XU LAB
Innovation through Catalysis

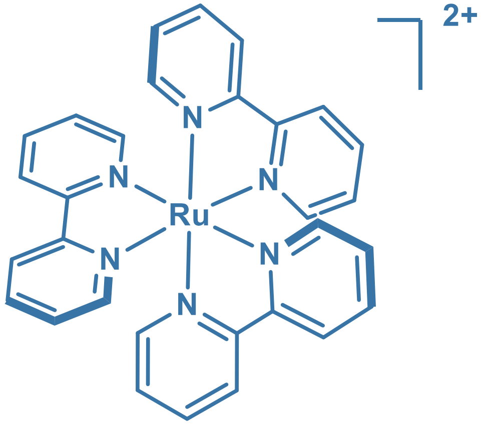
北京大學
PEKING UNIVERSITY

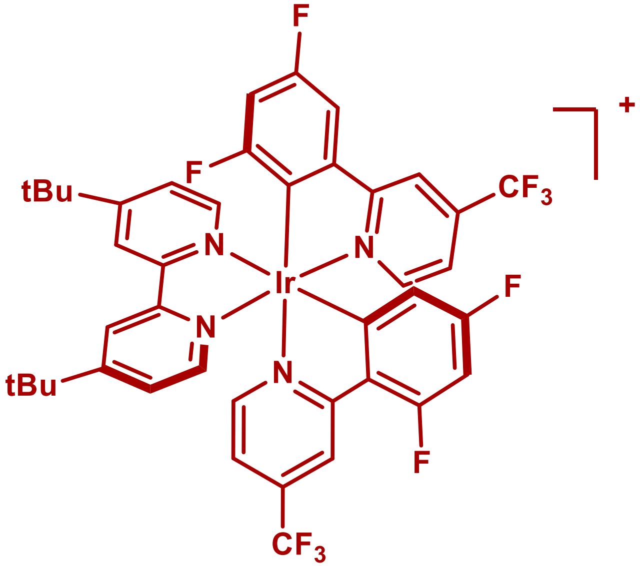
XU GROUP
Department of Chemistry, Peking University

Selected Weekly Literature Presentations

Disclaimer:
These slides contain personal interpretations and may include errors or subjective views.

A Story of Metal-based Photocatalysts with Photophysical Perspective



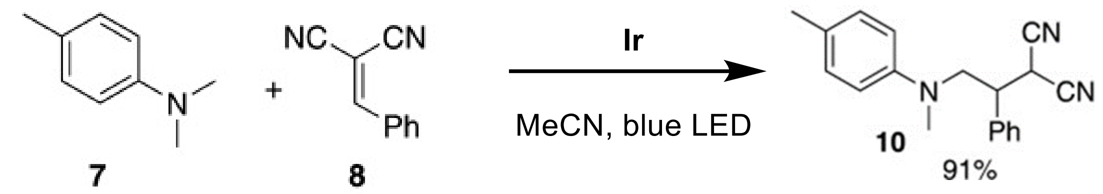


Tao Lu

Group Meeting

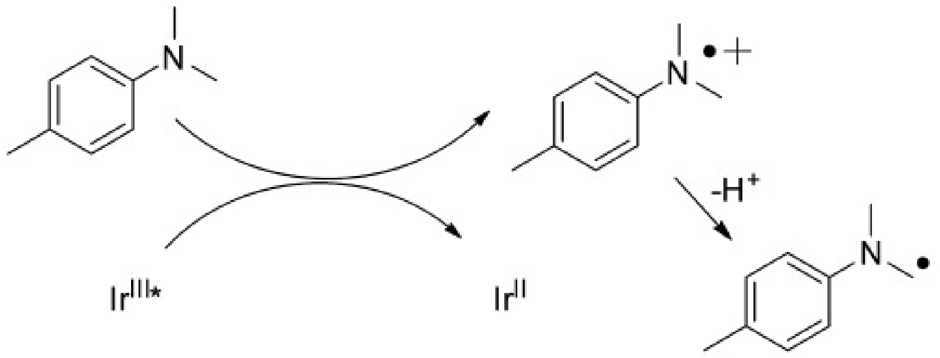
Mar. 7th, 2026

(1)

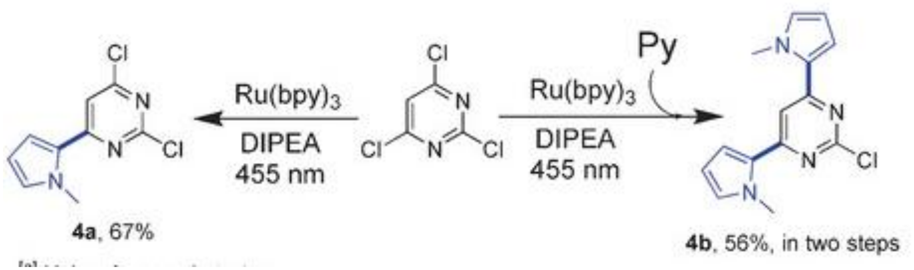


(3)

Choose the proper cat.: A Ir(ppy)3 B [Irppy2bpy]PF6



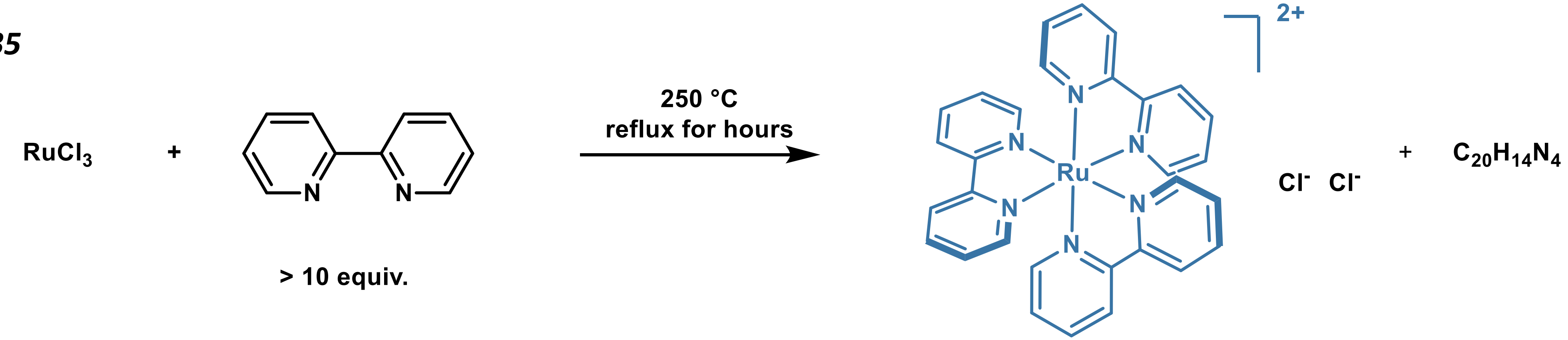
(2) *Explain the different reactivity*



CHAPTER I The Excited State of $[Ru(bpy)_3]^{2+}$

Ru(bpy)$_3$: The One that Started All

Burstall, 1935



- *Burstall's interest shifted to U and Th ores analysis after WW2.*

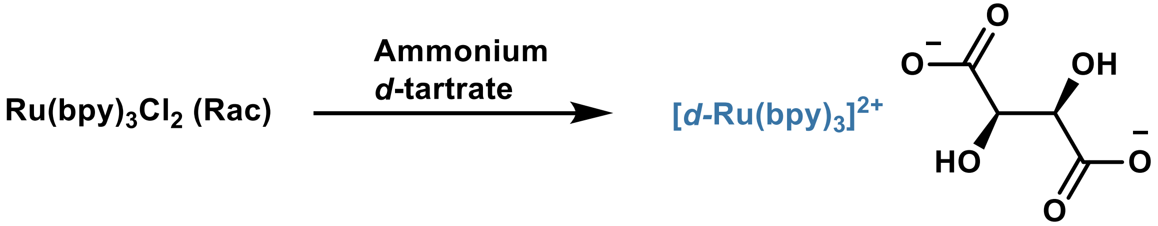
(In 1930s , topic of today lacked continuous interest)

- *External reductant accelerated the reaction to complete immediately.*

***RDS: Reduction of* Ru(bpy)$_2$$^{3+}$**

Puke et. al, 1954

- *dye silk and wool in orange-yellow shades.*

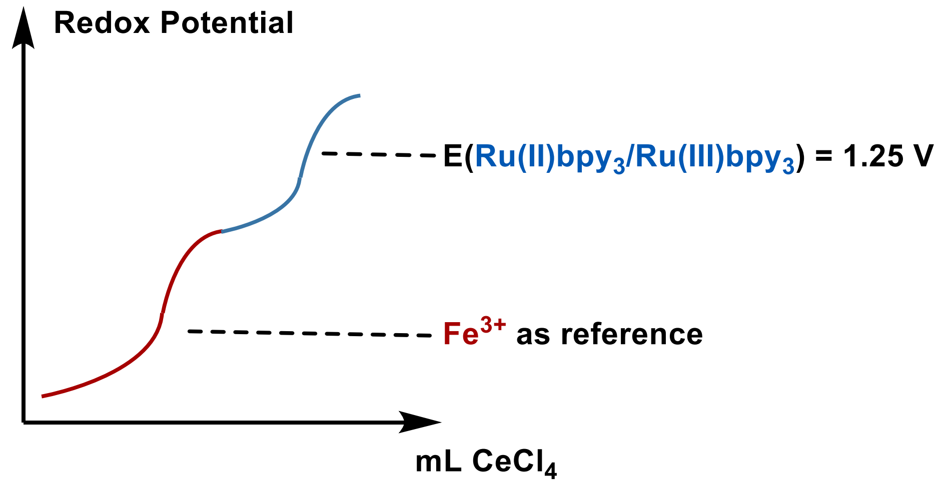


In comparison with **Fe(bpy)$_3$$^{2+}$** *and* **Ni(bpy)$_3$$^{2+}$***, racemization of* **Ru(bpy)$_3$$^{2+}$** *is extremely slow.*

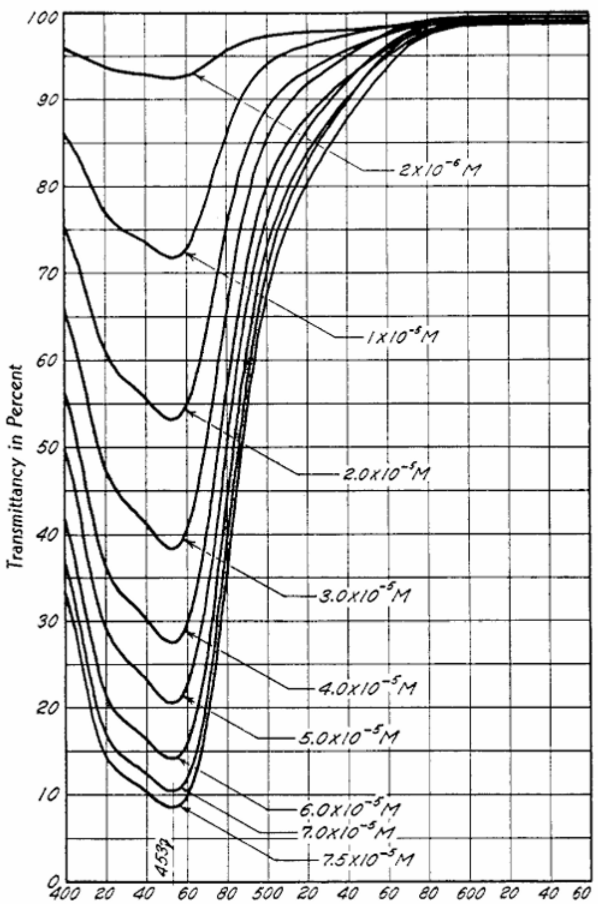
(1) Burstall, F. H. *J. Chem. Soc.* **1936**,173–175.

Before photophysics played a role: Ru-bpy as redox indicators and for spectrophotometric analysis

Brandt, 1949

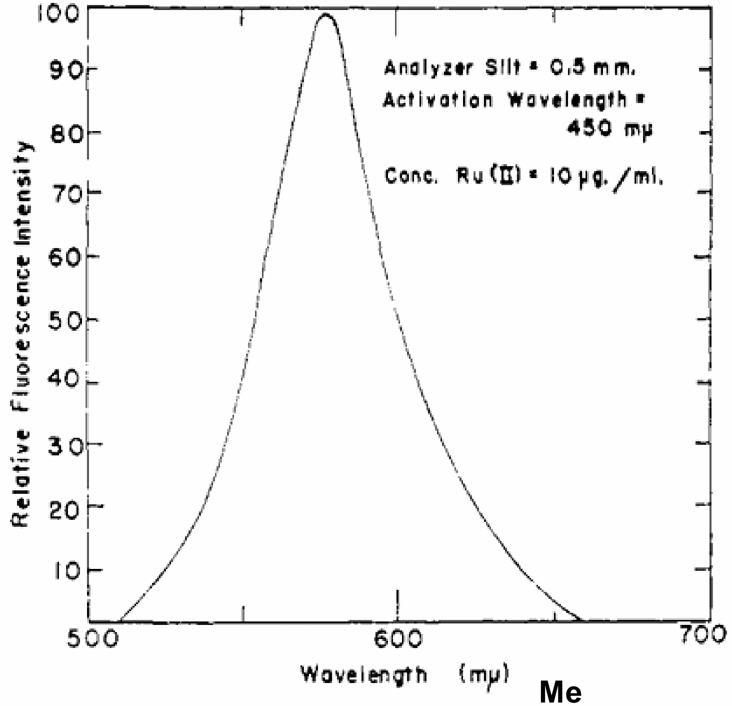


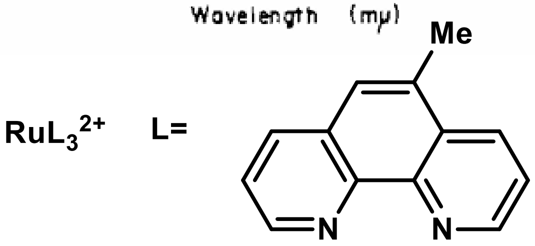
- *Previous analysis overestimated for* 1.33V
- *Good redox reversibility*



Maximum absorption: 453 nm

Brandt, 1960





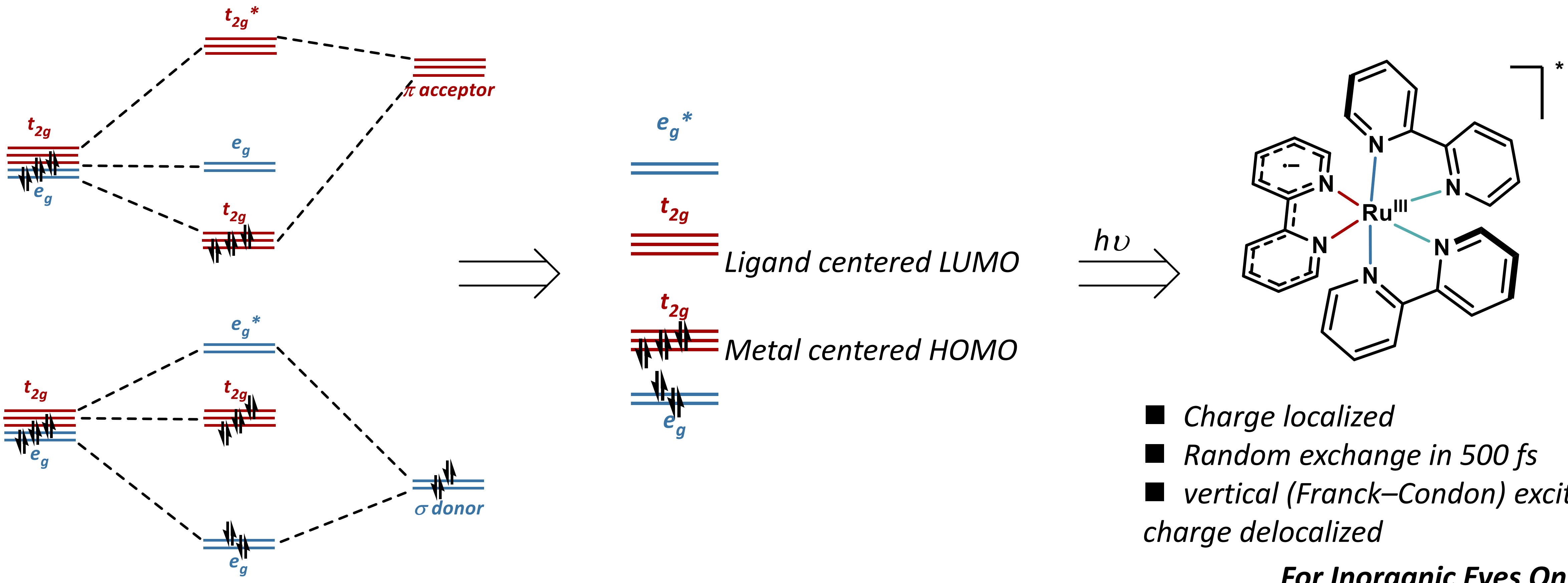
Maximum Fluorescence: 465 nm

(1) Steigman, J.; Birnbaum, N.; Edmonds, S. *Ind. Eng. Chem. Anal. Ed.* 1942, 14 (1), 30–30.
(2) Brandt, W. W.; Smith, G. F. *Anal. Chem.* 1949, 21 (11), 1313–1319.
(3) Veening, Hans.; Brandt, W. W. *Anal. Chem.* 1960, 32 (11), 1426–1428.

“The investigation of the area of ***charge transfer electronic transitions*** *in metal chelates was undertaken in an effort to increase the understanding and exploit the analytical utility of their absorption and luminescence spectra.”*

Paris, J. P. Studies on molecular electronic transitions, Ph.D. thesis; Purdue University: **1960**.

