vs. $[Q]$ is proportional to k_q

◆ protonated thiol shows no quenching

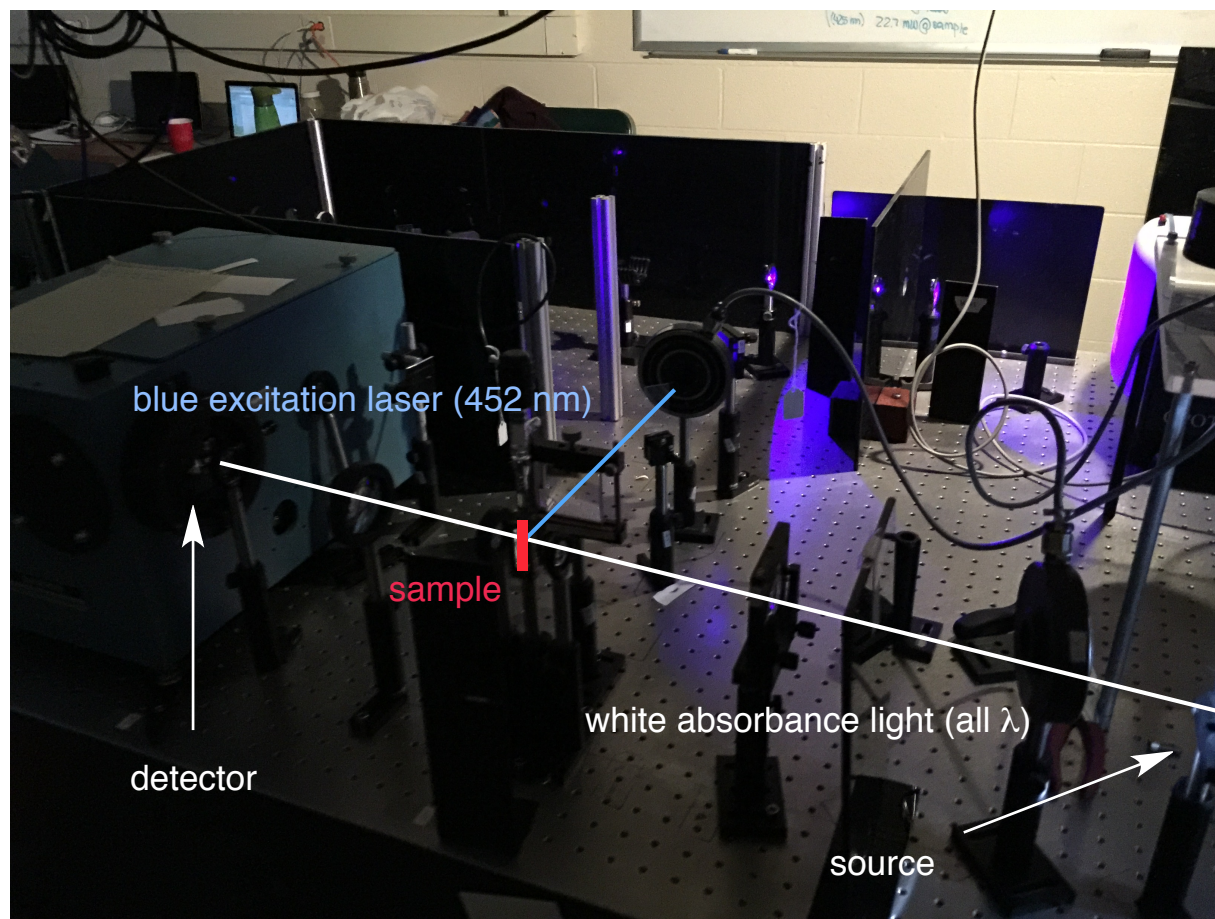
● deprotonated thiol shows clear, linear quenching

Stern-Volmer analysis makes quencher identification trivial

Studying the Photocatalysts through (Mostly) Spectroscopic Techniques

Transient Absorption Spectroscopy primer

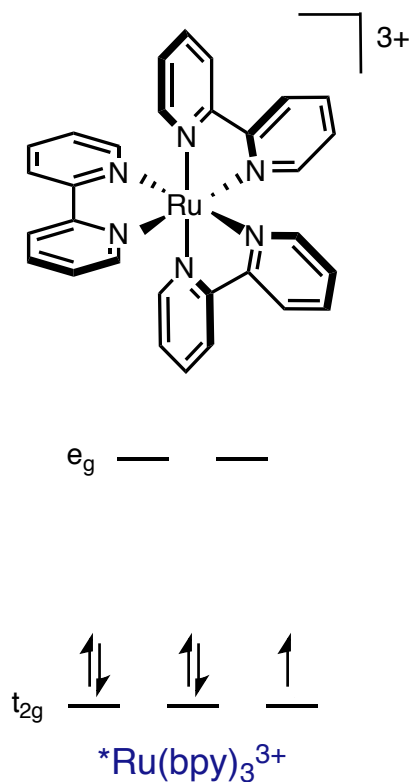
- 2 light sources are used:
 - excitation laser – tuned to MLCT absorption band
 - white absorption light – full visible spectrum
- laser excites sample with a 10 ns pulse; absorption at chosen λ every 10 ns thereafter
- first – record "difference spectra" to identify the excited photocatalyst's (T_1) signature absorptions



