BEHIND THE SCENES
with Transition Metal Photocatalysts

Eric R. Welin

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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

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Common Transition Metal Photocatalysts: the "Big 4"

For very useful reviews see:

Common Transition Metal Photocatalysts: the "Big 4"

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:

**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)$_2^+$*

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Photocatalyst Comparison: Choice of Metal Center

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

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:

  $E(M^+/M^-) = +0.77\, \text{V}$
  
  $E(M^+/M^-) = +1.81\, \text{V}$

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

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


Photocatalyst Comparison: Choice of Metal Center

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

- 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, $\Phi$)

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

\[
\text{Ir(ppy)}_3 \quad \text{Ir(ppy)}_2\text{(dtbbpy)}^{2+} \quad \text{Ir[dF(CF}_3\text{ppy)}_2\text{(dtbbpy)}^+}
\]

\[\text{strongly oxidizing} \quad \text{strongly reducing}\]

Ir photocatalysts are highly versatile and predictable  →  allows rational catalyst design
Photocatalyst Synthesis: Ruthenium

RuCl₃•xH₂O or Ru(DMSO)₆Cl₂ → excess bpy
100 °C

both salts are active catalysts
PF₆ shows greater solubility and stability towards deactivation

Photocatalyst Synthesis: Iridium Homoleptic

Ir(acac)$_3$ (excess ppy) $\rightarrow$ fac-Ir(ppy)$_3$

220 °C

fac-Ir(ppy)$_3$

mer-Ir(ppy)$_3$

140 °C

kinetic product
not light stable

fac isomer favored by $\sim$7 kcal/mol due to trans effect

Thompson, M. E. et al. J. Am. Chem. Soc. 2003, 125, 7377
Photocatalyst Synthesis: Iridium Heteroleptic

\[ \text{IrCl}_3 \xrightarrow{\text{excess ppy}} \text{IrCl}_3 \cdot \text{Ir(ppy)}_2(\text{dtbbpy}) \cdot \text{PF}_6 \xrightarrow{\text{120 °C}} \text{IrCl}_3 \cdot \text{Ir(ppy)}_2(\text{dtbbpy}) \cdot \text{PF}_6 \]

\[ \text{lower temperature yields exclusively dimer} \]

1.) excess dtbbpy, 200 °C

2.) NH\(_4\)PF\(_6\), rt

1.) AgPF\(_6\), MeCN, rt

2.) excess dtbbpy, rt

\[ \text{Ir(ppy)}_2(\text{dtbbpy})PF_6 \]

AgPF\(_6\) cracks dimer; increases yields (good for small scale)


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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 (i.e., no electrons in $e_g$ orbital)

This configuration is called "substitutionally inert" because $e_g$ is antibonding.

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

- The bigger $\Delta_0$, the more LFSE and the more overall stability
- Ir$^{3+}$ photocats. are more stable than Ru$^{2+}$

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

| the excited electron goes into LUMO (ligand $\pi^*$) – 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!) |

**Ground state - singlet**

"$S_0$"

**Excited state - singlet**

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

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Photon Absorption and Generation of Excited State

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

\[ \text{ground state - singlet } \quad "S_0" \]

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

\[ \text{excited state - triplet } \quad "T_1", \quad \tau = 1100 \text{ ns} \quad (10^{-9}) \]
Either Excited State can Relax through a Variety of Pathways

Jablonski diagram highlights ennumerates 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

singlet excited state

$S_0$ $\rightarrow$ $S_1$

abs (452 nm)

$S_1$ relaxations

$k_f \rightarrow$ fluorescence (452 nm)

$k_{ic} \rightarrow$ internal conversion

$k_{isc} \rightarrow$ intersystem crossing to $T_1$

$T_1$ relaxations

quantum mechanics forbids transformations where energy level and spin change at once; direct excitation from $S_0$ to $T_1$ is not allowed

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

\textbf{S}_1 relaxations

- \( k_f \to \text{fluorescence (452 nm)} \)
- \( k_{ic} \to \text{internal conversion} \)
- \( k_{isc} \to \text{intersystem crossing to } T_1 \)

\textbf{T}_1 relaxations

- \( k_p \to \text{phosphorescence (652 nm)} \)
- \( k_{isc}' \to \text{alternate intersystem crossing} \)
- \( k_q \to \text{intermolecular quenching} \)

Either Excited State can Relax through a Variety of Pathways

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\[ S_0 \rightarrow \text{k}_{\text{ic}} \rightarrow \text{internal conversion} \]

\[ S_0 \rightarrow \text{k}_{\text{isc}} \rightarrow \text{intersystem crossing to T}_1 \]

\[ S_1 \rightarrow \text{k}_f \rightarrow \text{fluorescence (452 nm)} \]

\[ S_1 \rightarrow \text{k}_{\text{isc}} \rightarrow \text{intersystem crossing to T}_1 \]

- fast emission of photon, quantum allowed, same \(\lambda\) as the one it absorbed
- nonradiative de-excitation through bond vibration, manifested as heat loss
- rapid conversion from singlet to triplet state; typically \(k_{\text{isc}} : (k_f + k_{\text{ic}}) = 100:1\)

Either Excited State can Relax through a Variety of Pathways

Jablonski diagram highlights enumerates relaxation pathways

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

Slow emission of photon, not quantum allowed, different (higher) λ than the one it absorbed.

Nonradiative de-excitation through bond vibration, manifested as heat loss (accompanied by spin flip).