^{3}MLCT - lowest excited state for $Ru(bpy)_3$

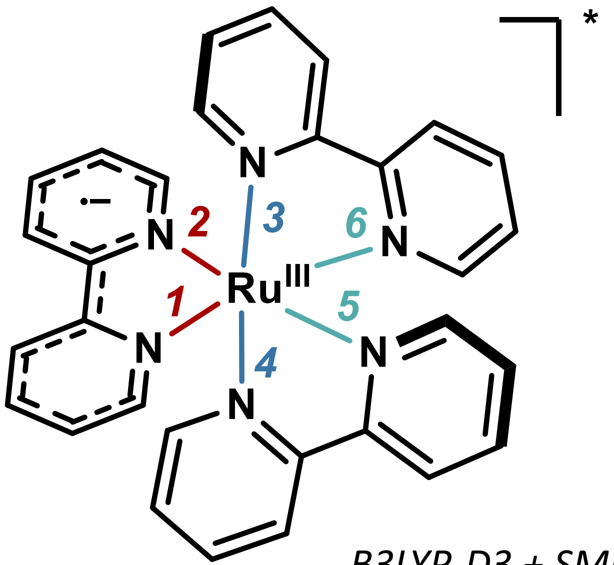


- *Charge localized*
- *Random exchange in 500 fs*
- *vertical (Franck–Condon) excitation, charge delocalized*

For Inorganic Eyes Only

Paris, J. P. Studies on molecular electronic transitions, Ph.D. thesis; Purdue University: **1960**.

Take a second look on the ^{3}LMCT excited state

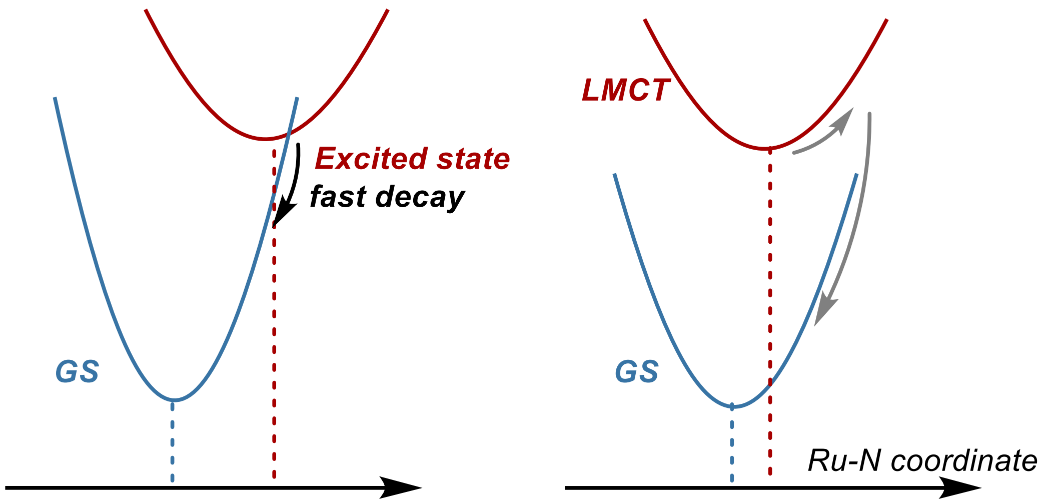


B3LYP-D3 + SMD-MeCN

Bond length (Å) for	***1***	***3***	***5***
LMCT state	**2.046**	**2.078**	**2.096**
S_0	**2.074**	**2.077**	**2.077**

Overall, the change of Bond length under 0.04 Å

LMCT state is long-lived

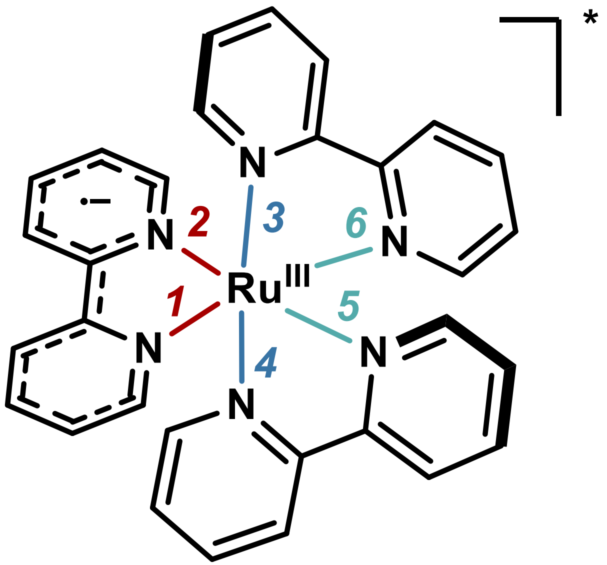


The similar lowest structure of GS and LMCT impede radiationless decay

Half-life 5 μs (77 K)

Adrien S., Isabelle M. D., Fabienne A., Jean-Louis H *Theoretical Chemistry Accounts: Theory, Computation, and Modeling*, 2018, 137 (37), 11-29.

Take a second look on the ^{3}LMCT excited state



Bond length (Å) for	1	3	6
LMCT state	2.046	2.078	2.096
S_0	2.074	2.077	2.077

Overall, the change of Bond length under 0.04 Å

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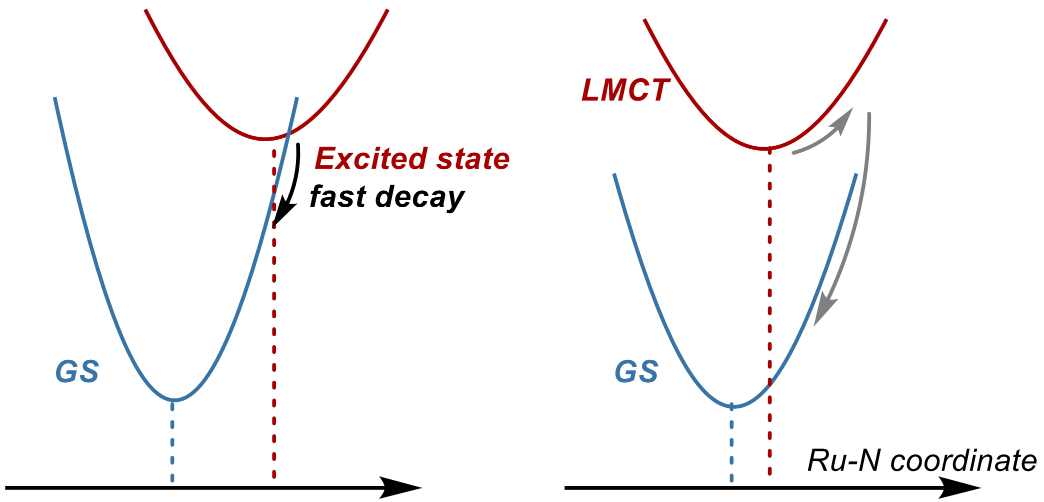


The similar lowest structure of GS and LMCT impede radiationless decay

Half-life 5 μs (77 K, crystal)

PRINCIPLE I: The photocatalyst should have long-lived excited state

Adrien S., Isabelle M. D., Fabienne A., Jean-Louis H *Theoretical Chemistry Accounts: Theory, Computation, and Modeling*, 2018, 137 (37), 11-29.

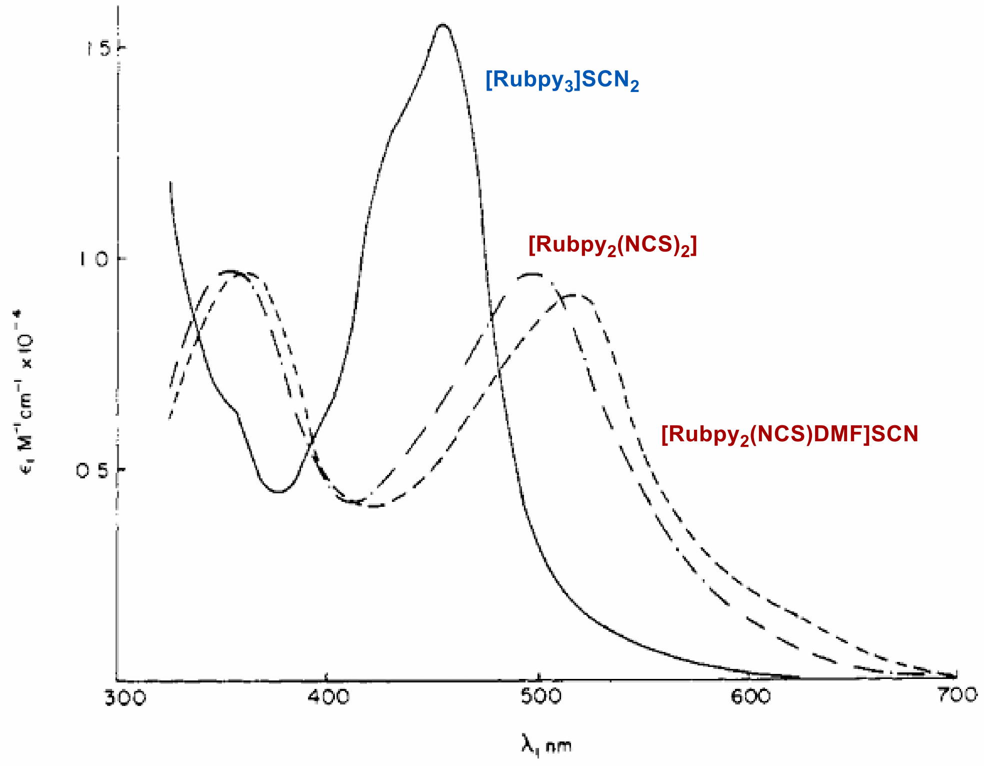
However, the stability changed with temperature and solvents…

1978 Hoggard

Half-life ~1 μs (r.t. , MeCN)

Patrick, move Rubpy3 from water to DMF.

$[Rubpy_3]SCN_2$ —(**Hg lamp**; **DMF**, **several minutes**)→ **$[Rubpy_2(NCS)DMF]SCN$** ***or*** **$[Rubpy_2(NCS)_2]$**



H_2O/O_2 shut down the reaction
$CHCl_3$ accelerate the reaction

With competing anion in organic solvents, photolysis proceeded in minutes.

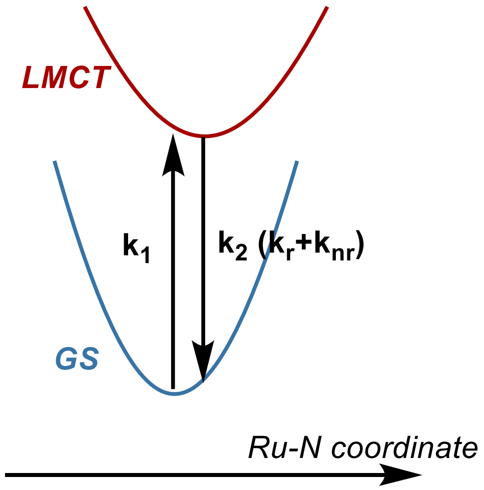
(1) Van Houten, J.; Watts, R. J. *J. Am. Chem. Soc.* **1976**, *98* (16), 4853–4858. (2) Van Houten, J.; Watts, R. J. *Inorg. Chem.* **1978**, *17* (12), 3381–3385. (3) Hoggard, P. E.; Porter, G. B. *J. Am. Chem. Soc.* **1978**, *100* (5), 1457–1463.

However, the stability changed with temperature and solvents…

1978 Watts

	Photo-decomposition rate in 0.1 M HCl			
T (K)	***HCl/Ru(bpy)$_3^{2+}$***	***HCl/Ru(bpy-d$_8$)$_3^{2}$***	***DCl/Ru(bpy)$_3^{2+}$***	***DCl/Ru(bpy-d$_8$)$_3^{2+}$***
313	***0.4***	***1.2***	***1.3***	***2.7***
323	***1.2***	***1.8***	***1.8***	***2.7***
333	***1.9***	***2.4***	***2.9***	***3.9***
343	***2.9***	***3.5***	***4.2***	***5.8***
353	***4.4***	***5.6***	***6.3***	***6.7***
363	***5.3***	***5.8***	***7.5***	***8.5***

($\Phi \times 10^{4}$)



- ***Temperature effect***
- ***Deuterium effect***

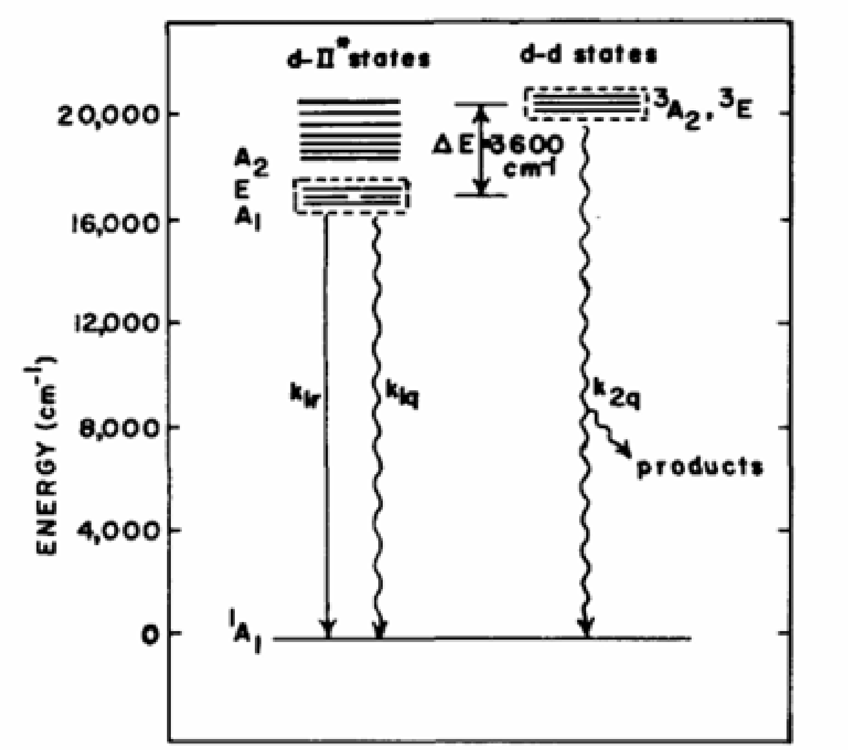
***Not** fitting with a simple two state model.*

Earlier work on the temperature dependence of luminescence enlightened them…

(1) Van Houten, J.; Watts, R. J. *J. Am. Chem. Soc.* **1976**, *98* (16), 4853–4858. (2) Van Houten, J.; Watts, R. J. *Inorg. Chem.* **1978**, *17* (12), 3381–3385. (3) Hoggard, P. E.; Porter, G. B. *J. Am. Chem. Soc.* **1978**, *100* (5), 1457–1463.

***Metal-centered states** introduced to explain the temperature-dependence.*

1978 Watts



Higher temperature accelerated the Internal conversion

- *Rationalize the influence of deuterium and temperature*

$$\mathrm{MLCT} \xrightarrow{k_1} \mathrm{GS} \qquad \mathrm{MC} \xrightarrow{k_3} \mathrm{GS}$$

$$\mathrm{MLCT} \xrightarrow{k_2} \mathrm{P} \qquad \mathrm{MC} \xrightarrow{k_4} \mathrm{P}$$

$$\mathrm{MLCT} \underset{k_{31}}{\overset{k_{13}}{\rightleftharpoons}} \mathrm{MC}$$

- ***HCl to DCl k1*** ↓
- ***d-bpy k13/k31*** ↑

- ***Metal-centered state accelerates photolysis of catalysts and lower quantum yield.***

(1) Van Houten, J.; Watts, R. J. *J. Am. Chem. Soc.* **1976**, *98* (16), 4853–4858. (2) Van Houten, J.; Watts, R. J. *Inorg. Chem.* **1978**, *17* (12), 3381–3385. (3) Hoggard, P. E.; Porter, G. B. *J. Am. Chem. Soc.* **1978**, *100* (5), 1457–1463.

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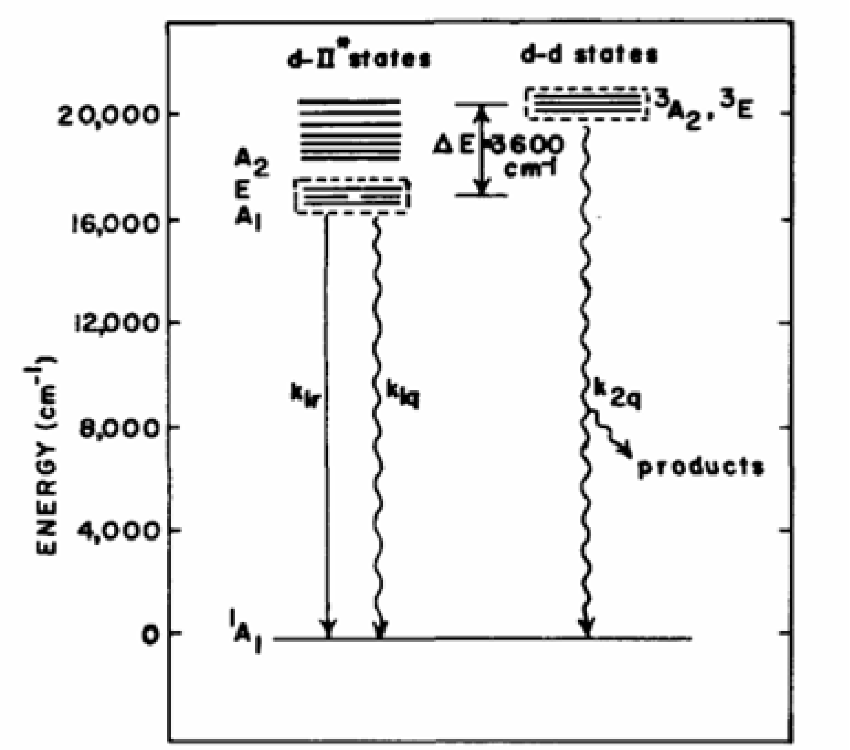


Higher temperature accelerated the Internal conversion

- *Rationalize the influence of deuterium and temperature*

$$MLCT \xrightarrow{k_1} GS \qquad MC \xrightarrow{k_3} GS$$

$$MLCT \xrightarrow{k_2} P \qquad MC \xrightarrow{k_4} P$$

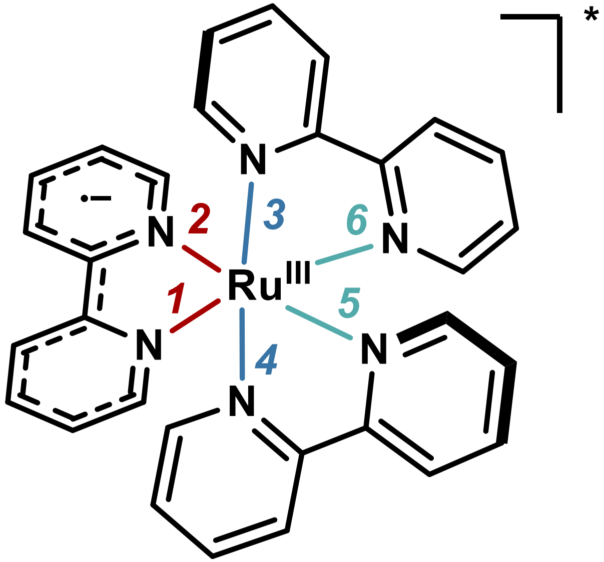
$$MLCT \underset{k_{31}}{\overset{k_{13}}{\rightleftharpoons}} MC$$

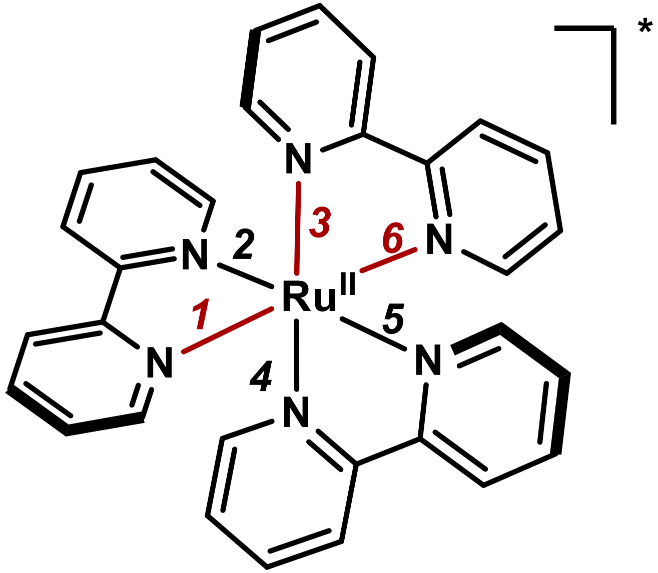
- ***HCl to DCl k1*** ↓
- ***d-bpy   k13/k31*** ↑

PRINCIPLE II: The metal-centered states are short-lived and always disfavored in catalyst design.