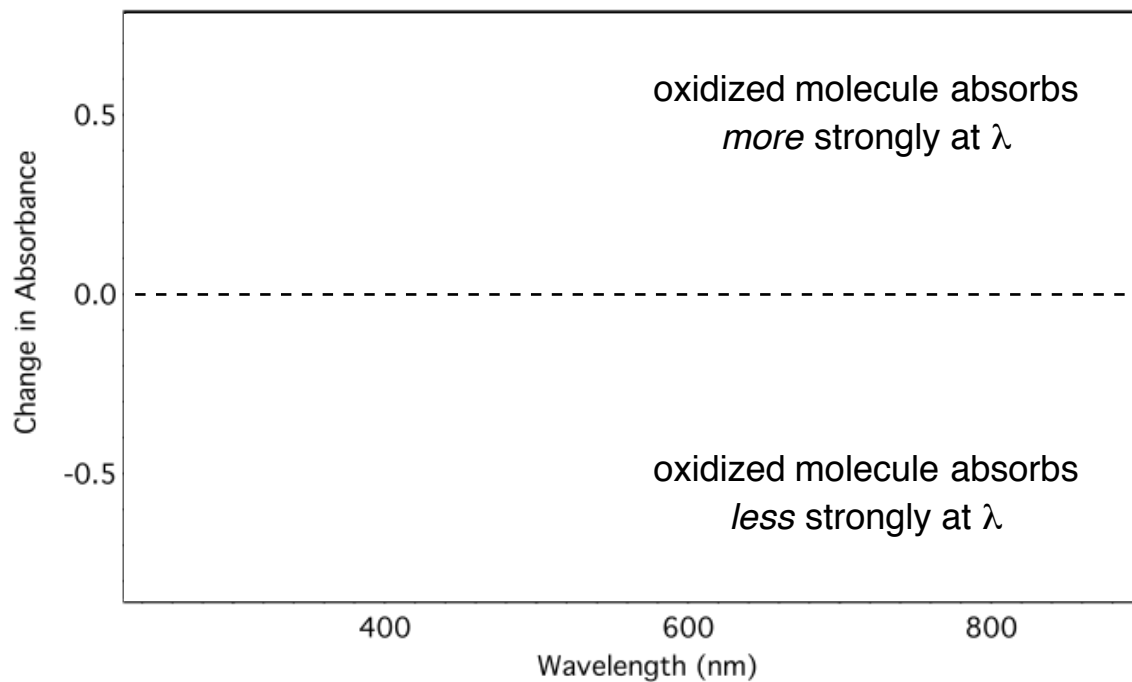
Studying the Photocatalysts through (Mostly) Spectroscopic Techniques

difference spectra (aka spectroelectrochemistry) shows how oxidation or reduction changes absorbances

- a voltage is applied to the photocatalyst, recording UV-Vis spectra along the way
- spectrum of the parent photocatalyst is subtracted out



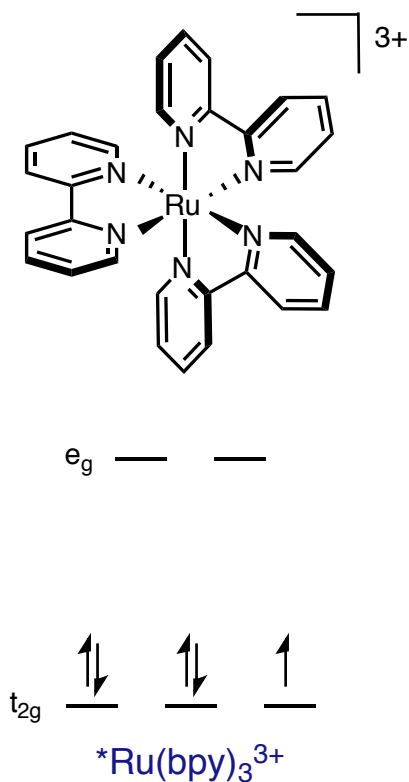
Oxidative Difference Spectrum



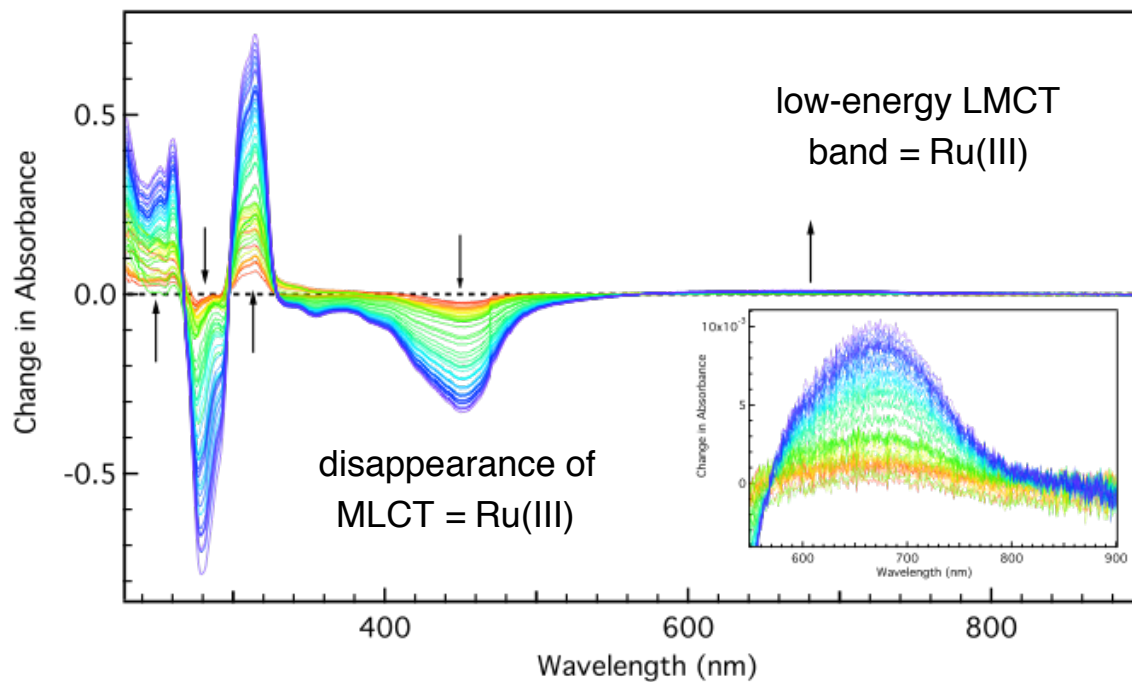
Studying the Photocatalysts through (Mostly) Spectroscopic Techniques

