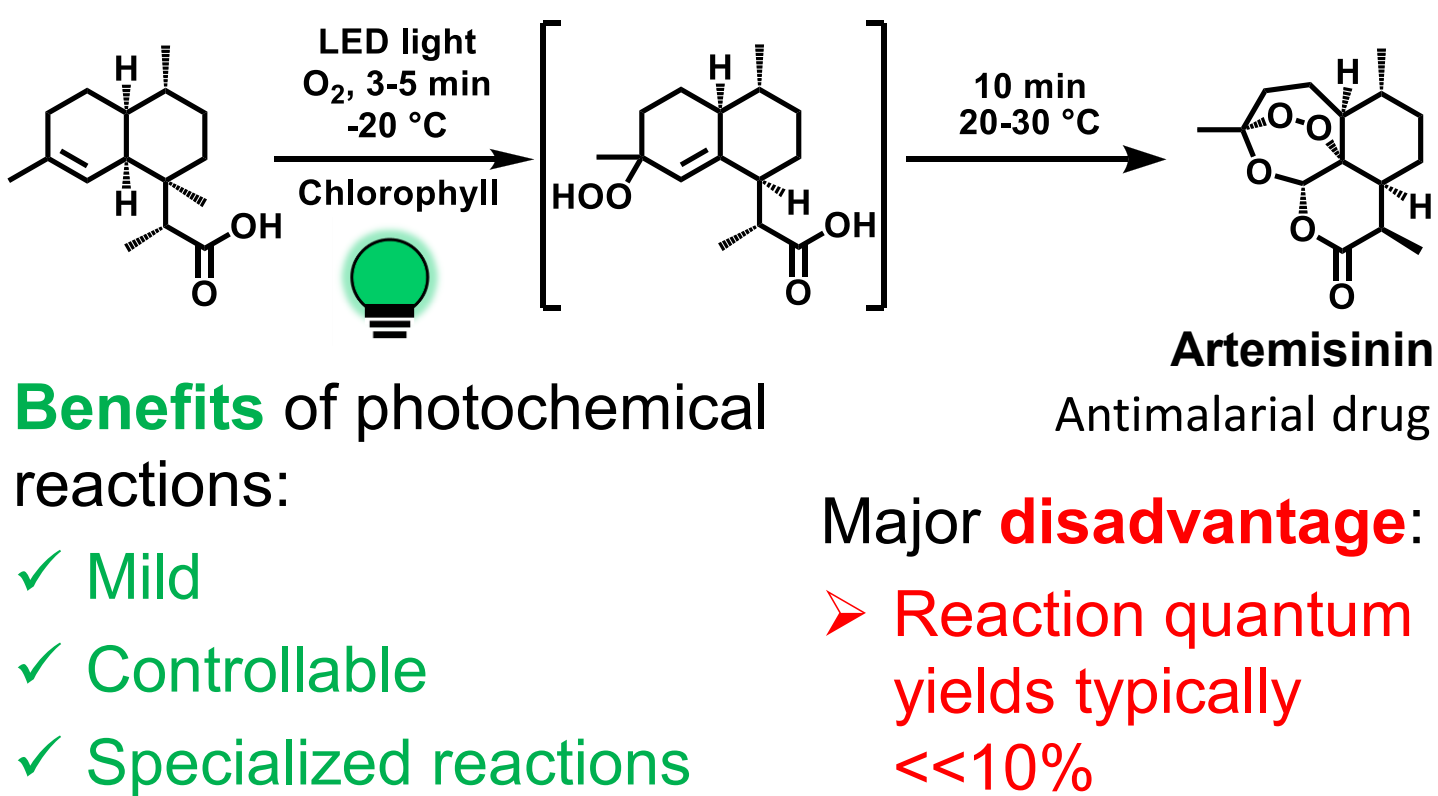# Increasing the Efficiency of Photochemical Elementary Steps