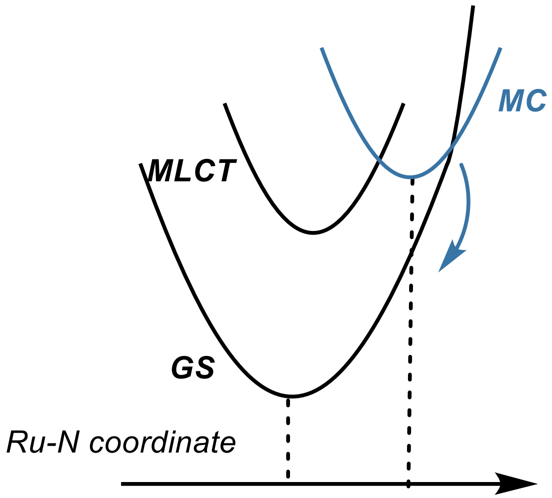
(1) Van Houten, J.; Watts, R. J. *J. Am. Chem. Soc.* **1976**, *98* (16), 4853–4858. (2) Van Houten, J.; Watts, R. J. *Inorg. Chem.* **1978**, *17* (12), 3381–3385. (3) Hoggard, P. E.; Porter, G. B. *J. Am. Chem. Soc.* **1978**, *100* (5), 1457–1463.

*Take a look on the MC excited state of **Rubpy3***





Bond length (Å) for	*1*	*3*	*6*
MLCT state	2.046	2.078	2.096
S_0	2.074	2.077	2.077
MC state	2.418	2.137	2.528



■ ***The highly twisted structure easily turned back to GS though MECP or went through ligand dissociation.***

(1)Adrien S., Isabelle M. D., Fabienne A., Jean-Louis H *Theoretical Chemistry Accounts: Theory, Computation, and Modeling*, 2018, 137 (37), 11-29. (2) Soriano-Díaz, I.; Dergachev, I. D.; Varganov, S. A.; Ortí, E.; Giussani, A. *J. Phys. Chem. Lett.* **2025**, *16* (35), 9004–9010.

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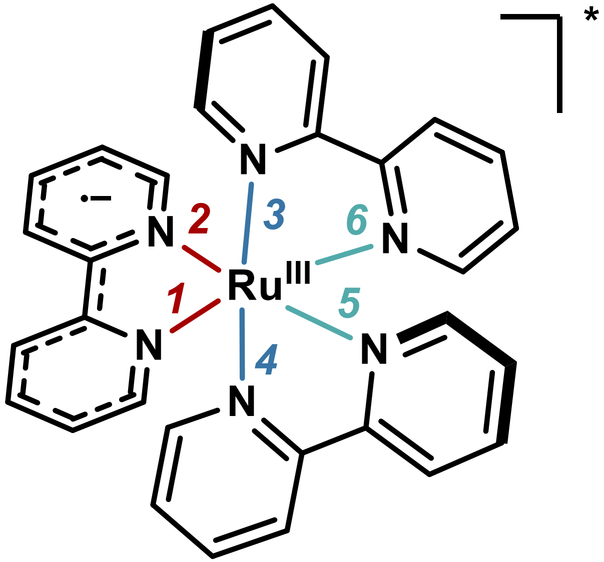

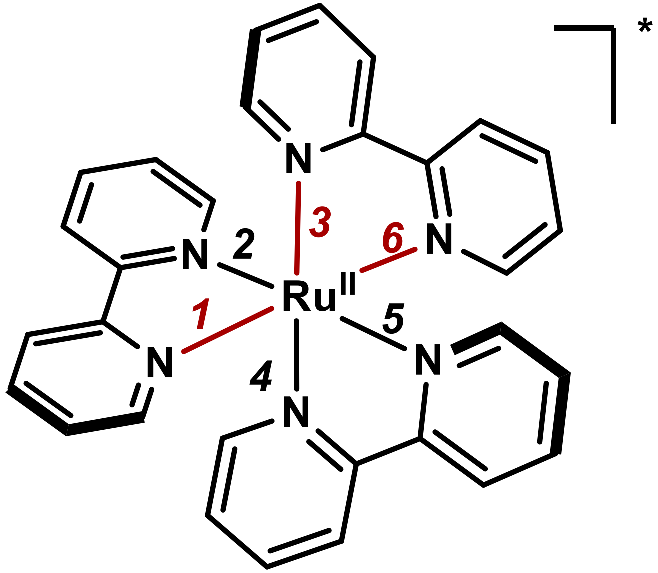

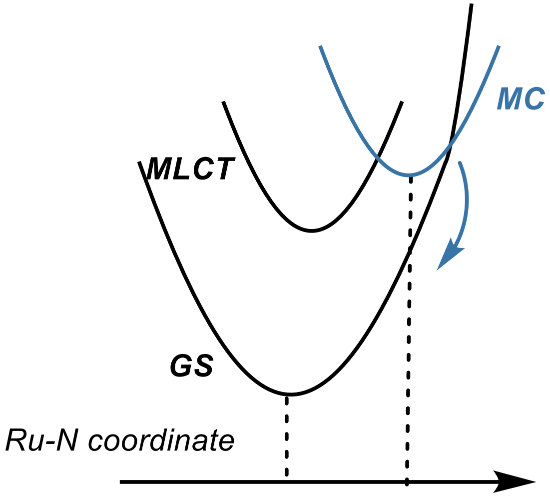

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MC state	**2.418**	**2.137**	**2.528**

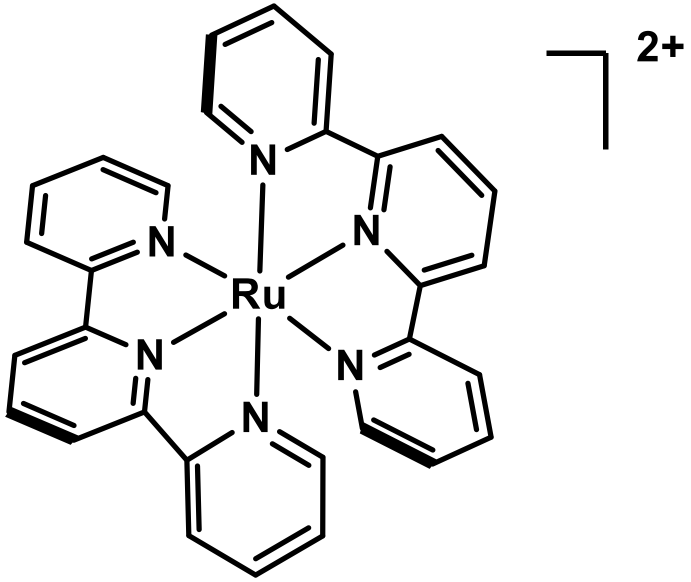
- ***The highly twisted structure easily turned back to GS though MECP or went through ligand dissociation.***

For Inorganic Eyes Only

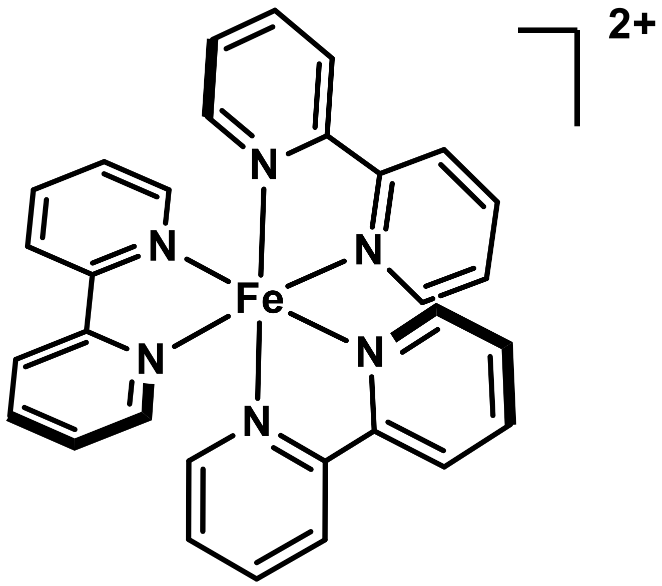
- *Tradition view: this ISC process is very fast*
- *New view: it's not a very fast process, but the MC state is "trapped" .*

(1)Adrien S., Isabelle M. D., Fabienne A., Jean-Louis H *Theoretical Chemistry Accounts: Theory, Computation, and Modeling*, 2018, 137 (37), 11-29. (2) Soriano-Díaz, I.; Dergachev, I. D.; Varganov, S. A.; Ortí, E.; Giussani, A. *J. Phys. Chem. Lett.* **2025**, *16* (35), 9004–9010.

MC excited state also quench reactivity of first-row photocatalyst and Rutpy2



Half-life ~200 ps (r.t. , MeCN)

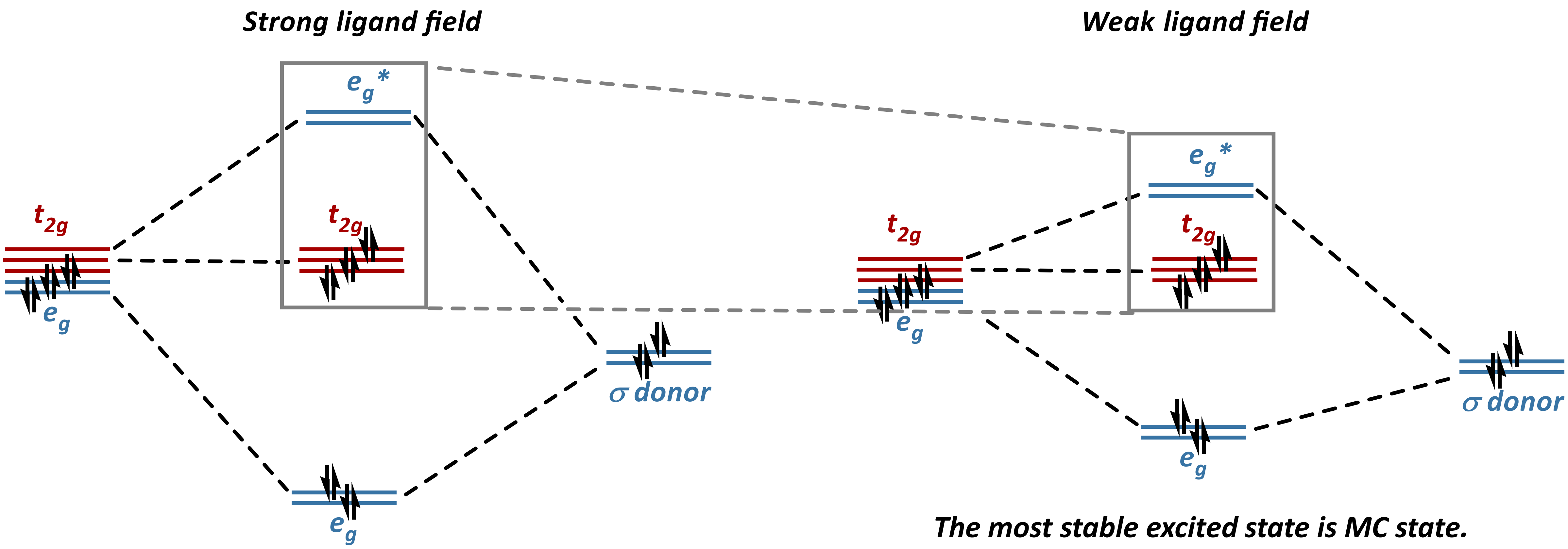


Half-life ~600 ps (r.t. , MeCN)

(1) Constable, E. C.; Cargill Thompson, A. M. W. *Inorganica Chimica Acta* **1994**, 223 (1), 177–179.
(2) Wenger, O. S. *Chemistry – A European Journal* **2019**, *25* (24), 6043–6052.

MC excited state also quench reactivity of first-row photocatalyst and Rutpy2

- ***The congested coordination structure** leads to weak ligand field split.*
- ***Contracted 3d orbital** leads to weak ligand field split.*

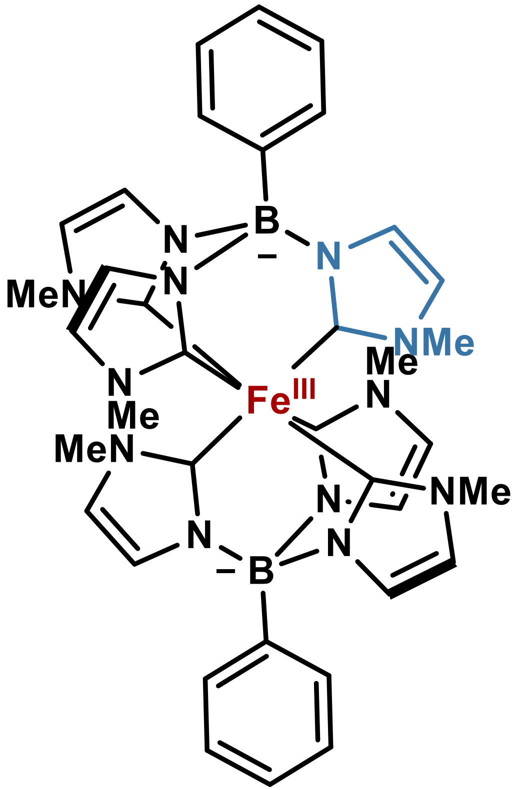


The most stable excited state is MC state.

(1) Constable, E. C.; Cargill Thompson, A. M. W. *Inorganica Chimica Acta* **1994**, 223 (1), 177–179.
(2) Wenger, O. S. *Chemistry – A European Journal* **2019**, *25* (24), 6043–6052.

State-of-art for iron photocatalyst and Rutpy2

2018 Wänmark



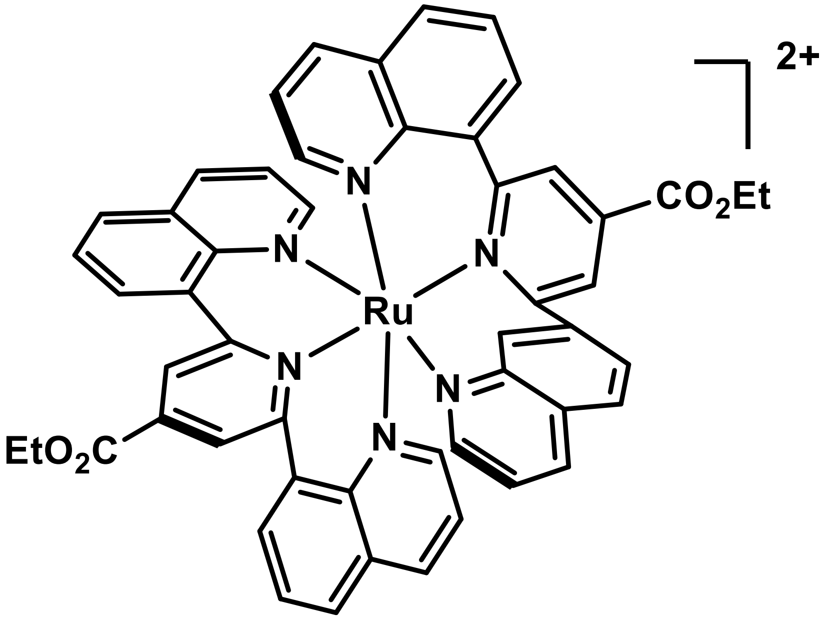
Strong ligand field *– NHC donor*
Well-aligned structure

Fe(III) instead of Fe(II) *– The IC from LMCT to MC spin-forbiddened*

Excited redox property	***1.6 V***	***-1.3 V***
Ru(bpy)3	***0.84 V***	***-0.86 V***

Half-life 2 ns (r.t. , MeCN)

2008 Hammarström



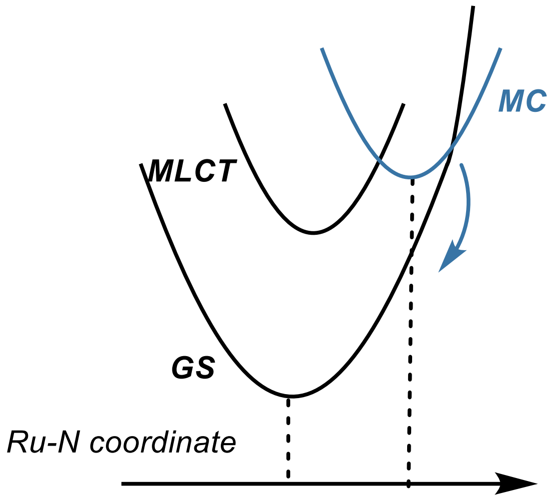
Well-aligned structure (Large bite angle)

Half-life 5.5 μs (r.t. , MeOH/EtOH)

(1) Kjær, K. S.; Wärnmark, K. *Science* **2019**, *363* (6424), 249–253. (2) Abrahamsson, M.; Hammarström, L. *J. Am. Chem. Soc.* **2008**, *130* (46), 15533–15542.