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Oxidative Difference Spectrum

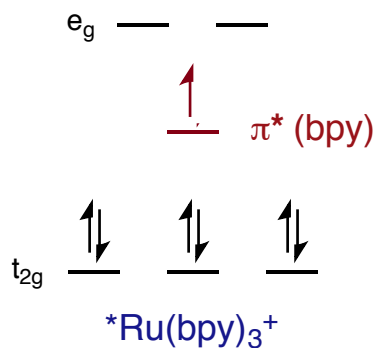
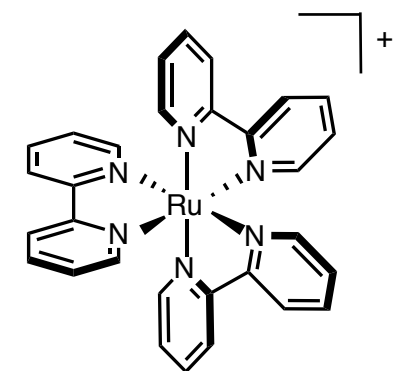


result is spectrum of a molecule with singly occupied HOMO (SHOMO) in t_{2g} orbital

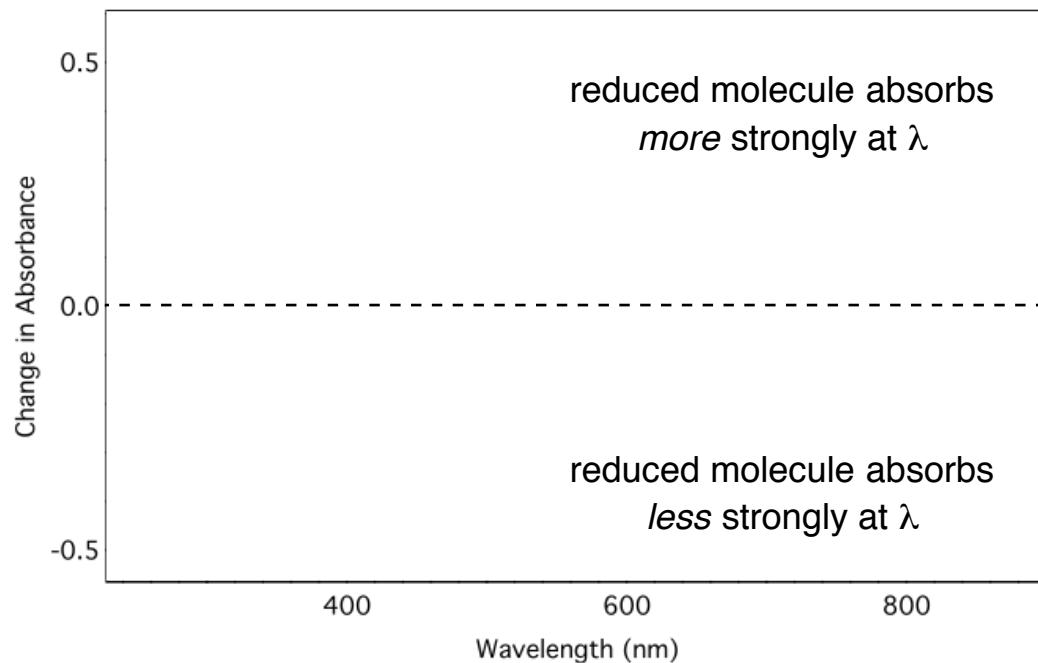
Studying the Photocatalysts through (Mostly) Spectroscopic Techniques

difference spectra (aka spectroelectrochemistry) shows how oxidation or reduction changes absorbances

- a voltage is applied to the photocatalyst, recording UV-Vis spectra along the way
- spectrum of the parent photocatalyst is subtracted out