Matthias Schmitz, Maria-Sophie Bertrams, Jun.-Prof. Dr. Christoph Kerzig
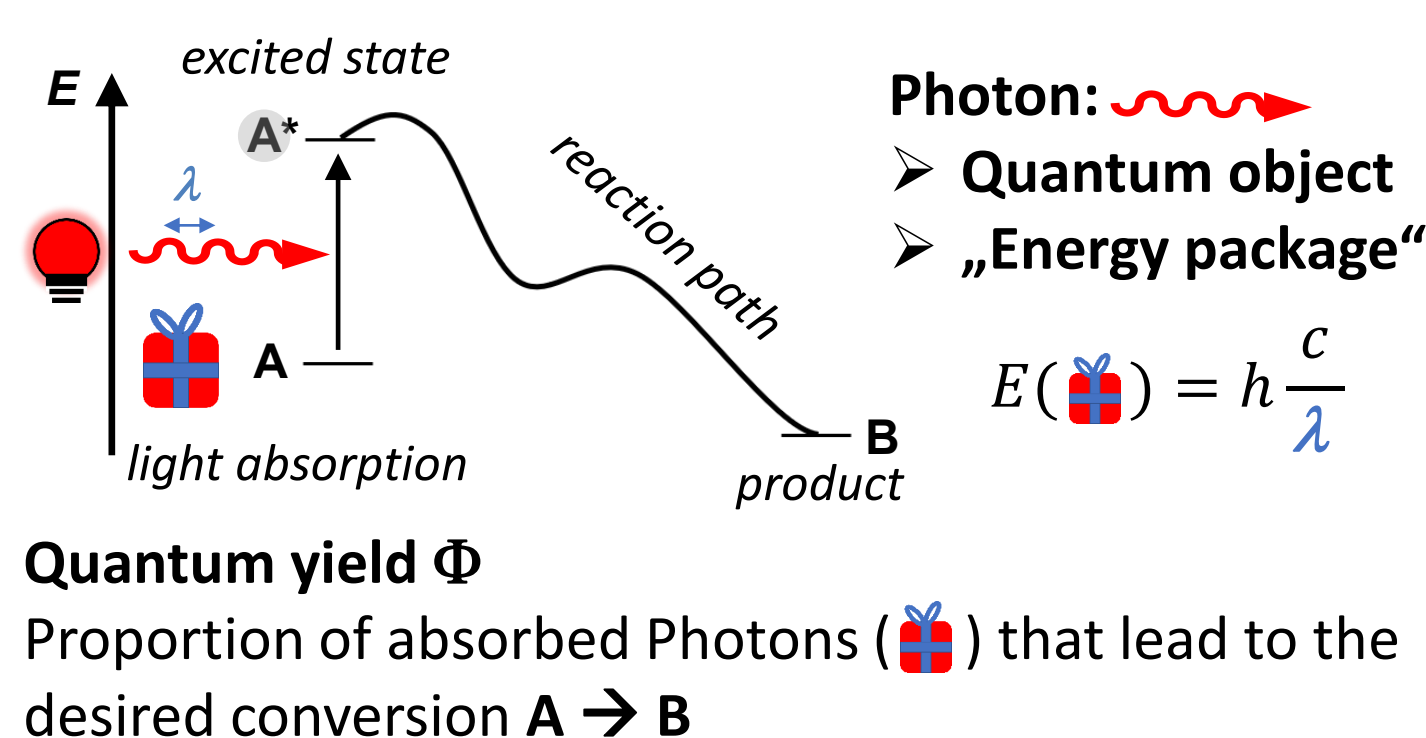Johannes Gutenberg University Mainz, Department of Chemistry