The reactivity-mattered photophysics of Ru-bpy completed

Take-home profile



- *None-important issues:*
  Ligand-centered state
  Singlet state

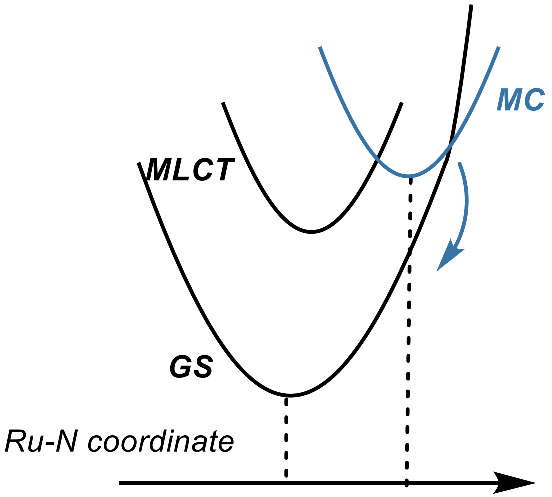
Take-home message

- *Ligand field strength, a* ***key determinant*** *of the profile, is modulated by* ***the donor properties of the ligand,*** ***the specific metal center****, and* ***its valence state***

For inorganic and spectroscopic chemists, the case was closed.

The reactivity-mattered photophysics of Ru-bpy completed

Take-home profile



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Take-home message

- *Ligand field strength, a **key determinant** of the profile, is modulated by* ***the donor properties of the ligand,*** ***the specific metal center****, and* ***its valence state***

For inorganic and spectroscopic chemists, the case was closed.

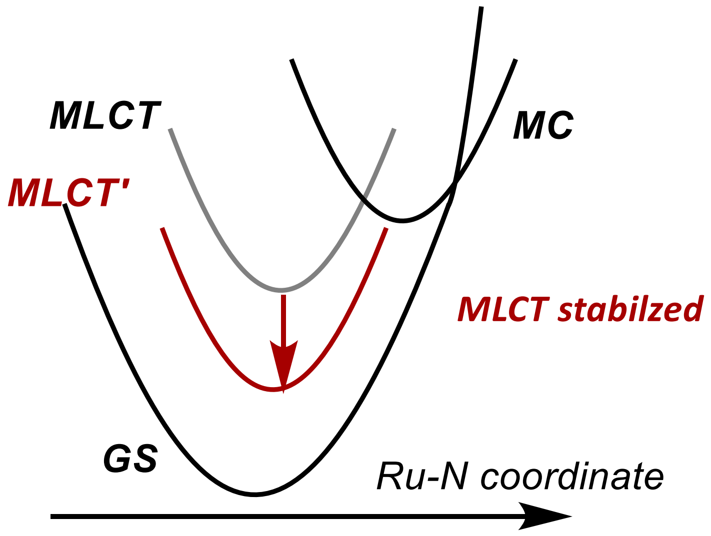
For those pursuing photochemical reactions, however, two critical questions remained open.

CHAPTER II The rational design of photocatalyst improvement

- *How to inhibit the non-radiative decay through the MC state?*
- *How to achieve stronger redox property/ improve EnT efficiency?*

For Ru(bpy)3, two sides of the same double-edged sword

- ***How to inhibit the non-radiative decay through the MC state.***



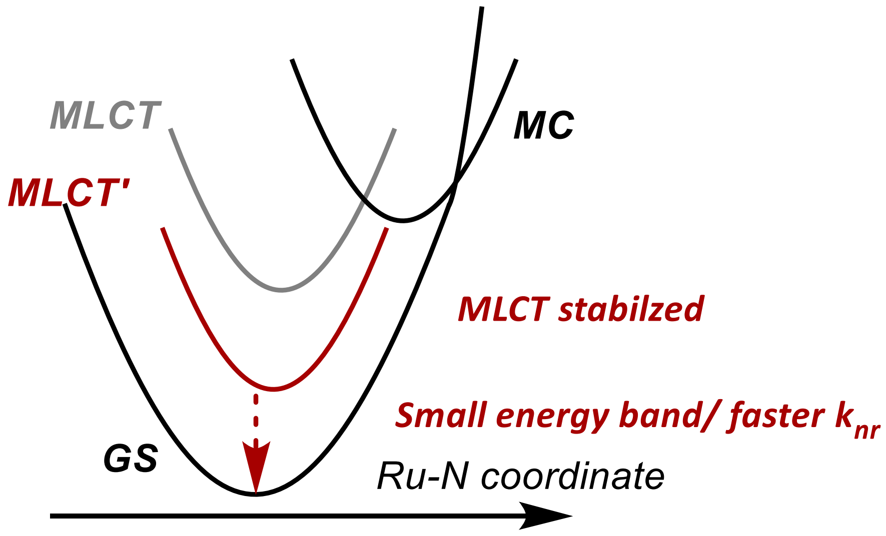
- ***Large barrier for LMCT/MC***

- ***How to achieve stronger redox property/ improve EnT efficiency.***

For Ru(bpy)3, two sides of the same double-edged sword

■ ***How to inhibit the non-radiative decay through the MC state.***

■ ***How to achieve stronger redox property/ improve EnT efficiency.***



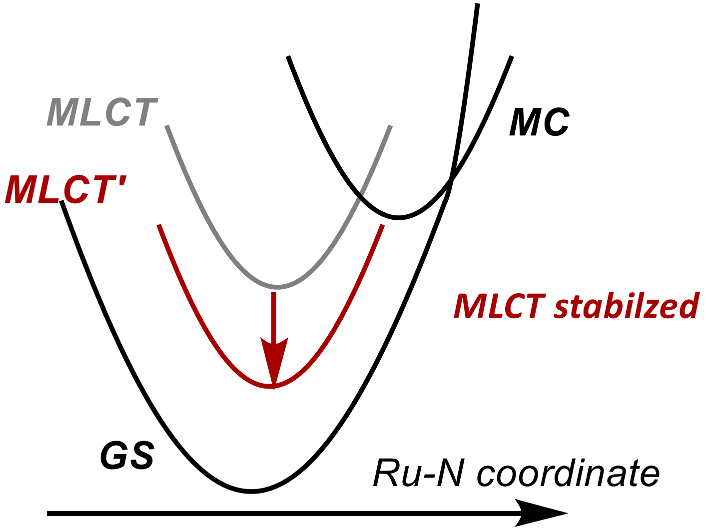
■ ***Large barrier for LMCT/MC***

■ ***More feasible for nonradiative relaxation***

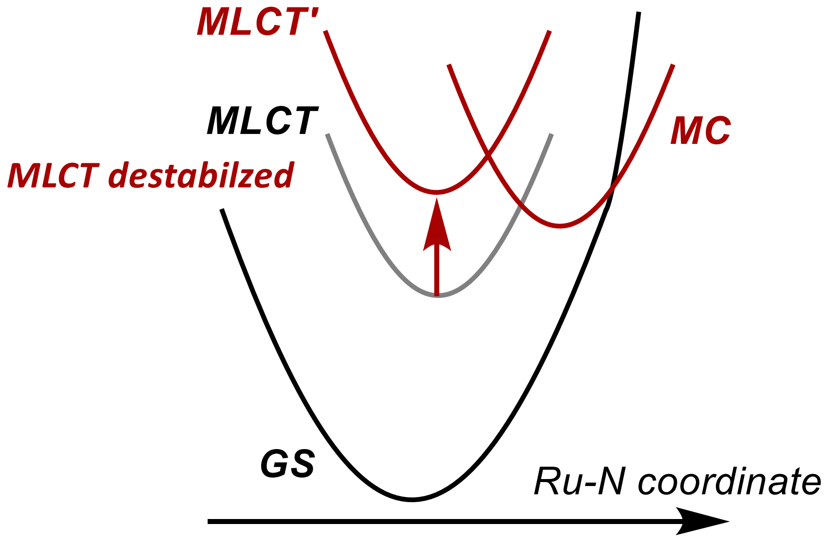
■ ***Weak redox/EnT property***

For Ru(bpy)3, two sides of the same double-edged sword

■ ***How to inhibit the non-radiative decay through the MC state.***



■ ***How to achieve stronger redox property/ improve EnT efficiency.***

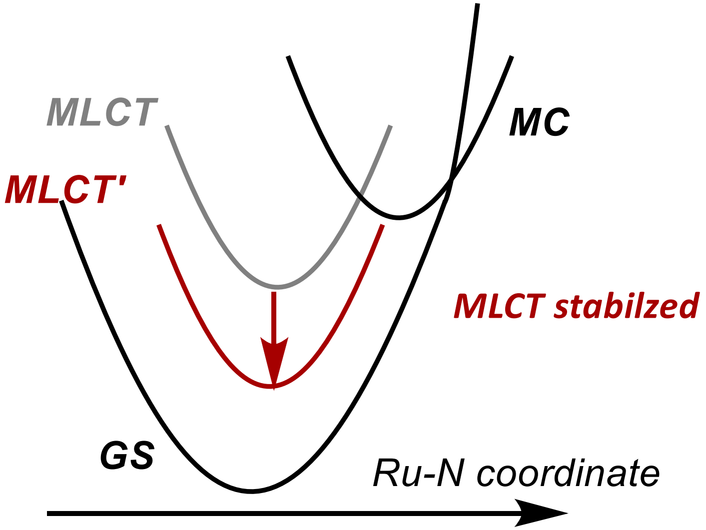


Another issue is that the HOMO and LUMO shift in concert.

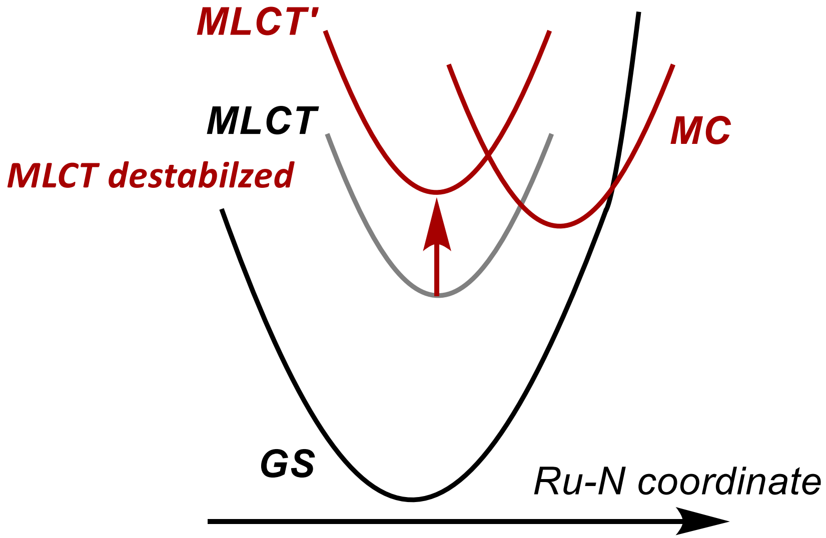
■ ***A trade-off dilemma if only modulating MLCT state through LIGAND modification***

For Ru(bpy)3, two sides of the same double-edged sword

- ***To inhibit the non-radiative decay through the MC state.***



- ***To achieve stronger redox property/ improve EnT efficiency.***

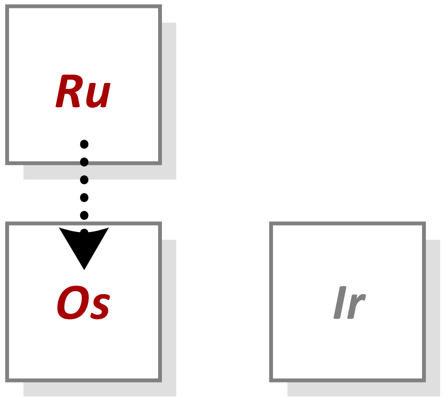


- ***A trade-off dilemma if only modulating LMCT state through LIGAND modification***

Another strategy: destabilizing the MC state higher energy.

From Ru to Fe, the MC state is stabilized.

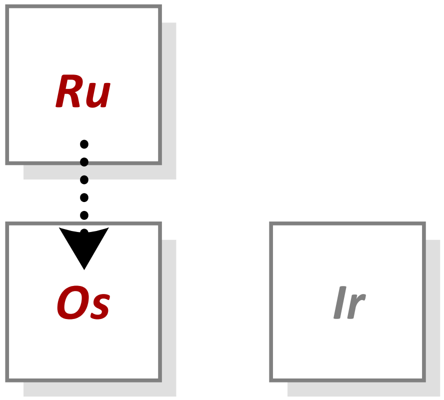
Replacing Ru(4d) with 5d metal



- *$Os(bpy)_3$(III/II) = 0.81 V (for Ru, 1.26 V) MLCT emission 1.6 eV (for Ru, 2.1 eV)*
  Os(II) more unstable comparing to Ru(II), low energy luminance.

(1) Lacky, D. E.; Pankuch, B. J.; Crosby, G. A. *J. Phys. Chem.* **1980**, *84* (16), 2068–2074. (2) Conradie, J. *Electrochimica Acta* **2025**, *514*, 145633.

Replacing Ru(4d) with 5d metal



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  Os(II) more unstable comparing to Ru(II), low energy luminance.

- *k_{nr} of $Os(bpy)_3^{2+}$ >> $Ru(bpy)_3^{2+}$*
  Spin-Orbital coupling stronger for 5d metal.

$Os(bpy)_3^{2+}$ exhibited low-energy excited state with lower quantum yield in higher temperature.

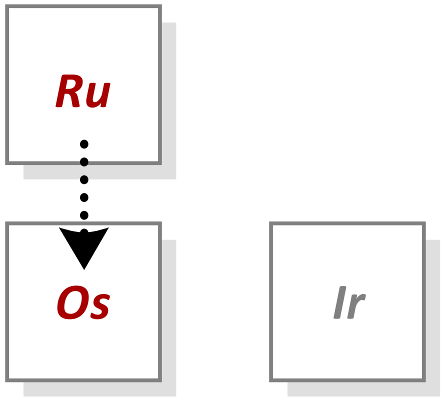
Apart from the mainline, narrow energy band enabled two areas for Os (II) photocatalyst.

1. *Red light photo catalyst (also benefits from SOC)*
2. *Energy accepter in Ru-Os complex*

Key players: Rovis, Landais, Campagna, Furue…

(1) Lacky, D. E.; Pankuch, B. J.; Crosby, G. A. *J. Phys. Chem.* **1980**, *84* (16), 2068–2074. (2) Conradie, J. *Electrochimica Acta* **2025**, *514*, 145633.

Replacing Ru(4d) with 5d metal



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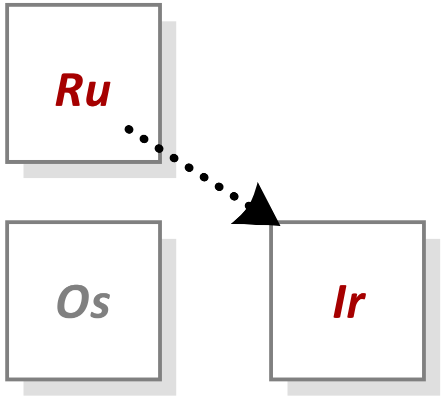
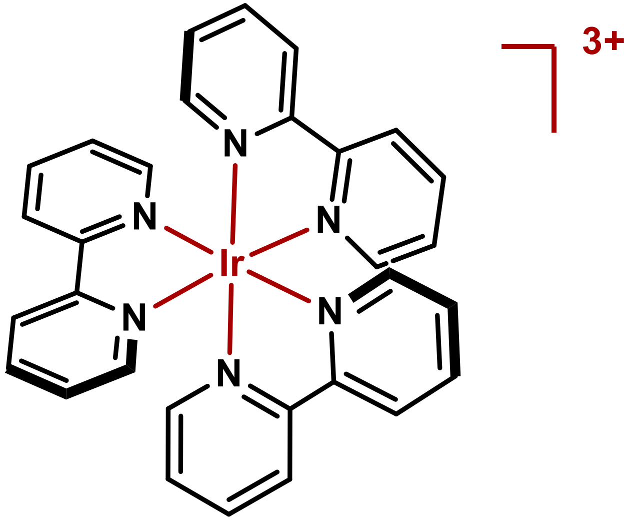


$Ir(bpy)_3^{3+}$-tricationic Ir(III) exhibited more obvious pronounced cation character compared to divalent ion.

(1) Flynn, C. M. Jr.; Demas, J. N. *J. Am. Chem. Soc.* **1974**, *96* (6), 1959–1960. (2) Kahl, J. L.; Hanck, K. W.; DeArmond, K. *J. Phys. Chem.* **1978**, *82* (5), 540–545.

Placing the redox potential right

1974 Demas



- *MLCT emission 2.1 - 3 eV (comparable wth Ru, 2.1 eV)*
- *Ir(bpy)$_3$(IV/III) = +2.1 V, too high for the net reductive reaction!*
- *Harder to synthesis.*

(1) Flynn, C. M. Jr.; Demas, J. N. *J. Am. Chem. Soc.* **1974**, *96* (6), 1959–1960. (2) Kahl, J. L.; Hanck, K. W.; DeArmond, K. *J. Phys. Chem.* **1978**, *82* (5), 540–545.

Placing the redox potential right

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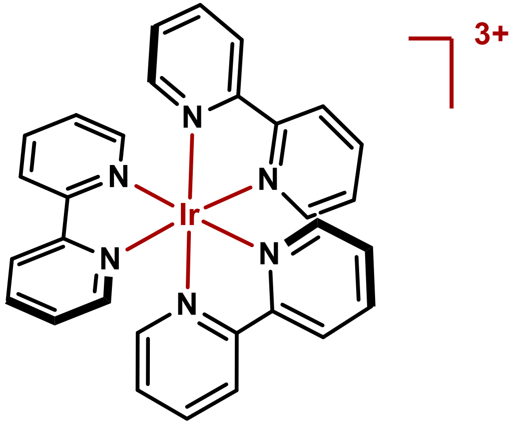
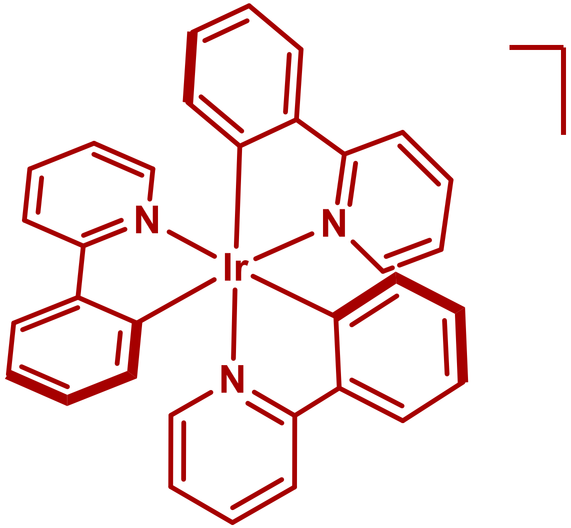


- *$Ir(bpy)_3$(IV/III) = +2.1 V,*

too high for
the net reductive reaction!