Reductive Difference Spectrum

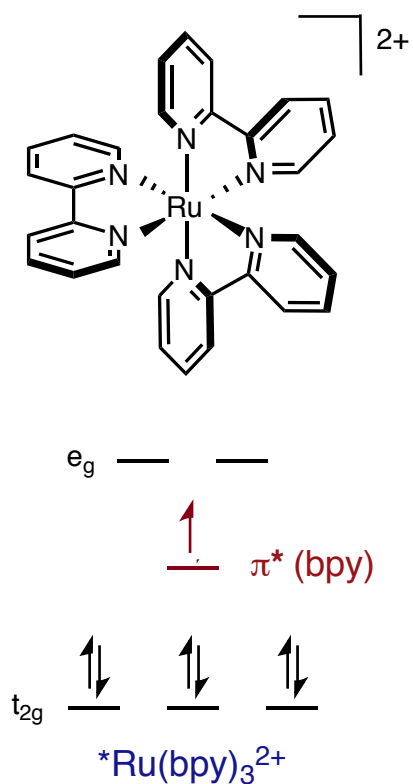


result is spectrum of a molecule with singly occupied LUMO (SLUMO) in π* orbital

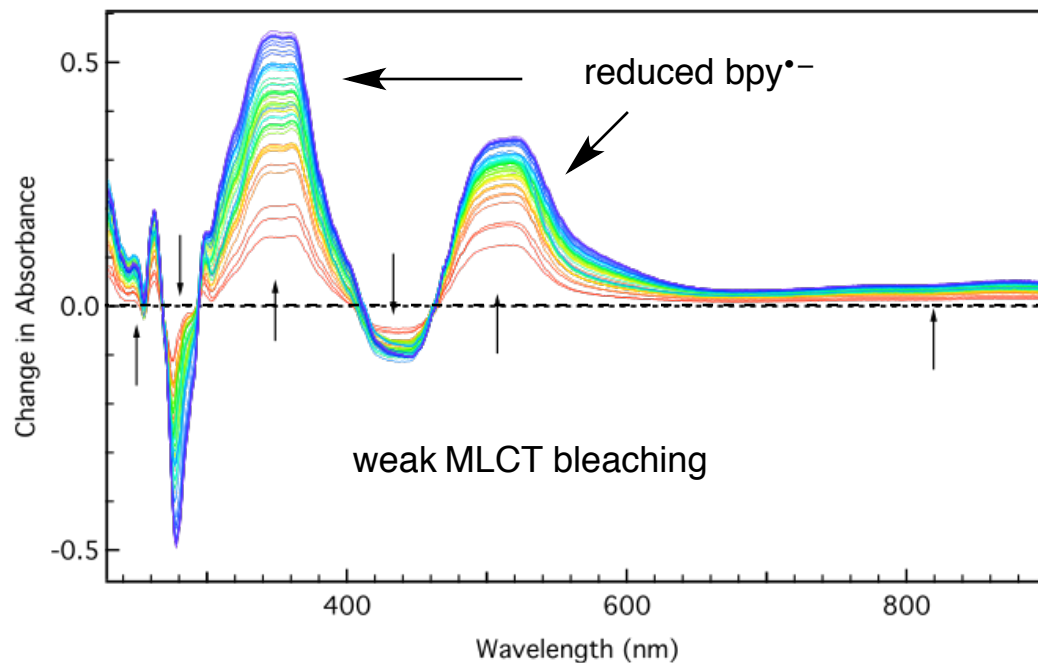
Studying the Photocatalysts through (Mostly) Spectroscopic Techniques

difference spectra (aka spectroelectrochemistry) shows how oxidation or reduction changes absorbances

- a voltage is applied to the photocatalyst, recording UV-Vis spectra along the way
- spectrum of the parent photocatalyst is subtracted out



Reductive Difference Spectrum

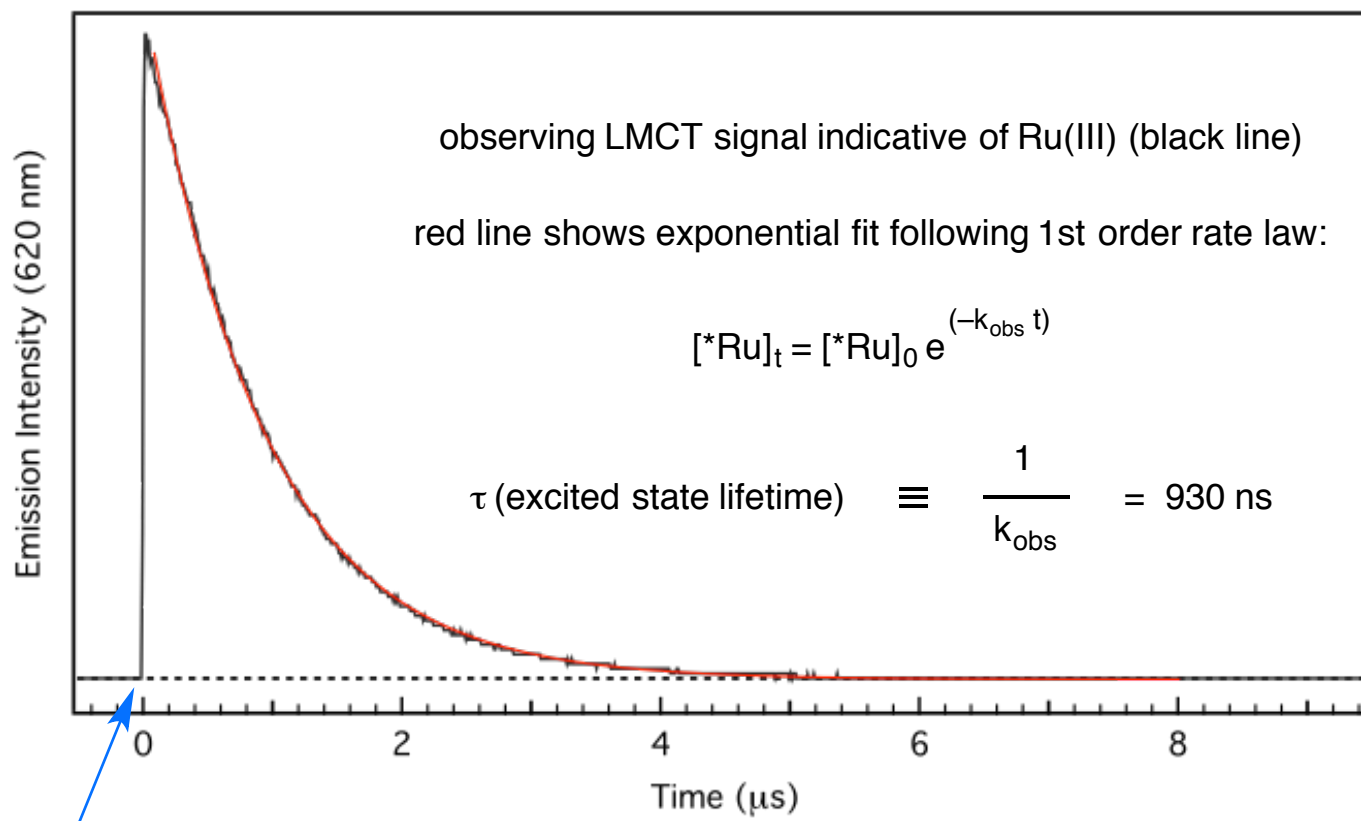


result is spectrum of a molecule with singly occupied LUMO (SLUMO) in π^* orbital