Abstract: Photocatalysis offers great potential for changing the synthesis of value-added molecules, yet many reactions suffer from low efficiencies hindering industrial scalability. Molecular dyads are attractive photocatalysts that enable milder conditions and higher reaction efficiencies for photochemical elemenraty steps (energy and electron transfer) by combining the properties of inorganic and organic chromophores.[1–3] In this study, we introduce a novel method for generating molecular dyads by mixing a cationic ruthenium complex with an anionic pyrene derivative in water, forming a salt bichromophore via electrostatic interactions. This Coulombic dyad exhibits long organic triplet lieftimes through energy transfer from the ruthenium complex, enabling efficient energy transfer catalysis. Compared to traditional molecular dyads and reference photosensitizers, the Coulombic dyad demonstrates similar reactivity and superior photostability in various photooxygenations. Furthermore, it enhances the quantum yield of photoredox reactions, attributed to higher cage escape quantum yields after photoinduced electron transfer.[2] Mechanistic insights gained from laboratory-scale experiments and spectroscopic investigations provide a comprehensive understanding of this easy-to-use photocatalyst class.

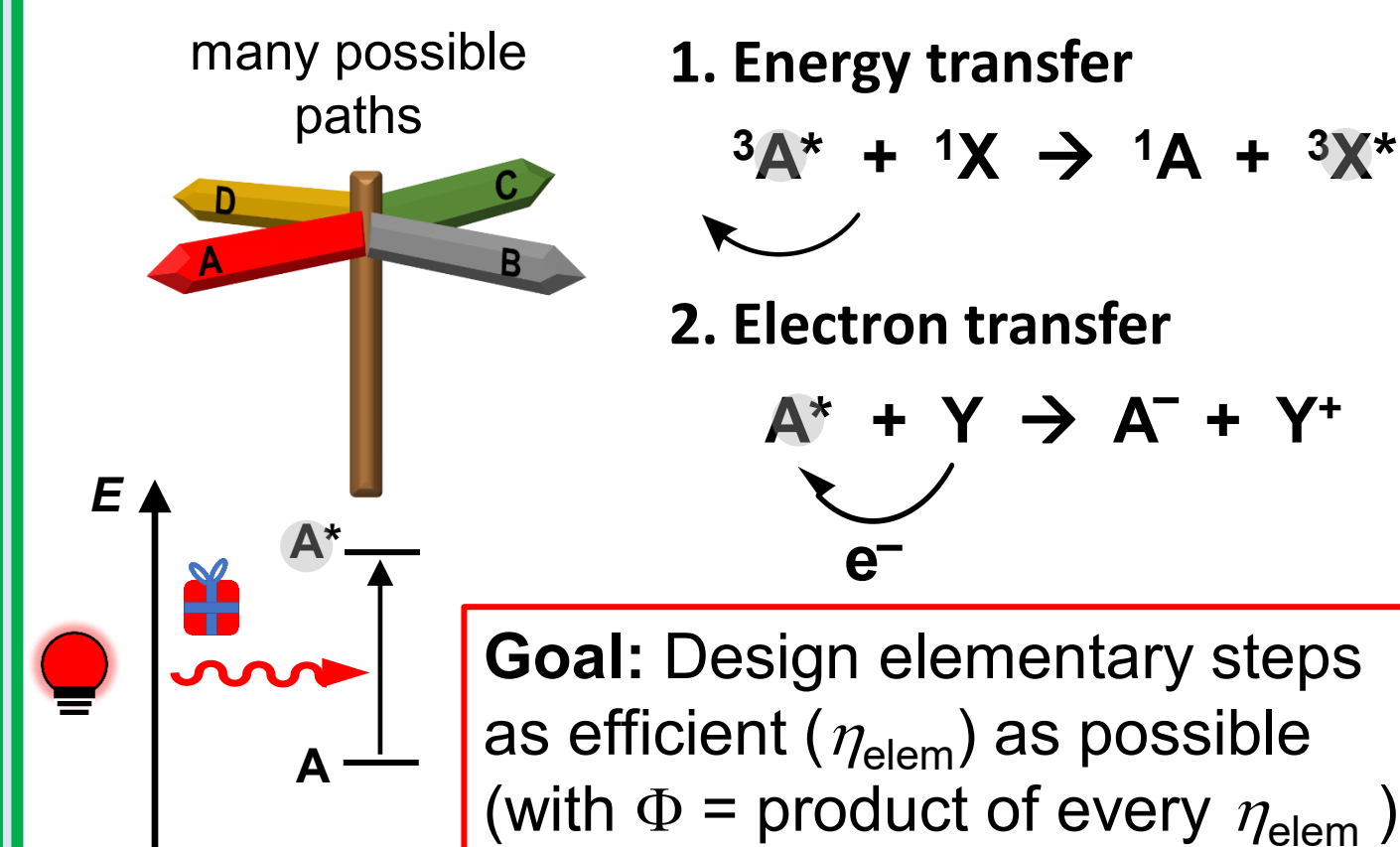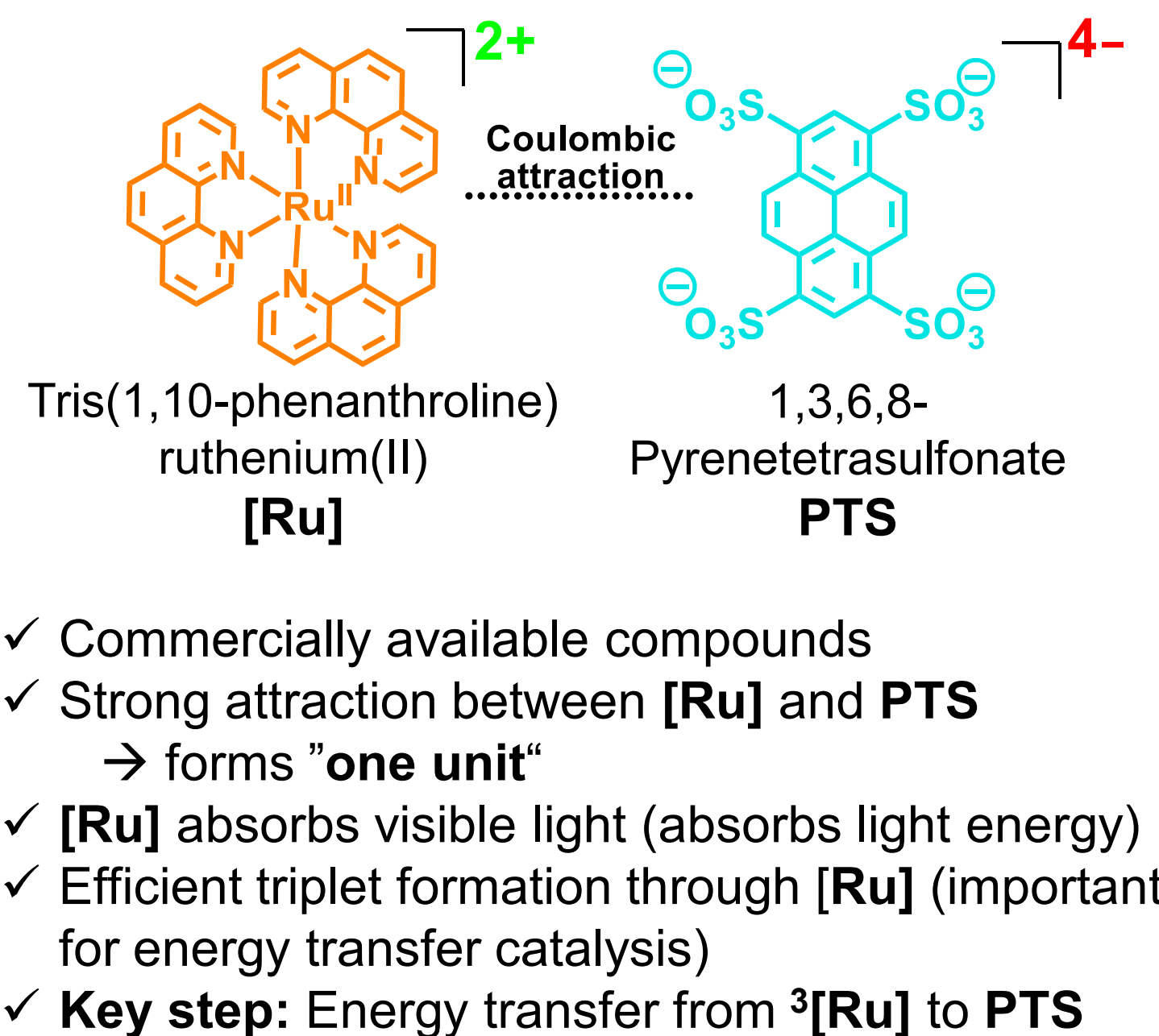## Photochemistry in Industry – Essentially the Only Example