1991 Watts



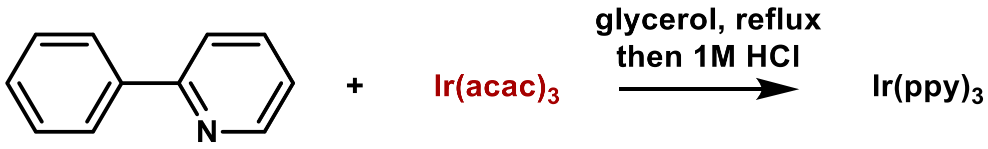
- *Fac-$Ir(ppy)_3$(IV/III) = +0.77 V*
- ***Fac-$Ir(ppy)_3$(II/III) = -2.2 V (MeCN,SCE)***

too low for
the net oxidative reaction!

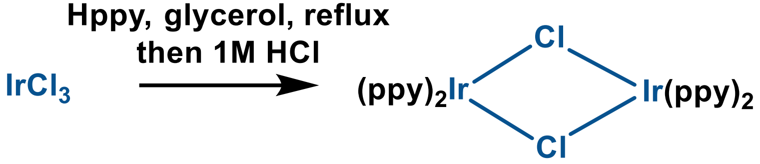
Synthesis consideration

- *Fac-isomer was obtained due to a so-called **trans-effect***

Strong σ donor and π acceptor destabilizing the trans bond kinetically.



- *With $IrCl_3$, only disubstituted.*

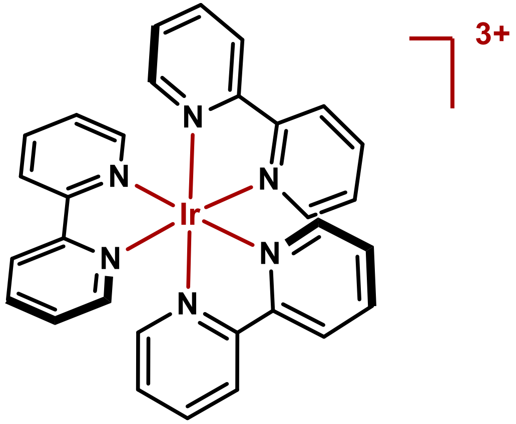


1984 Watts

(1) Sprouse, S.; King, K. A.; Spellane, P. J.; Watts, R. J. *J. Am. Chem. Soc.* **1984**, *106* (22), 6647–6653.
(2) Dedeian, K.; Djurovich, P. I.; Garces, F. O.; Carlson, G.; Watts, R. J. *Inorg. Chem.* **1991**, *30* (8), 1685–1687.

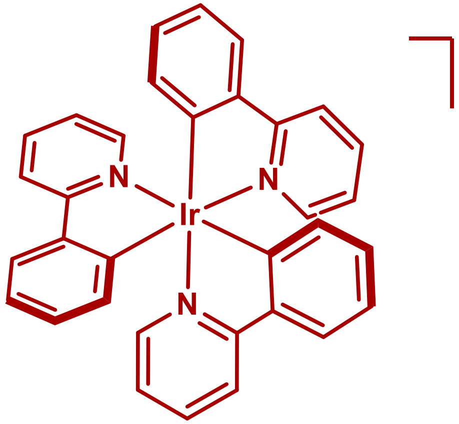
Placing the redox potential right

1974 Demas



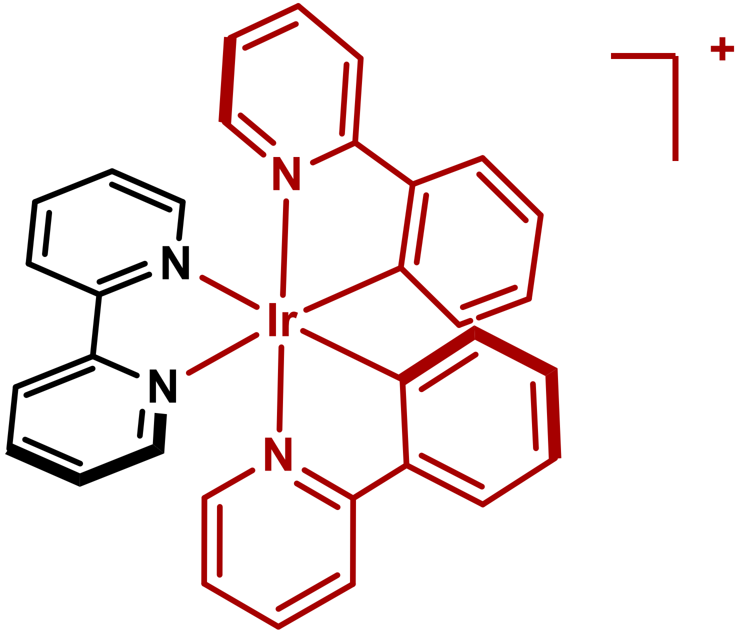
- *$Ir(bpy)_3$(IV/III) = +2.1 V, too high for the net reductive reaction!*

1991 Watts



- *Fac-$Ir(ppy)_3$(II/III) = -2.2 V (MeCN,SCE) too low for the net oxidative reaction!*

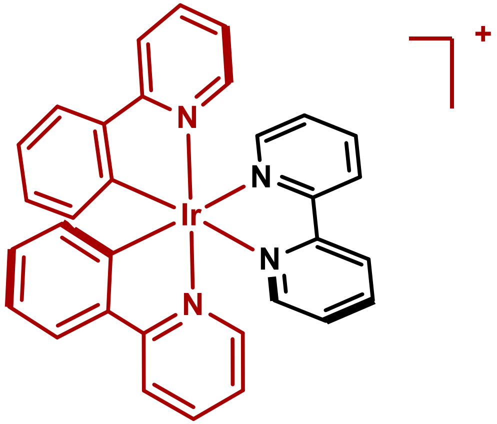
1988 Watts

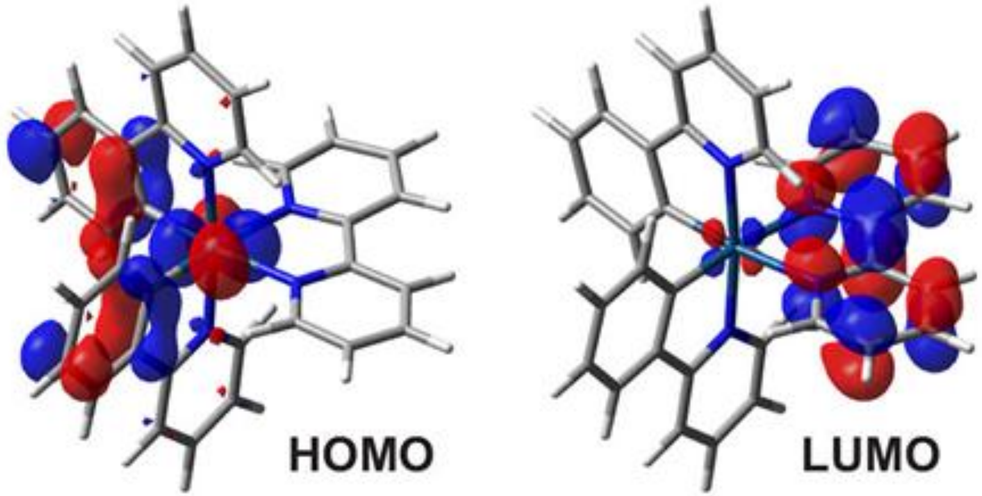


- *$Ir(ppy)_2$bpy(II/III) = -1.5 V*
  $Ir(ppy)_2$bpy(IV/III) = 1.2 V (SCE)

(1) Garces, F. O.; King, K. A.; Watts, R. J. *Inorg. Chem.* **1988**, *27* (20), 3464–3471. (2) https://pdf.benchchem.com/1429/An_In_depth_Technical_Guide_to_the_Redox_Potentials_of_Ir_dtbbpy_ppy_2_PF6.pdf

The heteroleptic structure decoupling HOMO and LUMO modulation





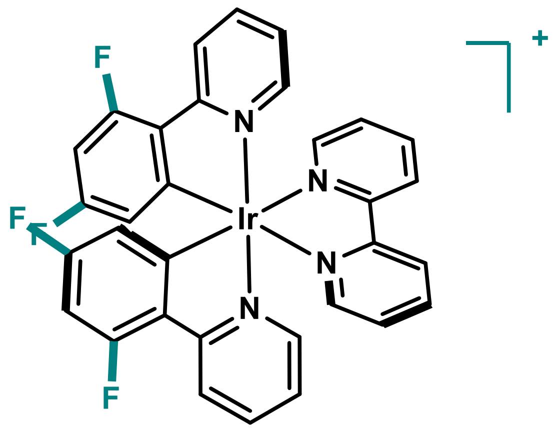
-5.88 eV

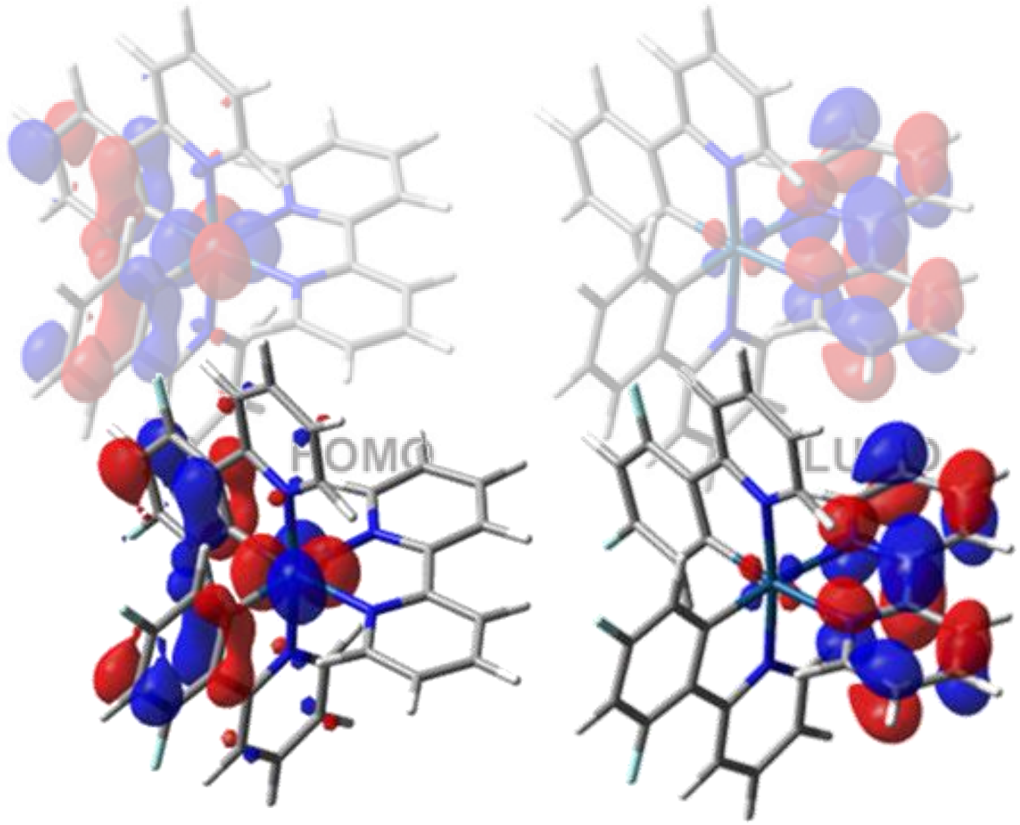
- 2.29 eV

Not only for inorganic eyes: The Ir-ppy displayed mixed LLCT(Ligand-ligand charge transfer)-MLCT state, while do no harm to the emission efficiency (sometimes even help).

(1) Monti, F.; Baschieri, A.; Sambri, L.; Armaroli, N. *Acc. Chem. Res.* **2021**, 54 (6), 1492–1505. (2) Colombo, M. G.; Hauser, A.; Guedel, H. U. *Inorg. Chem.* **1993**, 32 (14), 3088–3092.

The heteroleptic structure decoupling HOMO and LUMO modulation

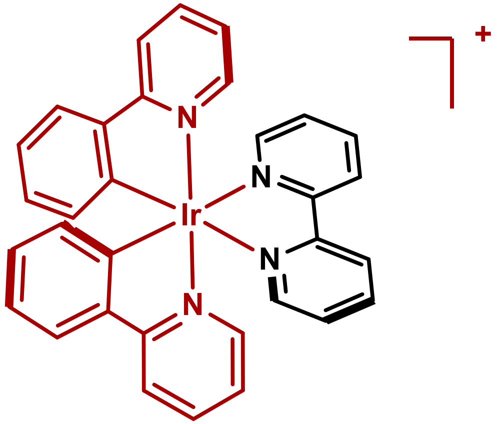


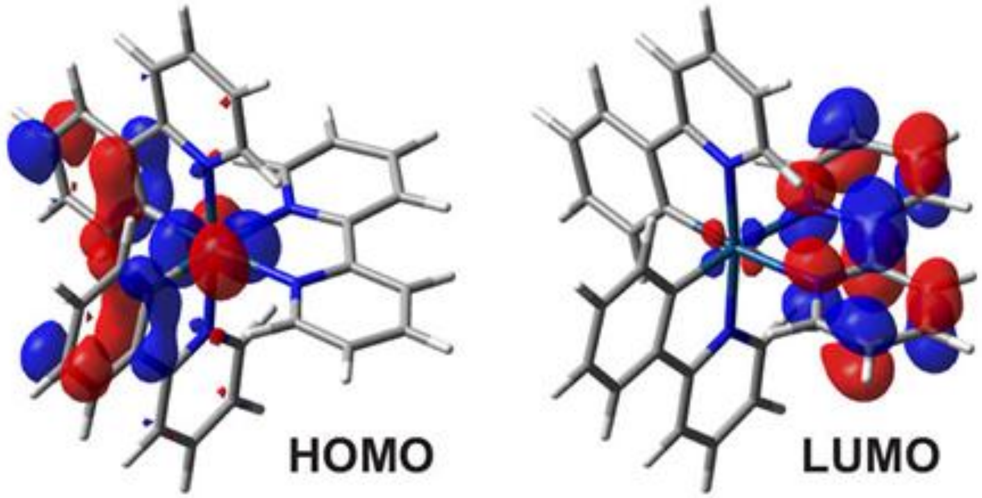


-5.88 eV	- 2.29 eV
-6.21 eV	- 2.38 eV

Monti, F.; Baschieri, A.; Sambri, L.; Armaroli, N. *Acc. Chem. Res.* **2021**, 54 (6), 1492–1505

The heteroleptic structure decoupling HOMO and LUMO modulation

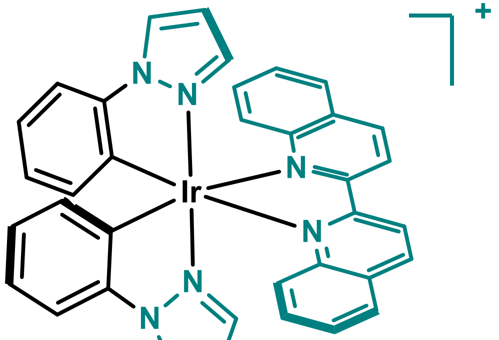




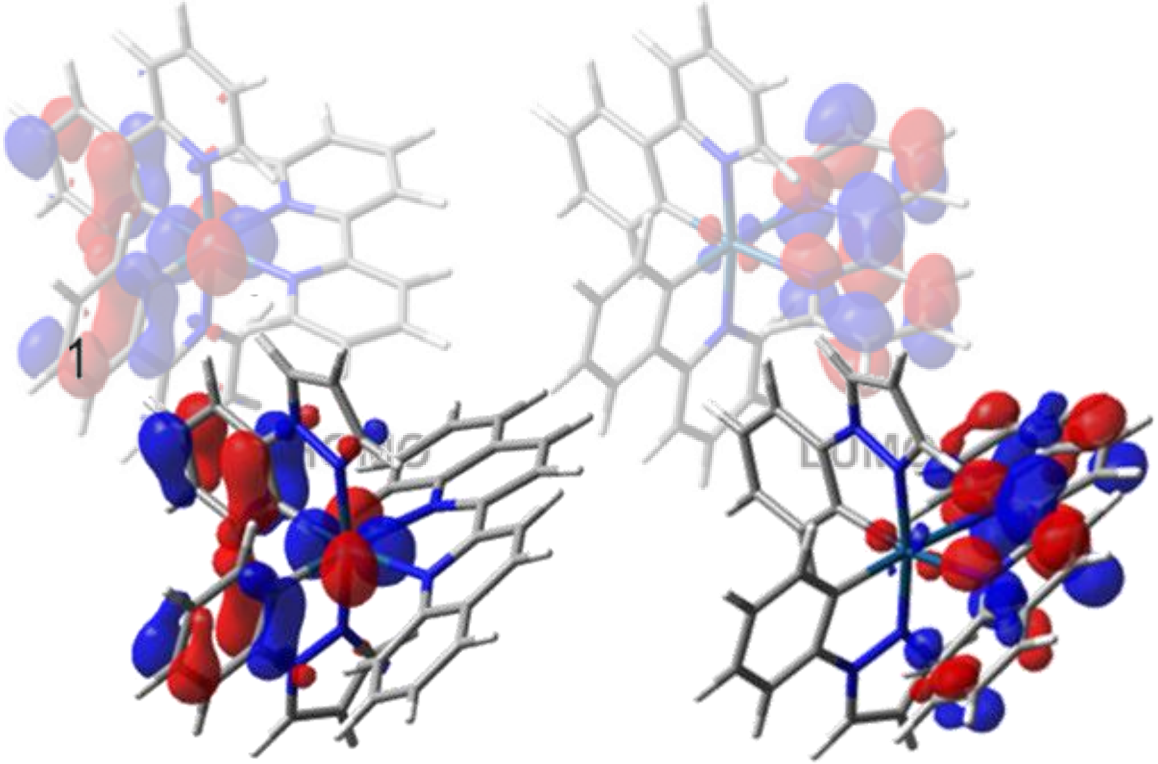
-5.88 eV ***- 2.29 eV***

Monti, F.; Baschieri, A.; Sambri, L.; Armaroli, N. *Acc. Chem. Res.* **2021**, 54 (6), 1492–1505

The heteroleptic structure decoupling HOMO and LUMO modulation



1



The ppz ligand originally designed for shifting the Ligand Centered (LC) excited state.