Studying the Photocatalysts through (Mostly) Spectroscopic Techniques

profile of a transient absorption (TA) spectrum

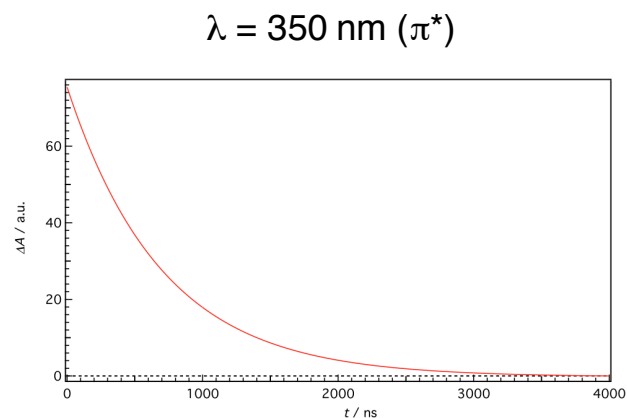
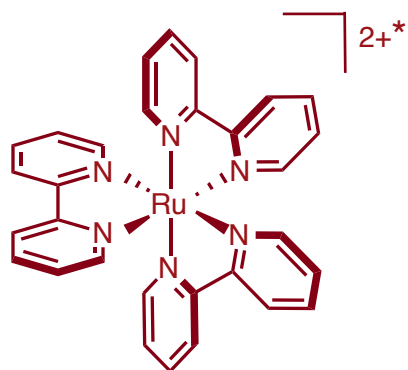
fast laser pulse excites the photocatalyst in absence of quencher, exponential (1st order) decay is observed



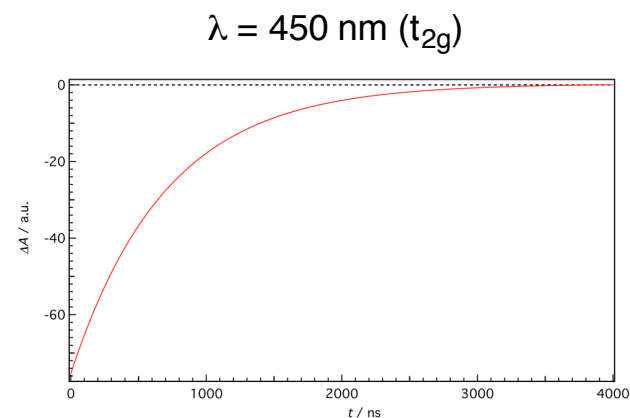
excitation pulse (10 ns)

Transient Absorption Spectroscopy: the Experiment

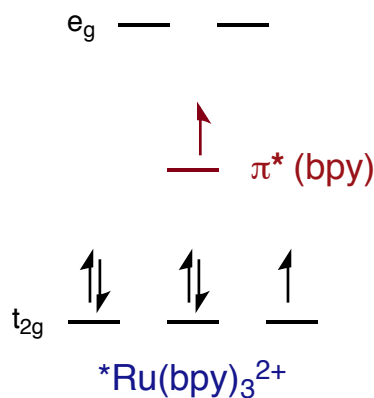
four limiting scenarios: no quenching, energy transfer, oxidative/reductive electron transfer



A) No quencher present



B) No quencher present

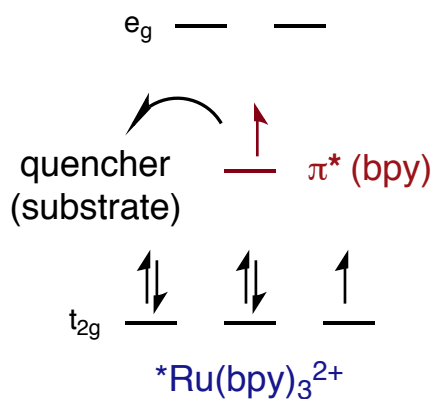
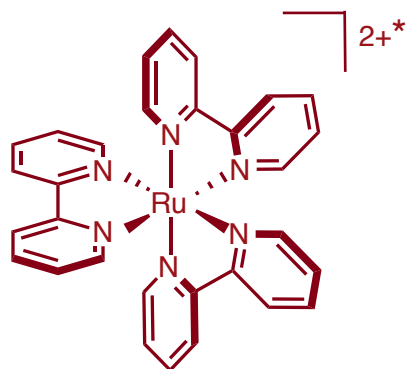


- without quencher, both signals are quenched at the same rate
- both signals return to 0 after quenching

excited state - triplet
"T₁", $\tau = 1100 \text{ ns } (10^{-9})$

Transient Absorption Spectroscopy: the Experiment

four limiting scenarios: no quenching, energy transfer, oxidative/reductive electron transfer

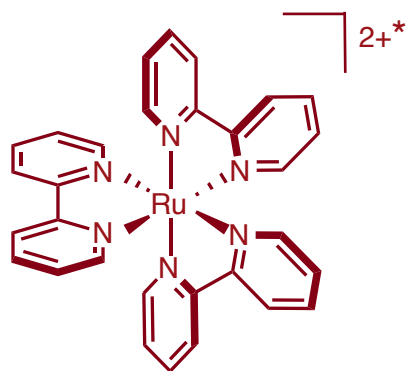


- now consider oxidative quenching (photocat. does reduction)
- remember – electron transfer is only 10-20% efficient

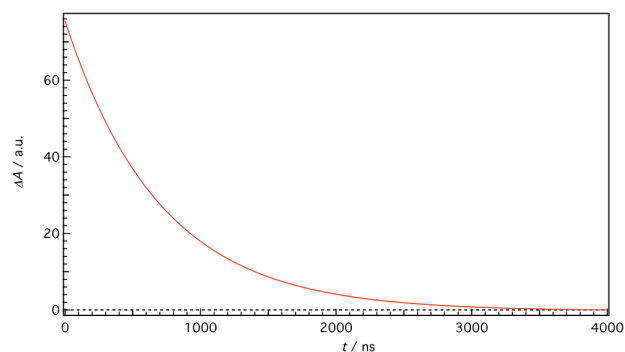
excited state - triplet
"T₁", $\tau = 1100 \text{ ns } (10^{-9})$

Transient Absorption Spectroscopy: the Experiment

four limiting scenarios: no quenching, energy transfer, oxidative/reductive electron transfer