LED light
O_2, 3-5 min
-20 °C
Chlorophyll

10 min
20-30 °C

Artemisinin
Antimalarial drug

Benefits of photochemical reactions:
- ✓ Mild
- ✓ Controllable
- ✓ Specialized reactions

Major **disadvantage**:
➤ Reaction quantum yields typically <<10%

Definition Quantum Yield

Simplyfied photochemical reaction

E
excited state
A*
λ
reaction path
A
light absorption
product
B

Photon:
➤ Quantum object
➤ „Energy package"

$$E = h \frac{c}{\lambda}$$

Quantum yield Φ
Proportion of absorbed Photons that lead to the desired conversion **A → B**

Most Important Elementary Steps

many possible paths

1. Energy transfer
$$^3A^* + {}^1X \rightarrow {}^1A + {}^3X^*$$

2. Electron transfer
$$A^* + Y \rightarrow A^- + Y^+$$
e^-

E
A*
A

Goal: Design elementary steps as efficient (η_{elem}) as possible (with Φ = product of every η_{elem})

Novel Catalyst System

2+

4−

Tris(1,10-phenanthroline) ruthenium(II)
[Ru]

1,3,6,8-Pyrenetetrasulfonate
PTS

- ✓ Commercially available compounds
- ✓ Strong attraction between **[Ru]** and **PTS** → forms "**one unit**"
- ✓ **[Ru]** absorbs visible light (absorbs light energy)
- ✓ Efficient triplet formation through [Ru] (important for energy transfer catalysis)
- ✓ **Key step:** Energy transfer from ^{3}**[Ru]** to **PTS**

Transient Absorption (TA) Spectroscopy – Most Important Measurement Technique in this Project

Laser flash photolysis

① I_0 — I — Detector "probe" Laser
② Detector "pump" Laser
③ I_0 — I — Detector "probe" Laser

100%
[Ru]
"pump"
40%
[Ru]
^{3}[Ru]*
0%
60%
^{3}[Ru]*

① absorption
$A = \lg(I_0/I)$
λ / nm

more absorption
less absorption

③ − ①

characteristic ("fingerprint") transient absorption spectrum for ^{3}**[Ru]***

LP 980

Time-resolved (~5 ns resolution)

$$\frac{I_0}{I} = e^{\frac{t}{\tau}}$$

emission
absorption
laser pulse
excited state lifetime
$\tau = 1.1\ \mu s$

Efficient Energy Transfer Catalysis

2+   4−

[Ru]   **PTS** ^{3}**[Ru]***   PTS   **[Ru]** ^{3}**PTS***
short lifetime   TTEnT   long lifetime