Relaxation through transfer of electron or energy to another molecule.

\[ T_1 \text{ relaxations} \]

- \( k_p \rightarrow \text{phosphorescence (652 nm)} \)
- \( k_{isc}' \rightarrow \text{alternate intersystem crossing} \)
- \( k_q \rightarrow \text{intermolecular quenching} \)

Intermolecular Quenching: Single Electron Transfer

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

\[ E_{1/2} = +0.77 \text{ V} \]

\[ E_{1/2} = -0.81 \text{ V} \]

\[ E_{1/2} = -1.33 \text{ V} \]

\[ E_{1/2} = +1.29 \text{ V} \]

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

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

\[ \text{Ru(bpy)}_3^{2+} \text{ – } S_1 \]

\[ \text{Ru(bpy)}_3^{3+} \]

\[ \text{Ru(bpy)}_3^{2+} \]

\[ \text{S}_0 \]

*PC + sub \rightarrow \text{PC}^- + \text{sub}^+

*PC + sub \rightarrow \text{PC}^+ + \text{sub}^-


**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)


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)

- T₁ and substrate form "encounter complex"
- T₁ relaxes through vibrational motion; this energy is funneled into a vibrational mode of the substrate
- electron is transferred from HOMO to LUMO

*S*Rul (T₁)

sub

HOMO

LUMO

π*

t₂g

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)

- Dexter Energy Transfer – simultaneous, double electron transfer mechanism
  - occurs through physical contact (< 0.01 nm)

**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)

  ![Förster Energy Transfer Diagram](image)

- **Dexter Energy Transfer** – simultaneous, double electron transfer mechanism
  - occurs through physical contact (<0.01 nm)

  ![Dexter Energy Transfer Diagram](image)

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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

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


King, K. A.; Spellane, P. J.; Watts, R. J. Am. Chem. Soc. 1985, 107, 1431
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 $E_m$)

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

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

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

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 measures the lifetime of each unpaired electron in T₁ 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)

\[
\begin{align*}
\text{phosphorescence:} & \quad *\text{Ir(ppy)}_3 \rightarrow [k_p] \rightarrow \text{Ir(ppy)}_3 + \lambda_{em} (518 \text{ nm}) \\
\text{intersystem crossing:} & \quad *\text{Ir(ppy)}_3 \rightarrow [k \text{isc}'] \rightarrow \text{Ir(ppy)}_3 + \text{heat} \\
\text{bimolecular quenching:} & \quad *\text{Ir(ppy)}_3 + Q \leftrightarrow [k_q] \rightarrow \text{Ir(ppy)}_3 + *\text{Q}
\end{align*}
\]

- $k_p$ and $k_{isc}'$ represent unimolecular reactions
  - varying $[Q]$ does not affect their rate laws

*however:*

- increasing $[Q]$ decreases $[^*\text{Ir(ppy)}_3]$ by Le Châtelier's principle
  - increasing $[Q]$ decreases intensity $I$ of phosphorescence

Verhoeven, J. W. Pure Appl. Chem. 1996, 68, 2223
Stern-Volmer phosphorescence quenching identifies quencher

\[ I_0 \equiv \text{phosphorescence intensity in the absence of quencher} \]
\[ I \equiv \text{phosphorescence intensity in the presence of quencher} \]

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 \( \lambda \) 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

oxidized molecule absorbs *more* strongly at \( \lambda \)
oxidized molecule absorbs *less* strongly at \( \lambda \)

Images courtesy of Daniela M. Arias-Rotondo, McCusker Group, Michigan State University
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

\[
\begin{align*}
\text{Oxidative Difference Spectrum} \\
\text{disappearance of MLCT } &= \text{Ru(III)} \\
\text{low-energy LMCT band } &= \text{Ru(III)}
\end{align*}
\]

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

Images courtesy of Daniela M. Arias-Rotondo, McCusker Group, Michigan State University
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

Images courtesy of Daniela M. Arias-Rotondo, McCusker Group, Michigan State University
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 $\pi^*$ orbital

Images courtesy of Daniela M. Arias-Rotondo, McCusker Group, Michigan State University
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

observing LMCT signal indicative of Ru(III) (black line)

red line shows exponential fit following 1st order rate law:

\[ [\text{^1Ru}]_t = [\text{^1Ru}]_0 e^{(-k_{\text{obs}} t)} \]

\[ \tau \text{ (excited state lifetime)} \equiv \frac{1}{k_{\text{obs}}} = 930 \text{ ns} \]

Images courtesy of Daniela M. Arias-Rotondo, McCusker Group, Michigan State University
Transient Absorption Spectroscopy: the Experiment

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

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

without quencher, both signals are quenched at the same rate

both signals return to 0 after quenching

Images courtesy of Daniela M. Arias-Rotondo, McCusker Group, Michigan State University
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

Images courtesy of Daniela M. Arias-Rotondo, McCusker Group, Michigan State University
Transient Absorption Spectroscopy: the Experiment

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

A) No quencher present

B) No quencher present

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

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

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

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

Images courtesy of Daniela M. Arias-Rotondo, McCusker Group, Michigan State University
Transient Absorption Spectroscopy: the Experiment

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

Images courtesy of Daniela M. Arias-Rotondo, McCusker Group, Michigan State University
Transient Absorption Spectroscopy: the Experiment

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

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

*Ru(bpy)_3^{2+} \ [excited state - triplet]

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

Images courtesy of Daniela M. Arias-Rotondo, McCusker Group, Michigan State University
Transient Absorption Spectroscopy: the Experiment

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

![Chemical structure](image)

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

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

finally, consider energy transfer (via either mechanism)

**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

- fast quenching of $t_{2g}$ and $\pi^*$, both baselines return to 0
- signals decaying at the same rate is highly indicative of energy transfer

Excited state - triplet
"$T_1$, $\tau = 1100$ ns (10^9)"

Images courtesy of Daniela M. Arias-Rotondo, McCusker Group, Michigan State University