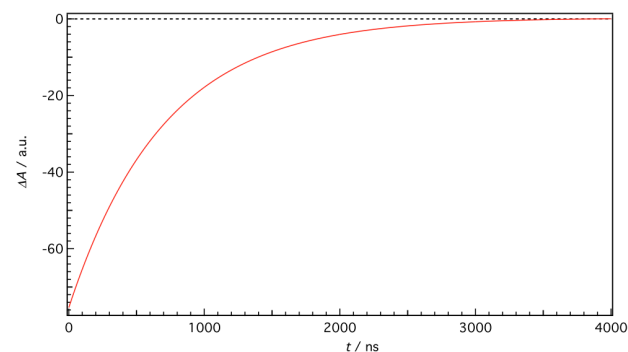


$\lambda = 350 \text{ nm } (\pi^*)$

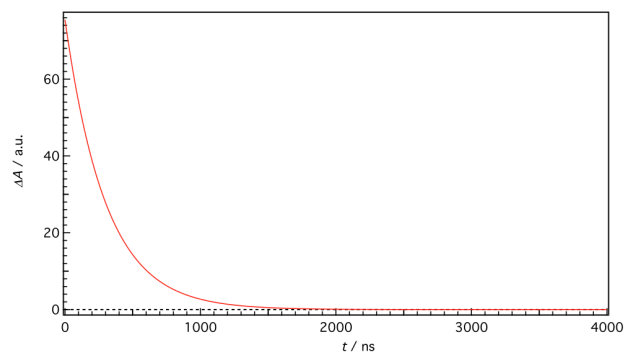
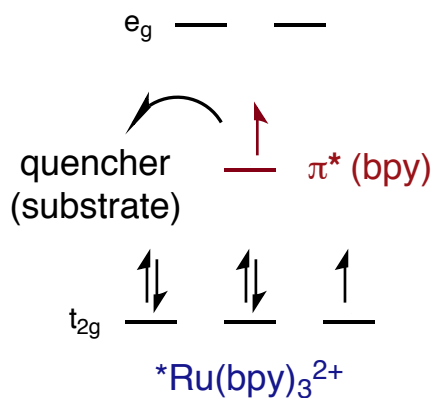


A) No quencher present

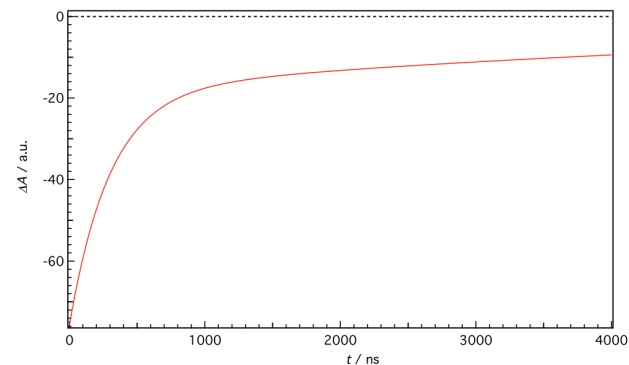
$\lambda = 450 \text{ nm } (t_{2g})$



B) No quencher present



Oxidative Quenching; $\lambda_{\text{probe}} = 350 \text{ nm}$



Oxidative Quenching; $\lambda_{\text{probe}} = 450 \text{ nm}$

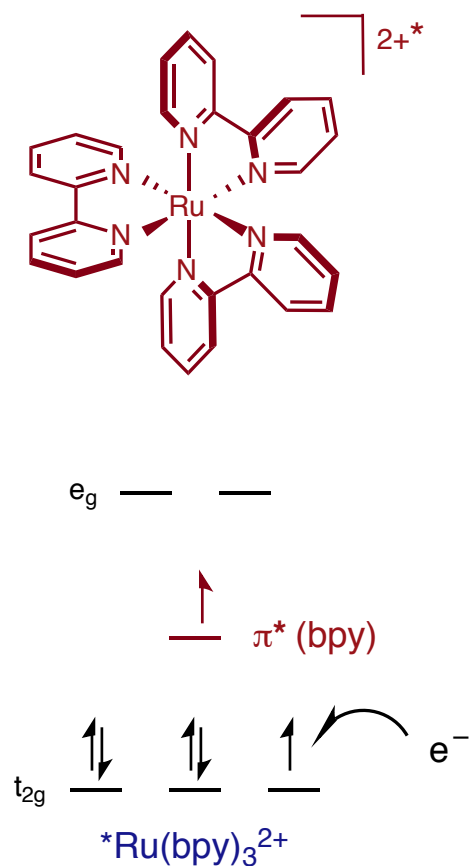
excited state - triplet

" T_1 ", $\tau = 1100 \text{ ns } (10^{-9})$

- fast quenching of π^* signal is observed, baseline returns to 0
- quenching of t_{2g} is accelerated, but 10-20% signal remains (π^* electron gone)

Transient Absorption Spectroscopy: the Experiment

four limiting scenarios: no quenching, energy transfer, oxidative/reductive electron transfer

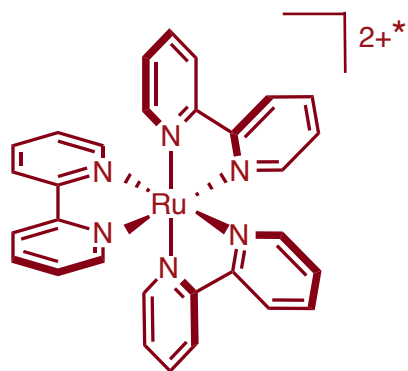


- now consider reductive quenching (photocat. does oxidation)
- remember – electron transfer is only 10-20% efficient

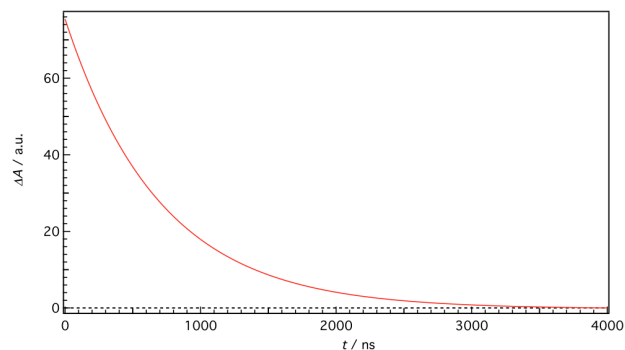
excited state - triplet
"T₁", $\tau = 1100 \text{ ns } (10^{-9})$