-5.88 eV ***- 2.29 eV***

-6.11 eV ***- 2.78 eV***

(1) Monti, F.; Baschieri, A.; Sambri, L.; Armaroli, N. *Acc. Chem. Res.* **2021**, 54 (6), 1492–1505. (2) Tamayo, A. B.; Garon, S.; Sajoto, T.; Djurovich, P. I.; Tsyba, I. M.; Bau, R.; Thompson, M. E. *Inorg. Chem.* **2005**, 44 (24), 8723–8732.

Bernhard developed the "familiar" Ir cat. for photoredox

Stefan Bernhard

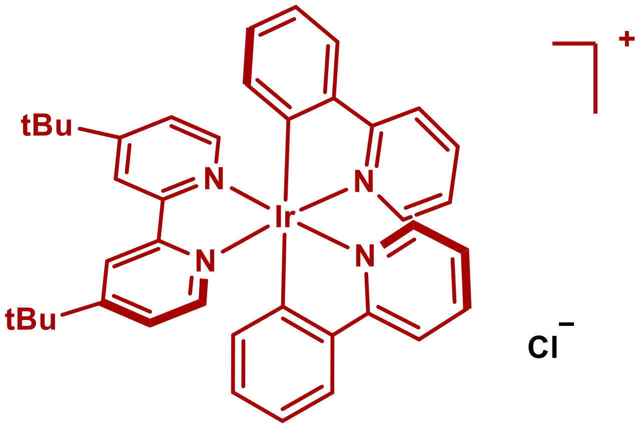
Carnegie Mellon University

- *Started his career in Chocolat Tobler®*

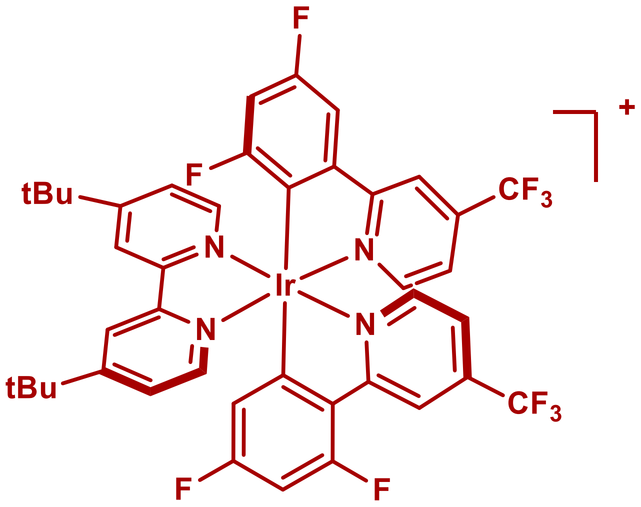
- *Received training in synthetic chemistry, laser spectroscopy, and electrochemistry.*
- *Investigating light-to-electrochemical energy conversions using synthetically tunable transition metal photosensitizers.*

Bernhard developed the "familiar" Ir cat. for photoredox

2004 Gen 1



2005 Gen 2



As electroluminescent devices, emission wacelength and quantum yield matters.

- *Single layer OLED.*
- *tert-Bu decrease solid self-quenching.*

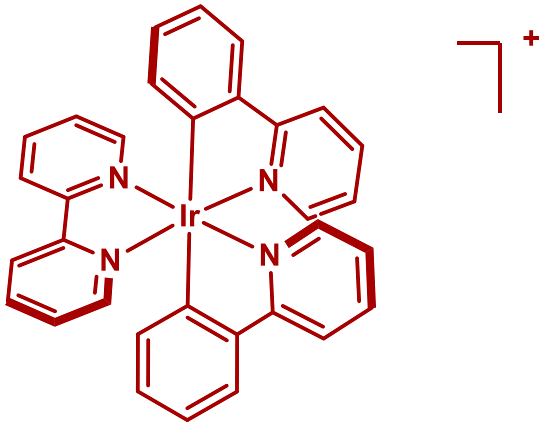
Φ 0.06 to 0.18

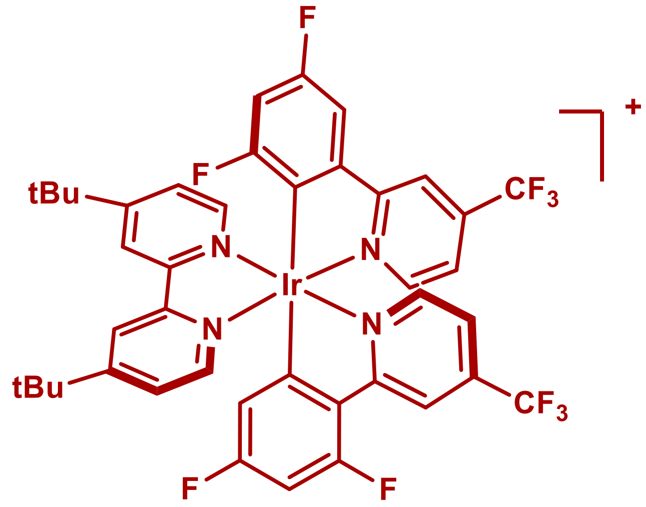
- *Blue-to-green OLED.*
- *Most electron-deficient ligand Tested*

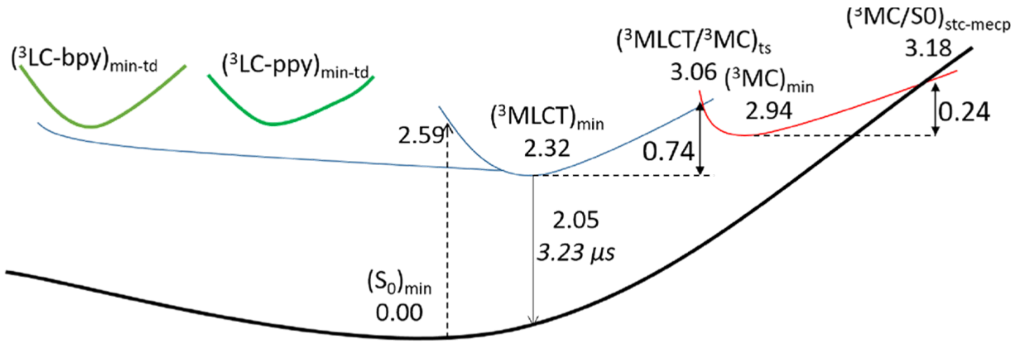
Φ(PF_6) 0.18 to 0.68

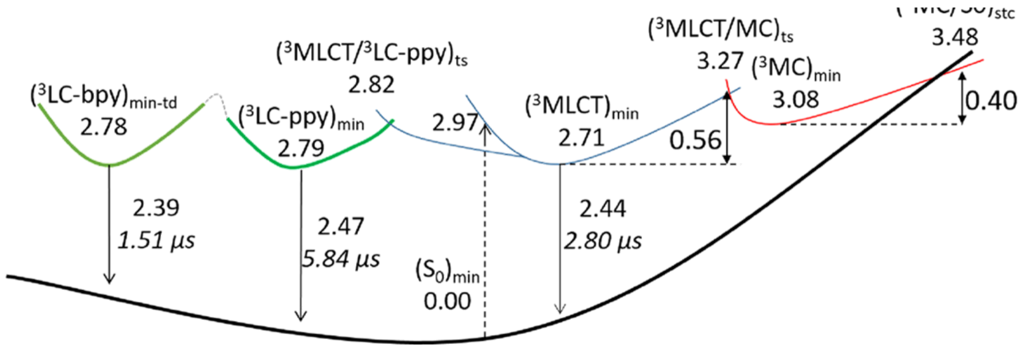
(1) Lowry, M. S.; Goldsmith, J. I.; Slinker, J. D.; Rohl, R.; Pascal, R. A.; Malliaras, G. G.; Bernhard, S. Chem. Mater. **2005**, 17 (23), 5712–5719. (2) Slinker, J. D.; Gorodetsky, A. A.; Lowry, M. S.; Wang, J.; Parker, S.; Rohl, R.; Bernhard, S.; Malliaras, G. G. J. Am. Chem. Soc. **2004**, 126 (9), 2763–2767.

Bernhard developed the "familiar" Ir cat. for photoredox









LC state participated in emission

(1) Lowry, M. S.; Goldsmith, J. I.; Slinker, J. D.; Rohl, R.; Pascal, R. A.; Malliaras, G. G.; Bernhard, S. Chem. Mater. **2005**, 17 (23), 5712–5719. (2) Slinker, J. D.; Gorodetsky, A. A.; Lowry, M. S.; Wang, J.; Parker, S.; Rohl, R.; Bernhard, S.; Malliaras, G. G. J. Am. Chem. Soc. **2004**, 126 (9), 2763–2767. (3) Soriano-Díaz, I.; Ortí, E.; Giussani, A. *Inorg. Chem.* **2021**, 60 (17), 13222–13232.

Finally, the lightbulb is ready to work…

Stefan Bernhard

Assistant Professor
Princeton,
2002

tBubpy, F-ppy
2004**, **2005

Assistant Professor
CMU
2009

David Macmillan

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Assistant Professor
Princeton,
2002

tBubpy, F-ppy
2004, 2005

Assistant Professor
CMU
2009

The renaissance of photoredox

Professor of chem.
Princeton,
2006

The ground-breaking work of photoredox, using Rubpy3
2008

Aldehyde benzylation, using tBubpy, F-ppy
2010

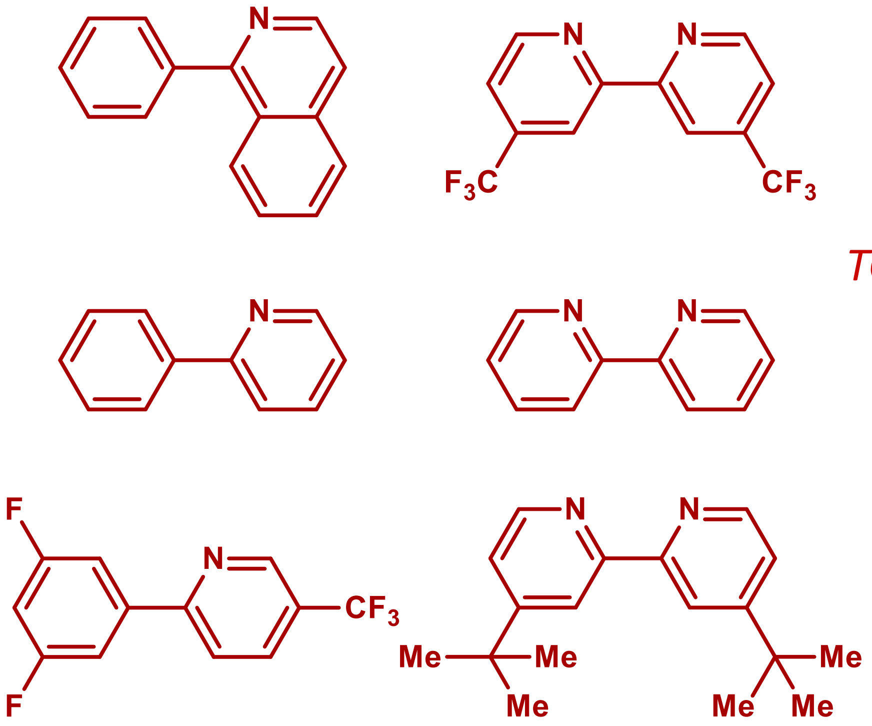
David Macmillan

CHAPTER III How to define the ultimate catalyst in photoreaction?

This is an open question, for real-world problem, there are always more than one answers…

Commercially available? YES, we don't do organometallics.

Normally, we don't tend to screen the PC delicately
Because the reactivity-property-structure relationship
Is hard to predict.



TCI available Iridium complex (PF_6)
1g > 1900 ¥

…ist keine Frage der Theorie, soudern einepraktische Frage.

PRINCIPLE III: Good photo physics don’t always lead to good reactivity

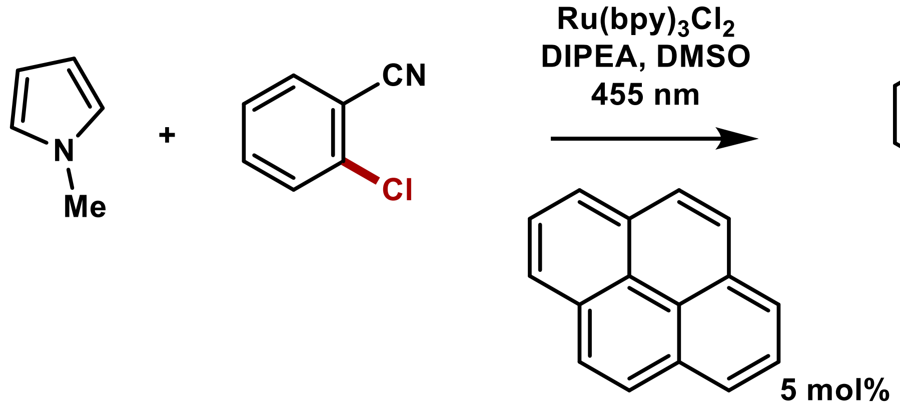
Cage effect is so important while we’ll skip this due to the limited time.

(1) *Bianco, A.; Natali, M.; Bergamini, G. When Better Quenching Means Lower Yields: Electrostatic Control of Cage Escape. ACS Phys. Chem Au* ***2026****, 6 (1), 185–195.*

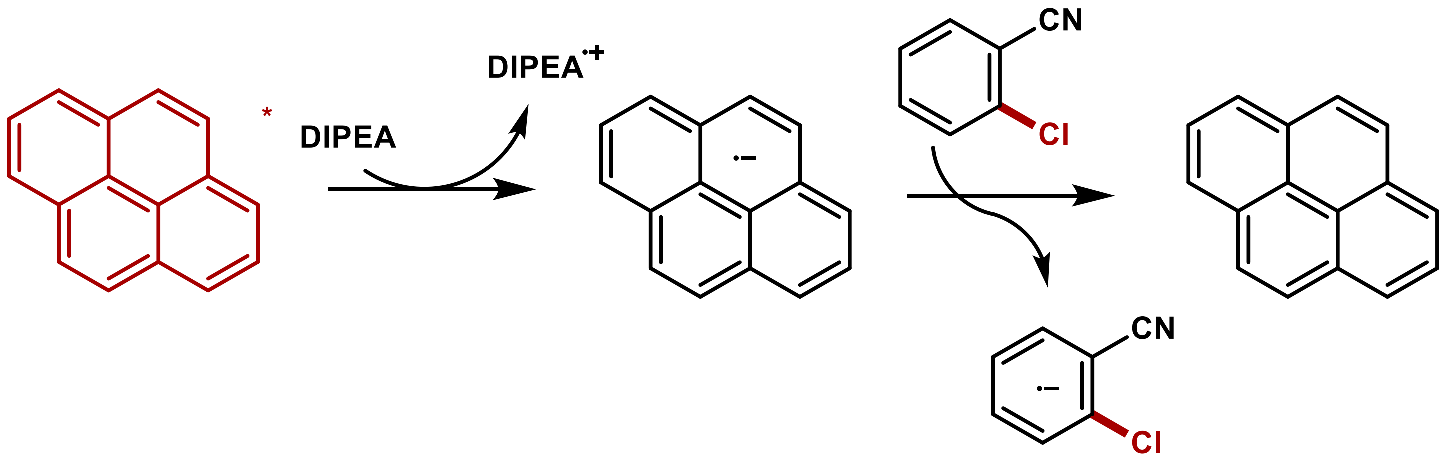
(2) *Wang, C.; Li, H.; Bürgin, T. H.; Wenger, O. S. Cage Escape Governs Photoredox Reaction Rates and Quantum Yields. Nature Chemistry* ***2024****, 16 (7), 1151–1159.*

Topic I: *Multi photon process*

2017 König



Initial proposed mechanism



(1) Ghosh, I.; Shaikh, R. S.; König, B. *Angew. Chem. Int. Ed.* **2017**, *56* (29), 8544–8549. (2) Marchini, M.; Bergamini, G.; Cozzi, P. G.; Ceroni, P.; Balzani, V. *Angew. Chem. Int. Ed.* **2017**, *56* (42), 12820–12821. (3) Coles, M. S.; Quach, G.; Beves, J. E.; Moore, E. G. *Angew. Chem. Int. Ed.* **2020**, *59* (24), 9522–9526.