Transient Absorption Spectroscopy: the Experiment

four limiting scenarios: no quenching, energy transfer, oxidative/reductive electron transfer

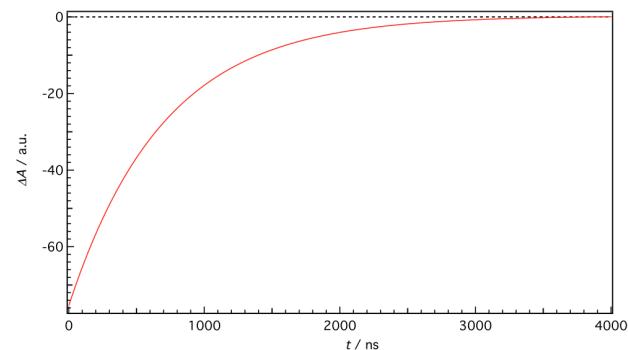


$\lambda = 350 \text{ nm } (\pi^*)$

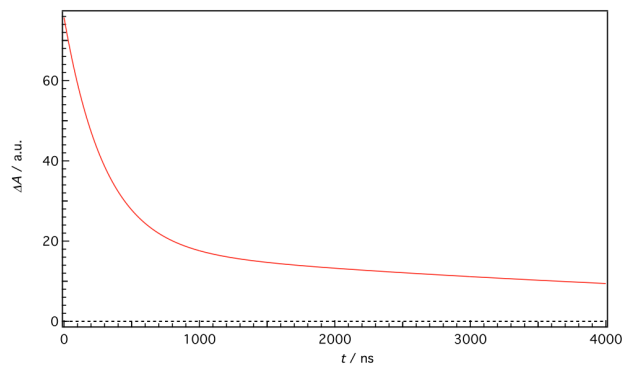
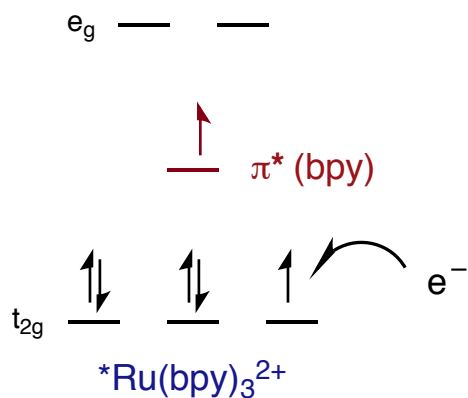


A) No quencher present

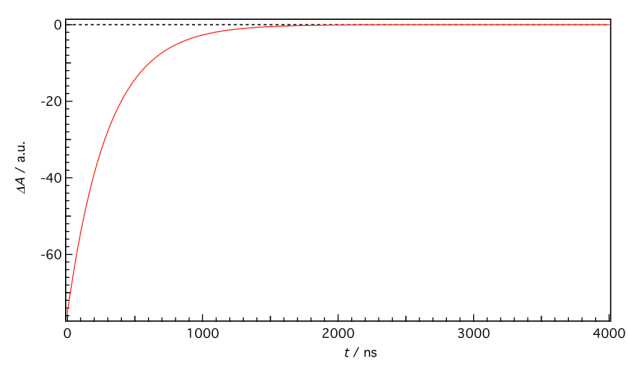
$\lambda = 450 \text{ nm } (t_{2g})$



B) No quencher present



Reductive Quenching; $\lambda_{\text{probe}} = 350 \text{ nm}$



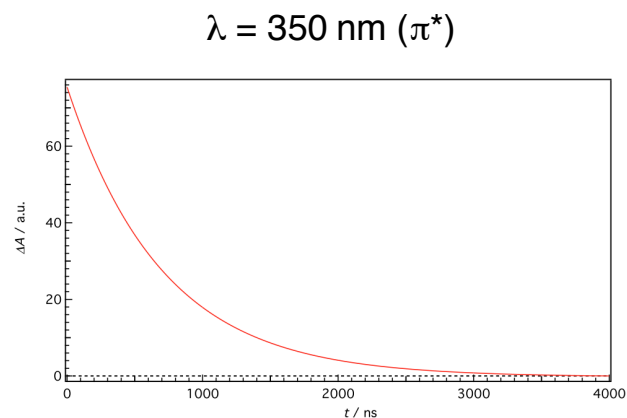
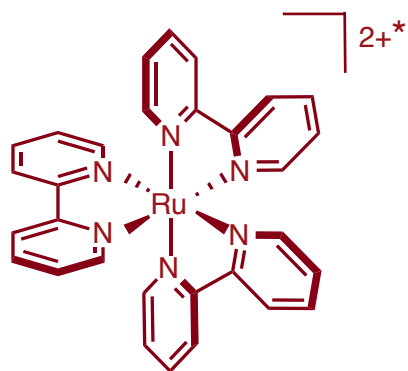
Reductive Quenching; $\lambda_{\text{probe}} = 450 \text{ nm}$

excited state - triplet
"T₁", $\tau = 1100 \text{ ns } (10^{-9})$

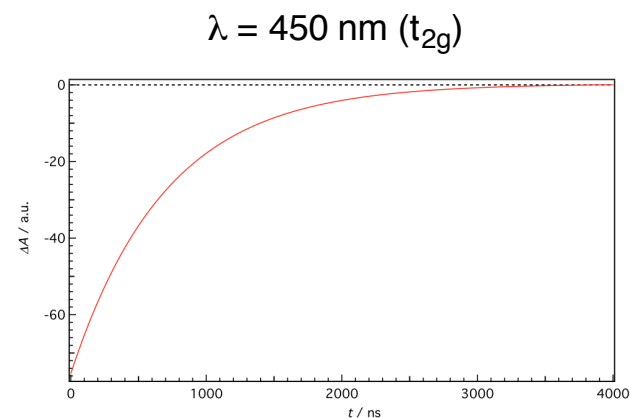
- fast quenching of t_{2g} signal is observed, baseline returns to 0
- quenching of π^* is accelerated, but signal cannot return to 0 (t_{2g} hole filled)