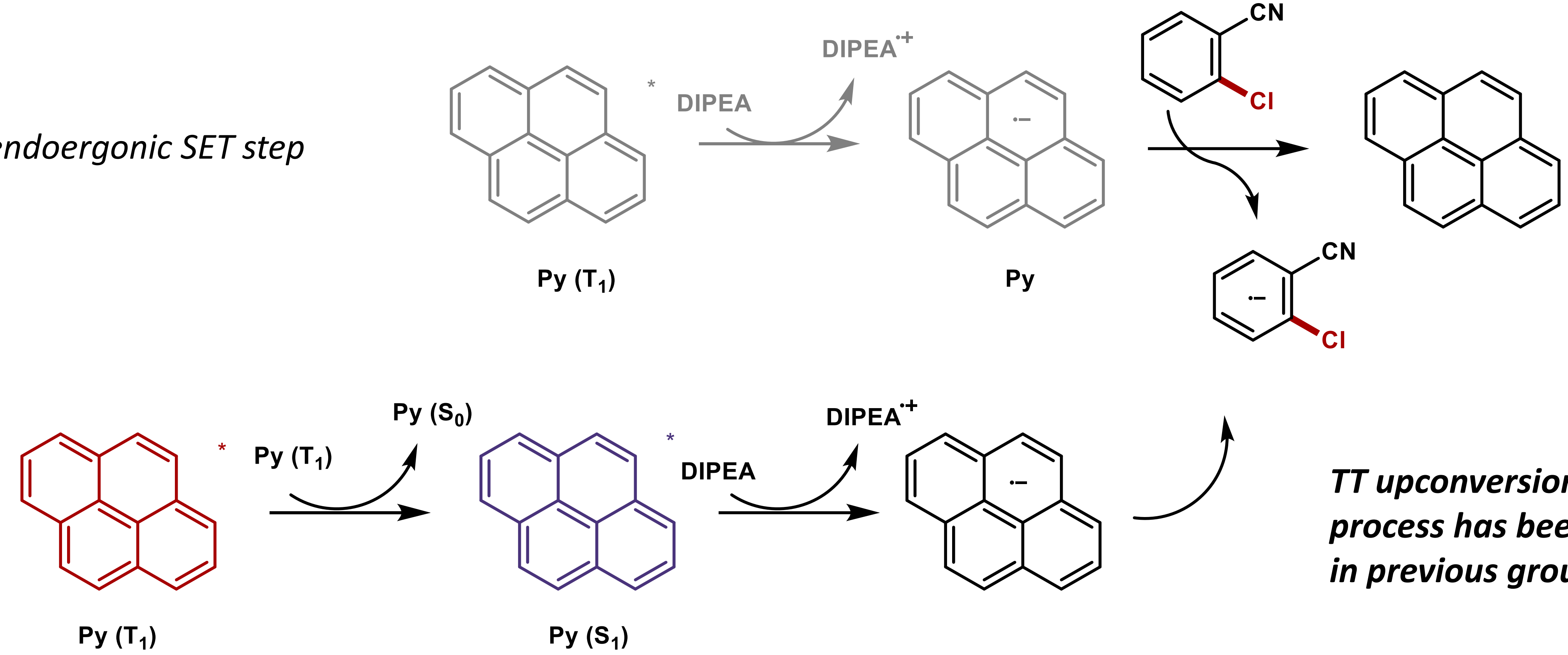
Topic I: *Multi photon process*

2017 Balzani

$$E[\mathrm{Py(T_1)/Py^-}] = E[\mathrm{Py/Py^-}] + E_{00}[\mathrm{Py/Py(T_1)}] = -2.1 + 2.0 = -0.1\ \mathrm{V}$$

$$E[\mathrm{DIPEA^+/DIPEA}] = +0.9\ \mathrm{V\ vs.\ SCE}^{[7]}$$

Highly endoergonic SET step



TT upconversion process has been discussed in previous group meeting.

SoA: Moore proposed T1-Ru(I) SET.

(1) Ghosh, I.; Shaikh, R. S.; König, B. *Angew. Chem. Int. Ed.* **2017**, *56* (29), 8544–8549. (2) Marchini, M.; Bergamini, G.; Cozzi, P. G.; Ceroni, P.; Balzani, V. *Angew. Chem. Int. Ed.* **2017**, *56* (42), 12820–12821. (3) Coles, M. S.; Quach, G.; Beves, J. E.; Moore, E. G. *Angew. Chem. Int. Ed.* **2020**, *59* (24), 9522–9526.

Topic I: *Multi photon process*

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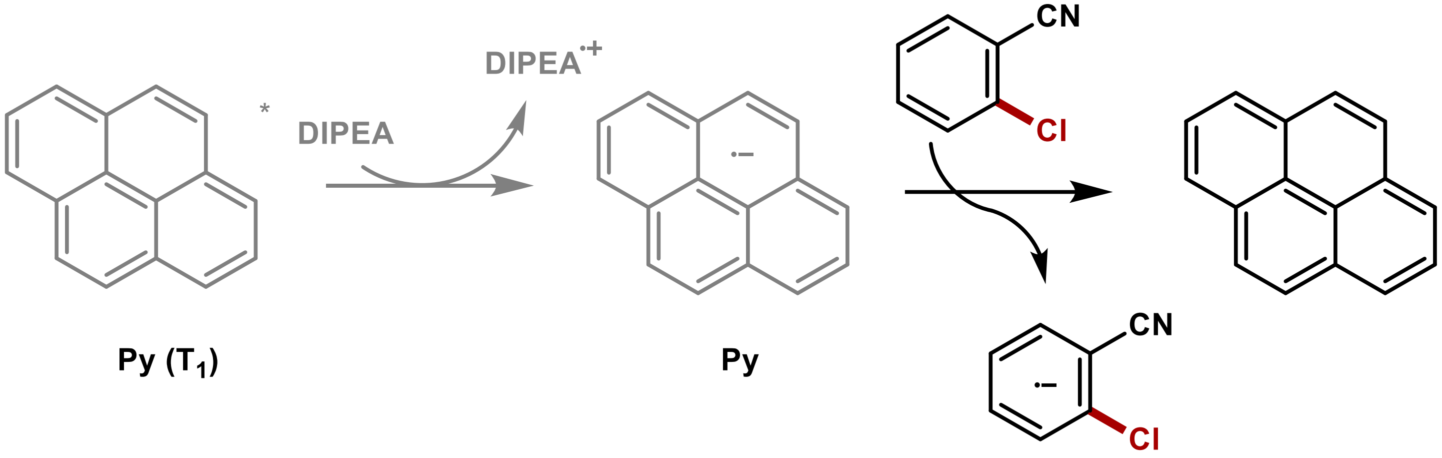
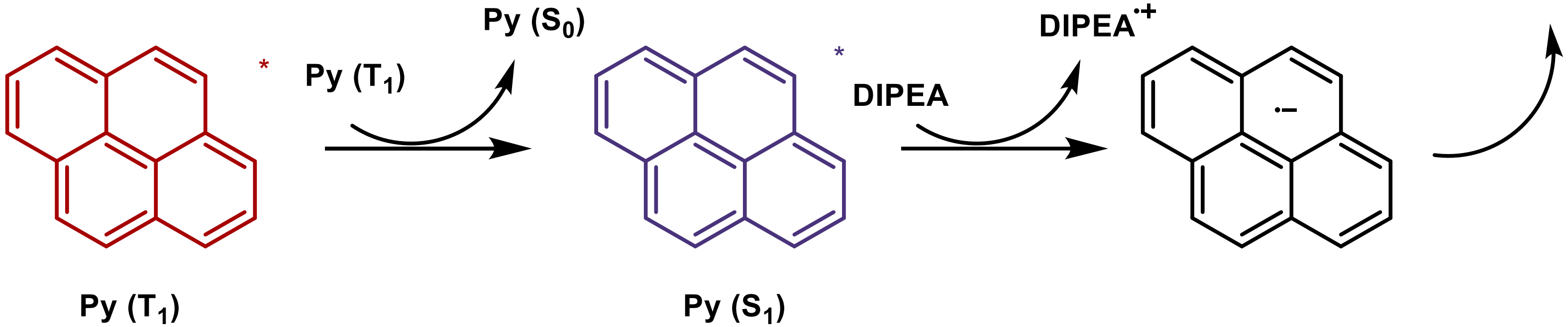




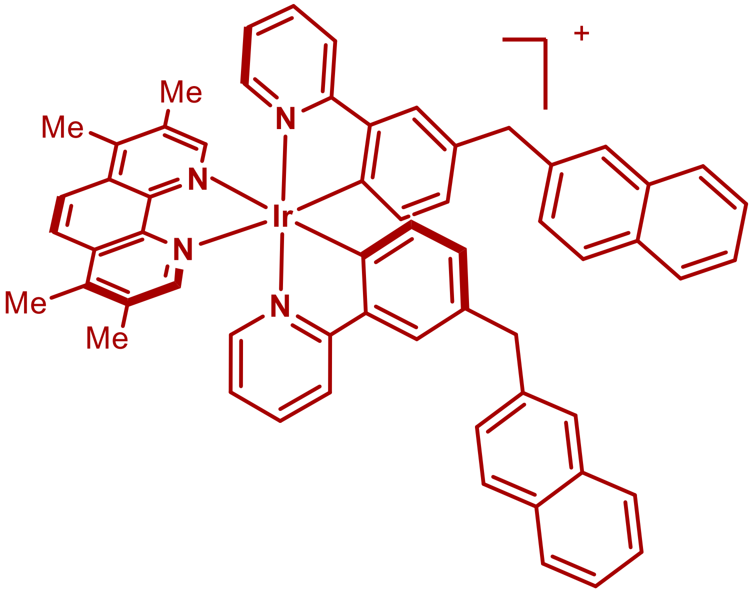
TT upconversion process has been discussed in previous group meeting.

Two-photon process delivered the product.

(1) Ghosh, I.; Shaikh, R. S.; König, B. *Angew. Chem. Int. Ed.* **2017**, *56* (29), 8544–8549. (2) Marchini, M.; Bergamini, G.; Cozzi, P. G.; Ceroni, P.; Balzani, V. *Angew. Chem. Int. Ed.* **2017**, *56* (42), 12820–12821. (3) Coles, M. S.; Quach, G.; Beves, J. E.; Moore, E. G. *Angew. Chem. Int. Ed.* **2020**, *59* (24), 9522–9526.

Topic I: *Multi photon process*

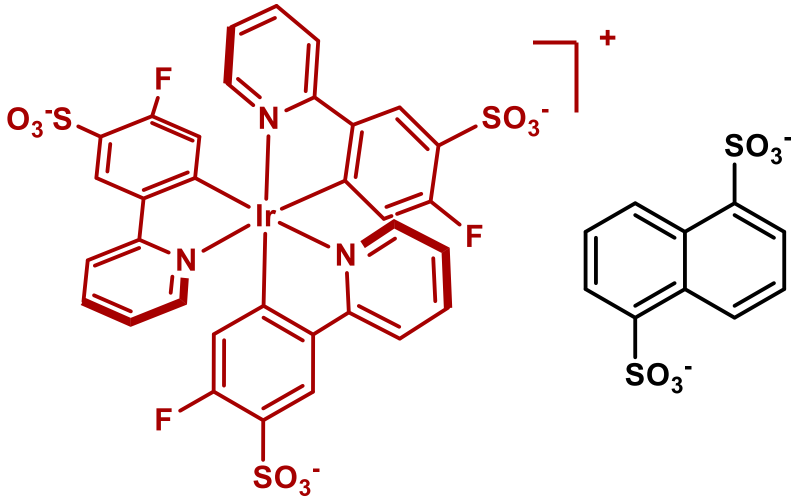
2025 Maestri



Key ideas:

- ***Diradical stabilization, no external pyrene needed.***
- ***Reaction focus***

2020 Kerzig



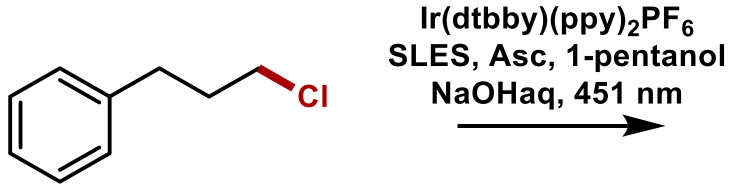
Key ideas:

- ***Water-soluble system enable longer LMCT lifetime.***
- ***Strongest upconversion (447 nm to 4 eV, 310 nm)***

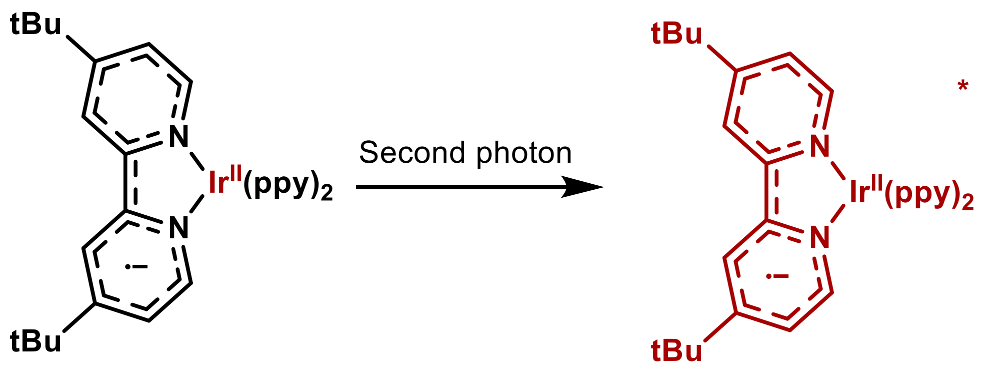
(1) Pfund, B.; Steffen, D. M.; Schreier, M. R.; Bertrams, M.-S.; Ye, C.; Börjesson, K.; Wenger, O. S.; Kerzig, C. *J. Am. Chem. Soc.* **2020**, *142* (23), 10468–10476. (2) Ruggeri, D.; Hoch, M.; Spataro, D.; Marchiò, L.; Protti, S.; Cauzzi, D.; Tegoni, M.; Lanzi, M.; Maestri, G. *Chemistry – A European Journal* **2025**, *31* (18), e202403309.

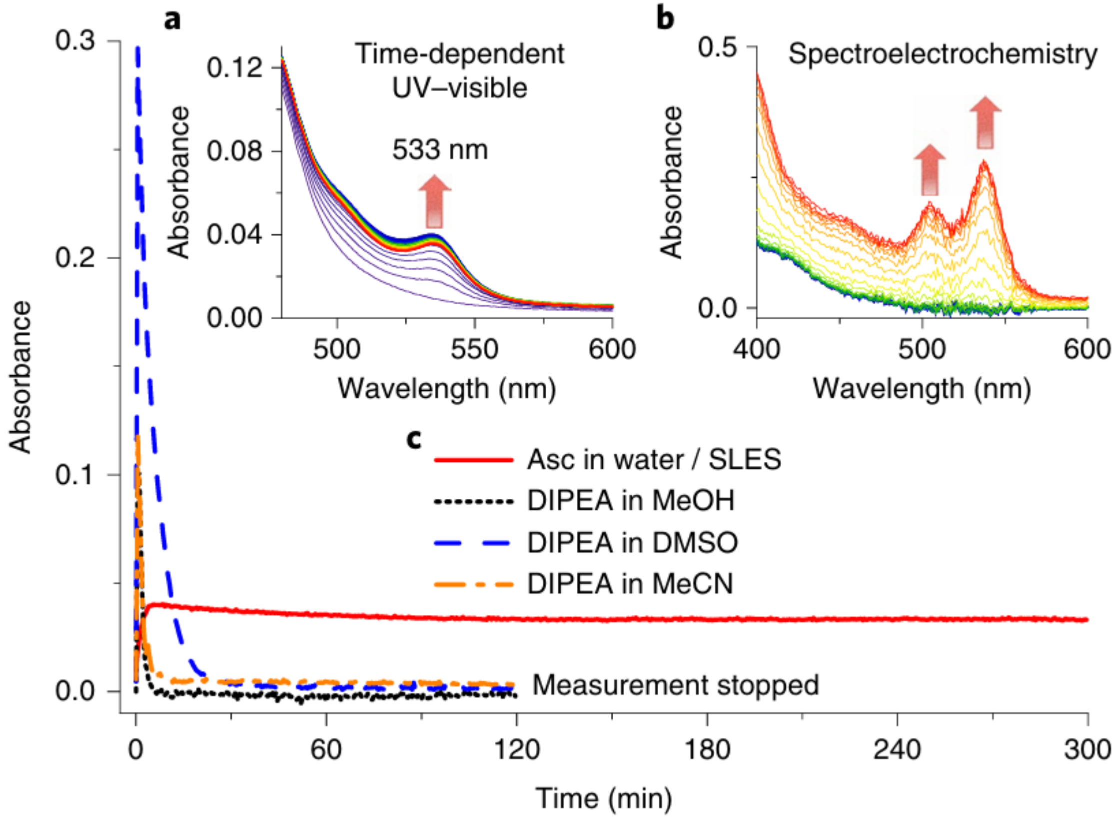
Topic I: *Multi photon process*

2020 König



- 2.8 V vs. SCE

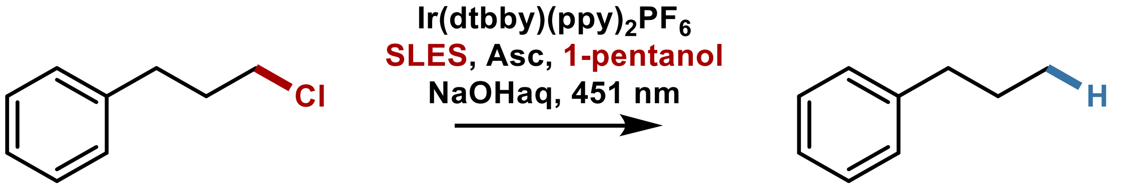




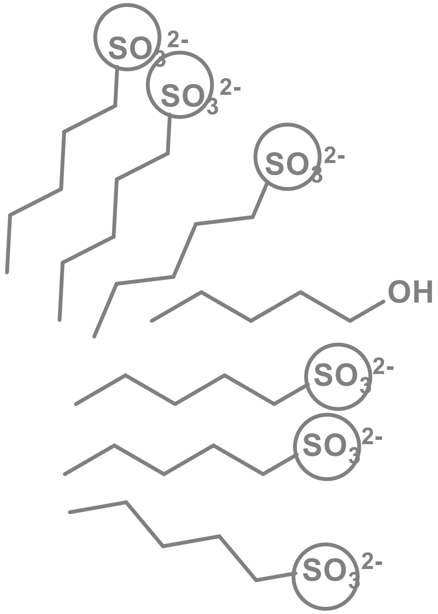
(1) Giedyk, M.; Narobe, R.; Weiß, S.; Touraud, D.; Kunz, W.; König, B. *Nature Catalysis* **2020**, *3* (1), 40–47.

König's tree is very elegant

2020 König



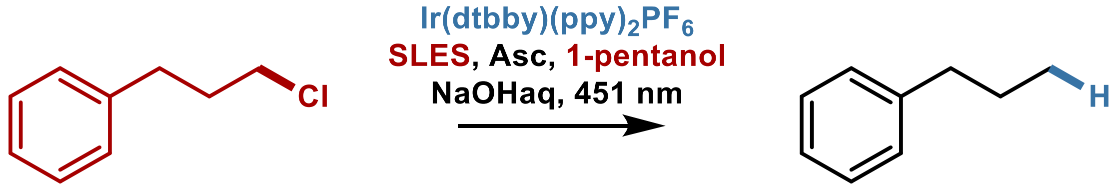
Micelles improve microstructure and pre-aggression.



(1) Giedyk, M.; Narobe, R.; Weiß, S.; Touraud, D.; Kunz, W.; König, B. *Nature Catalysis* **2020**, *3* (1), 40–47.

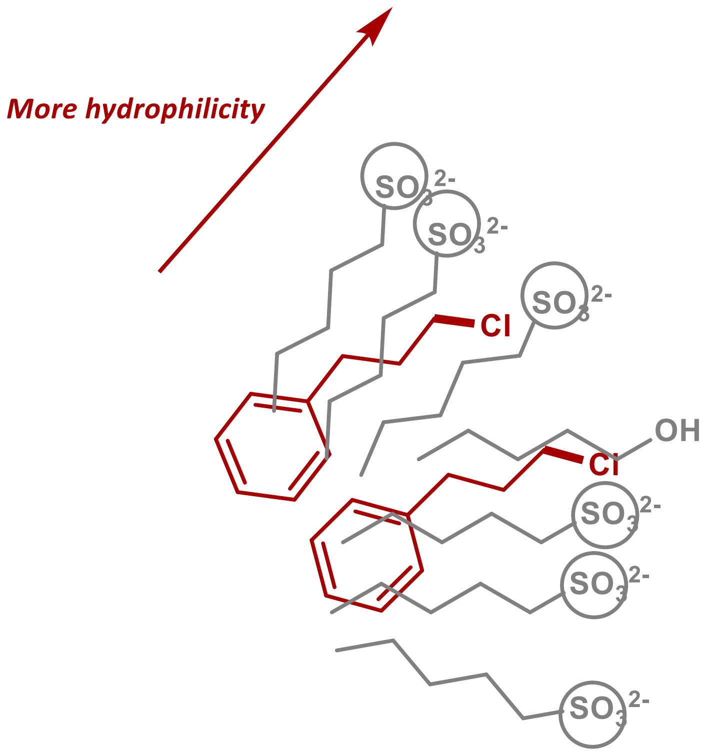
König's tree is very elegant

2020 König



Micelles improve microstructure and pre-aggression.

Chloride pointed out because of polarity



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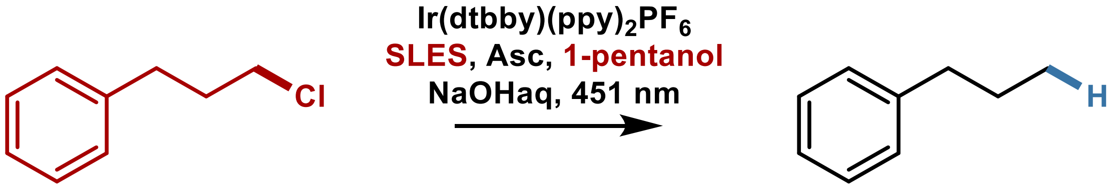
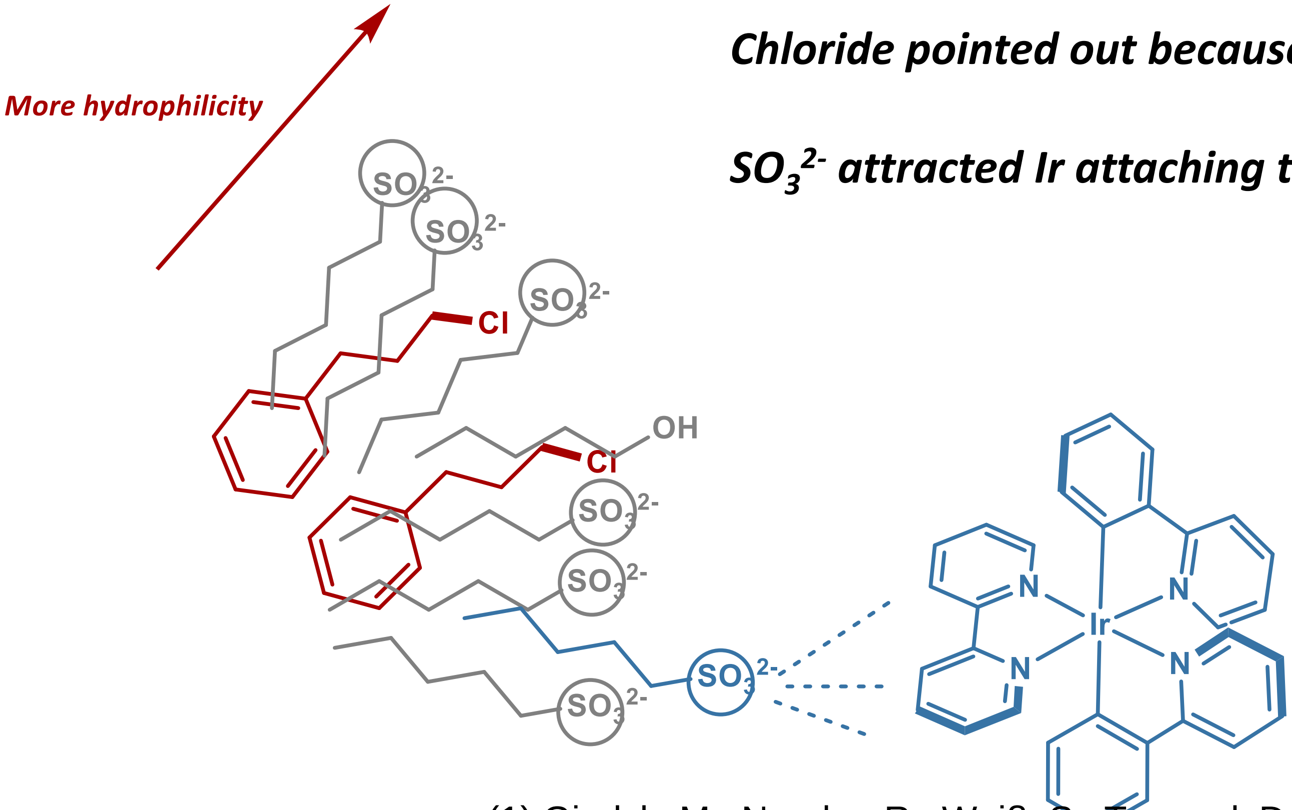


Micelles improve microstructure and pre-aggression.

Chloride pointed out because of polarity

SO_3^{2-} attracted Ir attaching to surface of micelles

SLES > SDS > Potassium Laurate



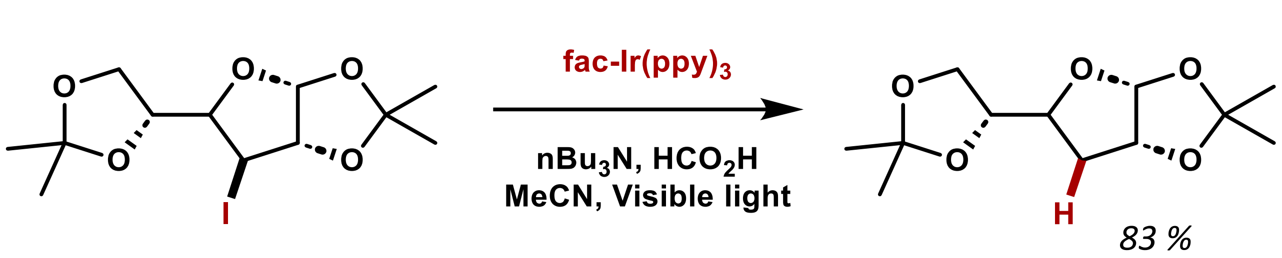
The micelles-Ir/Ru system
also produce solvated electrons
~ -2.9 V   Key player: Goez

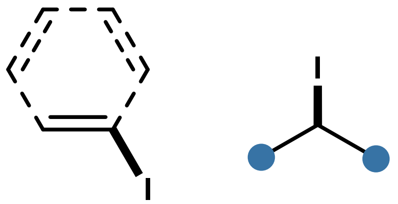
(1) Giedyk, M.; Narobe, R.; Weiß, S.; Touraud, D.; Kunz, W.; König, B. *Nature Catalysis* **2020**, *3* (1), 40–47.

***Topic II**: Highly reductive photocatalytic systems*

(1) Shon, J.-H.; Teets, T. S. *Chem. Sci.* **2021**, *12* (11), 4069–4078. (2) Giedyk, M.; Narobe, R.; Weiß, S.; Touraud, D.; Kunz, W.; König, B. *Nature Catalysis* **2020**, *3* (1), 40–47. (3) Nguyen, J. D.; Stephenson, C. R. *Nat. Chem.* **2012**, *4* (10), 854–859.

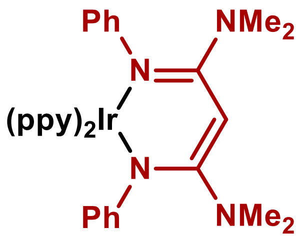
2012 Stephenson

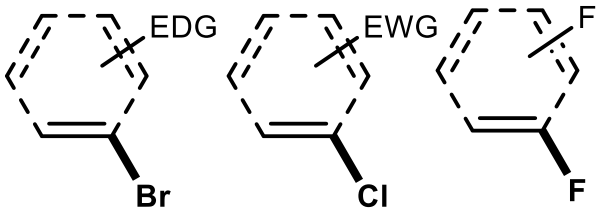




Ir(ppy)$_3$ (IV/III) = -1.73 V vs. SCE (-1.49 V)*

2021 Teets

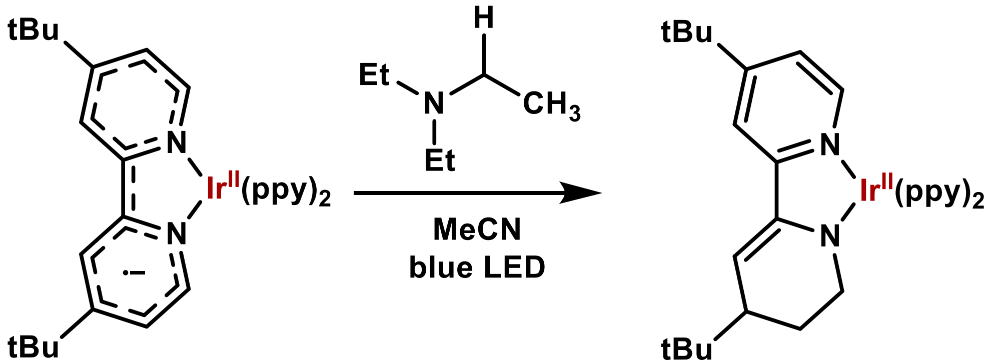




Ir(ppy)$_2$L (IV/III) = -2.6 V vs. Fc (-1.9 V)*

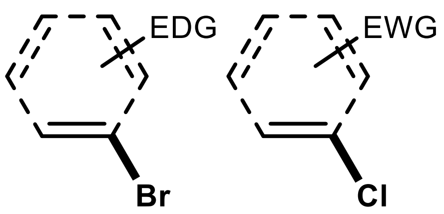
Ligand engineering: NacNac

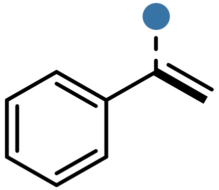
2019 Francis



Ir(ppy)$_2$H-bpy (IV/III) = -1.70 V vs. SCE (-1.46 V)*

Tandem Iridium cycle

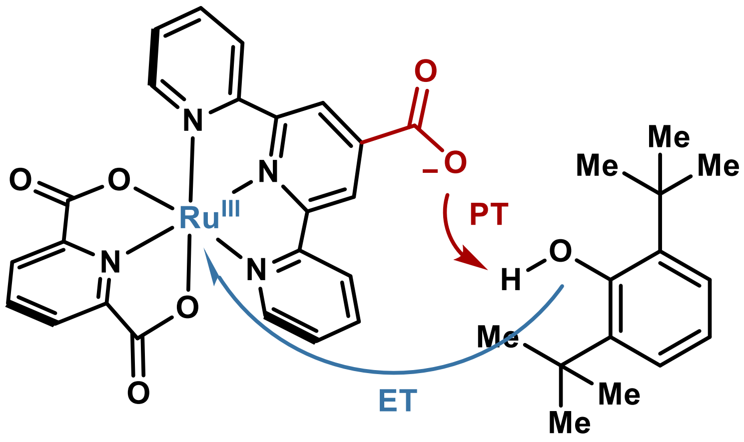




-2.25 V vs. SCE (-2.01 V)

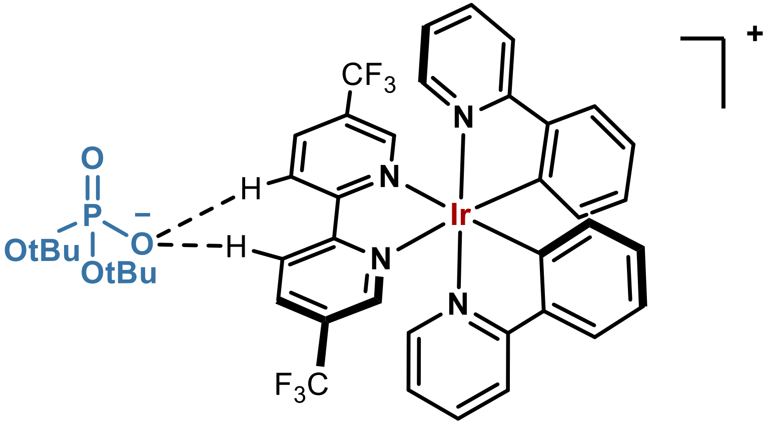
Topic III:*PCET-guided Engineering* ***Can Ru/Ir photocatalyst undergo direct HAT process?***

2008 Meyer

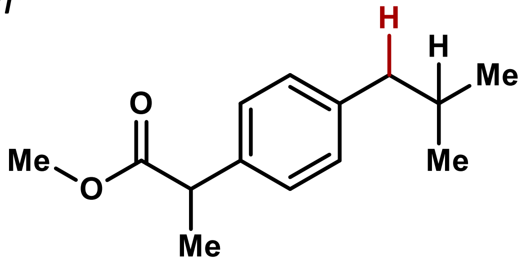


- *Fundamental state reaction*
- *When Pai system extended, PCET rate uncorrelated to BDE*

2019 Alexanian



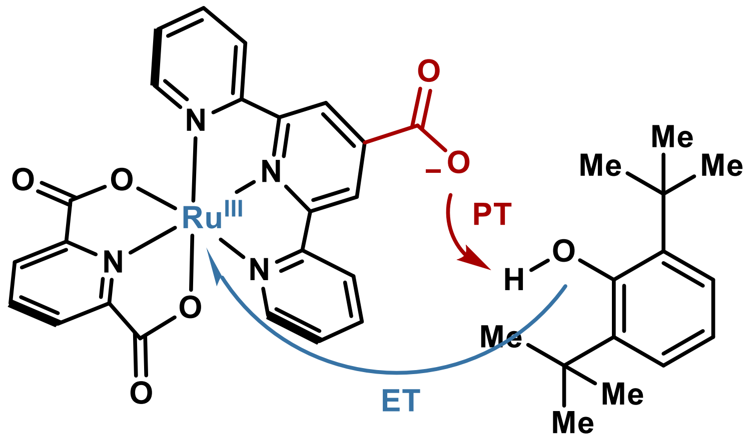
- *Secondary, tertiary alkyl radical*
- *Giese reaction*
- *No PKa preference shown.*



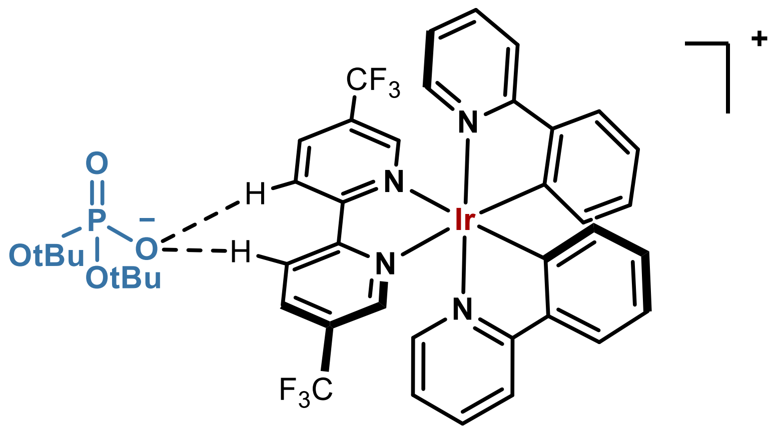
83% yield, single product

Topic III**: PCET-guided Engineering*   ***Can Ru/Ir photocatalyst undergo direct HAT process?

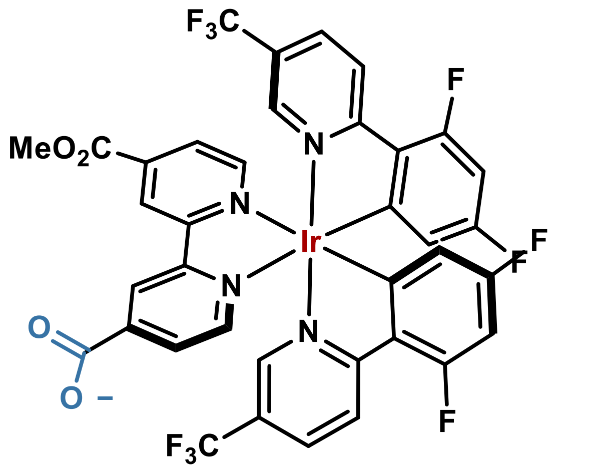
2008 Meyer



2019 Alexanian



2025 Knowles

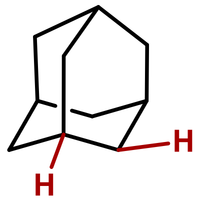


- *Fundamental state reaction*
- *When Pai system extended, PCET rate uncorrelated to BDE*

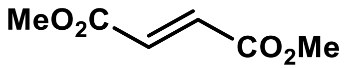
- *Secondary, tertiary alkyl radical*
- *Giese reaction*
- *No PKa preference shown.*

- *Secondary, tertiary alkyl radical*
- *KIE ~ 1.3 (For Alexanian, 2.0)*
- *Very poor regioselectivity!*

(1) Granados, D. A.; Knowles, R. R. *J. Am. Chem. Soc.* **2025**, *147* (24), 20703–20715. (2) Manner, V. W.; Mayer, J. M*J. Am. Chem. Soc.* **2008**, *130* (23), 7210–7211. (3) Manner, V. W.; Mayer, J. M. *J. Am. Chem. Soc.* **2009**, *131* (29), 9874–9875. (4) Morton, C. M.; Alexanian, E. *J. Am. Chem. Soc.* **2019**, *141* (33), 13253–13260.



67% yield, 1:1,



Summary: We have come a long way!

PRINCIPLE I: The photocatalyst should have long-lived excited state

PRINCIPLE II: The metal-centered states are short-lived and always disfavored in catalyst design. (State-mixing is acceptable, unless leading to non-radiative decay)

PRINCIPLE III: Good photo physics don’t always lead to good reactivity