Transient Absorption Spectroscopy: the Experiment

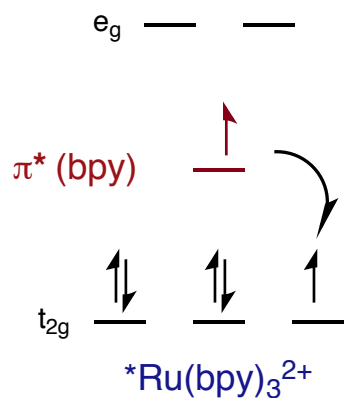
four limiting scenarios: no quenching, energy transfer, oxidative/reductive electron transfer



A) No quencher present



B) No quencher present



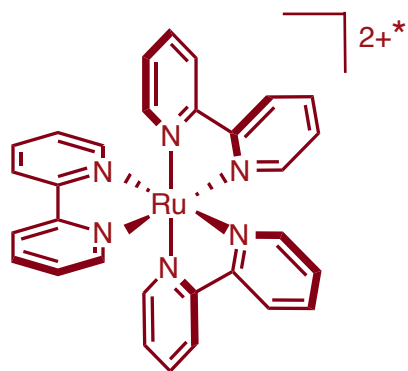
■ finally, consider energy transfer (via either mechanism)

excited state - triplet

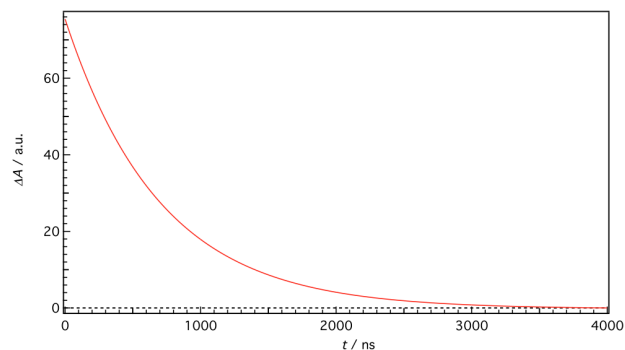
" T_1 ", $\tau = 1100 \text{ ns } (10^{-9})$

Transient Absorption Spectroscopy: the Experiment

four limiting scenarios: no quenching, energy transfer, oxidative/reductive electron transfer

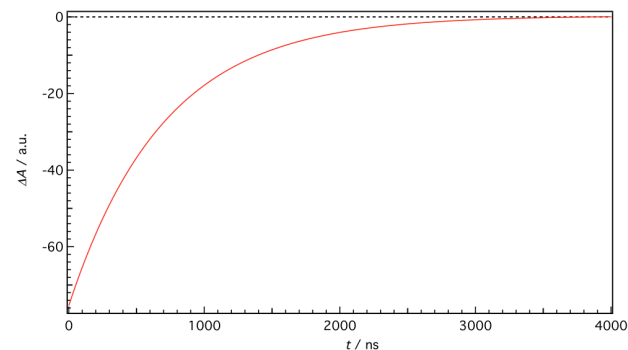


$\lambda = 350 \text{ nm } (\pi^*)$

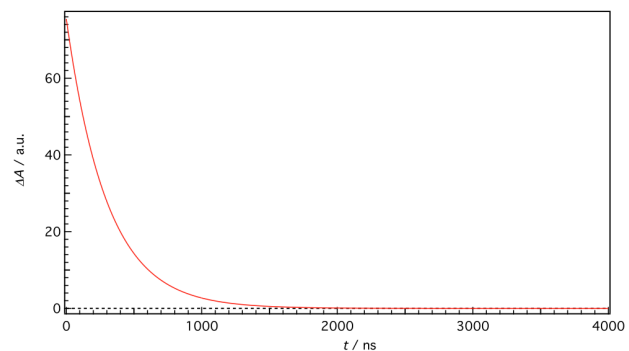
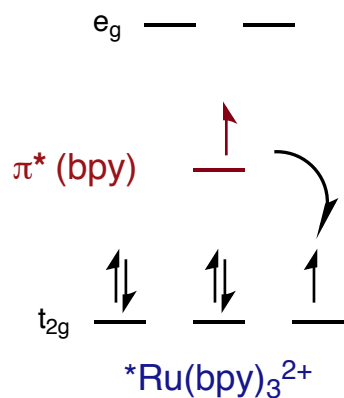


A) No quencher present

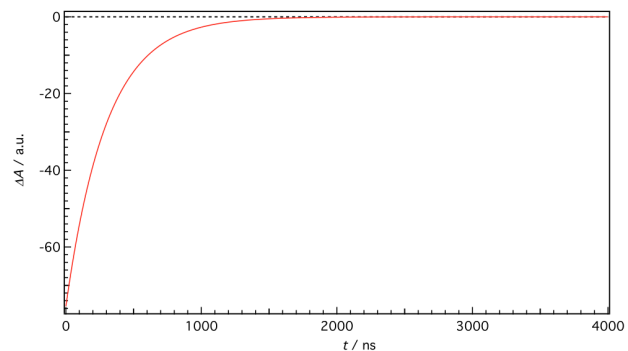
$\lambda = 450 \text{ nm } (t_{2g})$



B) No quencher present



Energy Transfer



Energy Transfer

excited state - triplet

" T_1 ", $\tau = 1100 \text{ ns } (10^{-9})$

■ fast quenching of t_{2g} and π^* , both baselines return to 0

■ signals decaying at the same rate is highly indicative of energy transfer