quantitative, key step

Proof that ^{3}PTS is the key species

^{3}(Ruphen···PTS) $\tau_T = 214\ \mu s$
$^3(\pi\pi^*)$
λ_{det}
^{3}Ruphen
ΔA
λ / nm
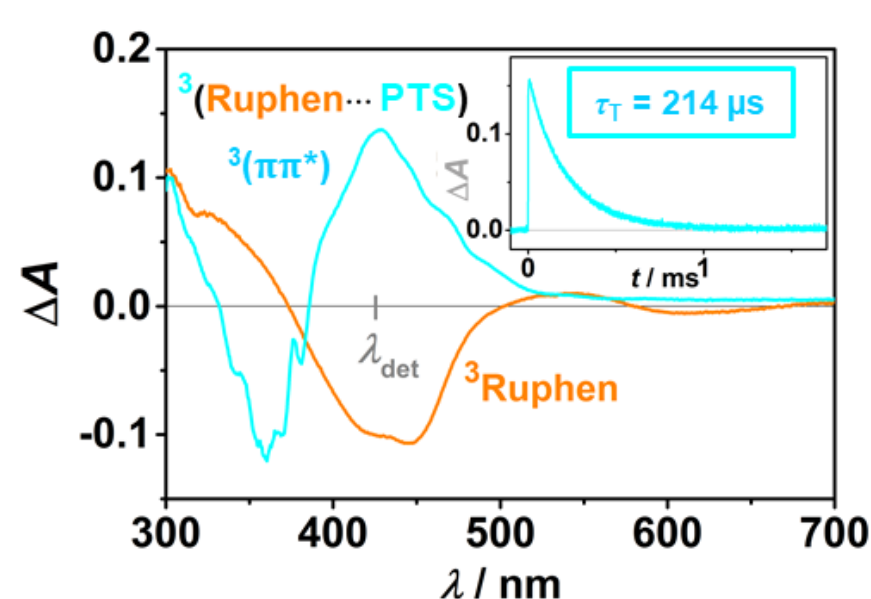
Connection between lifetime and reaction efficiency

$c(O_2) = 0.27$ mM
air-saturated water
$k_q = 5 \cdot 10^9\ M^{-1}\ s^{-1}$

214 μs
1.1 μs

η (triplet quenching)
$\tau_{0,triplet}$ / s
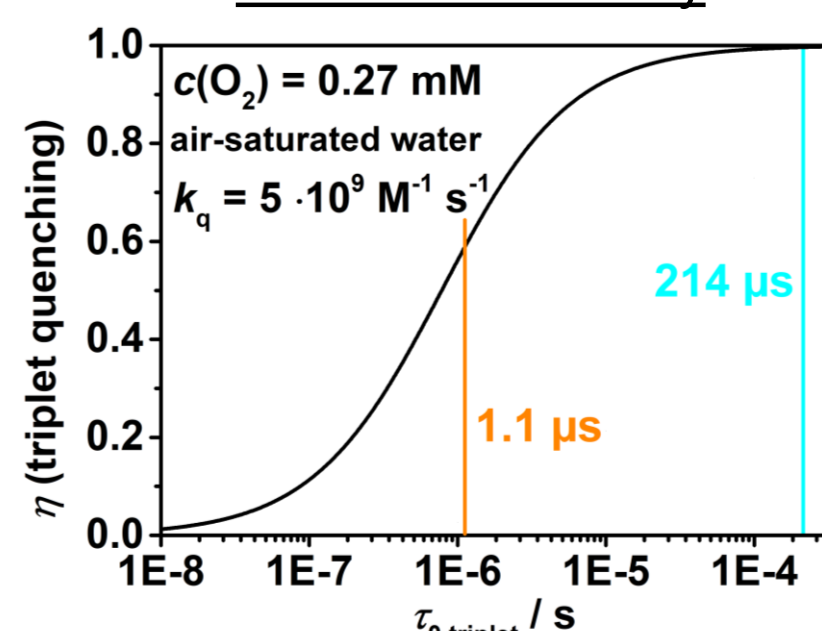
Formation and utilization of $^1O_2$

[Ru]
(+ PTS)
O_2
via $^1O_2$
biopolymer precursor

product yield / %
with PTS
only [Ru]
t / min
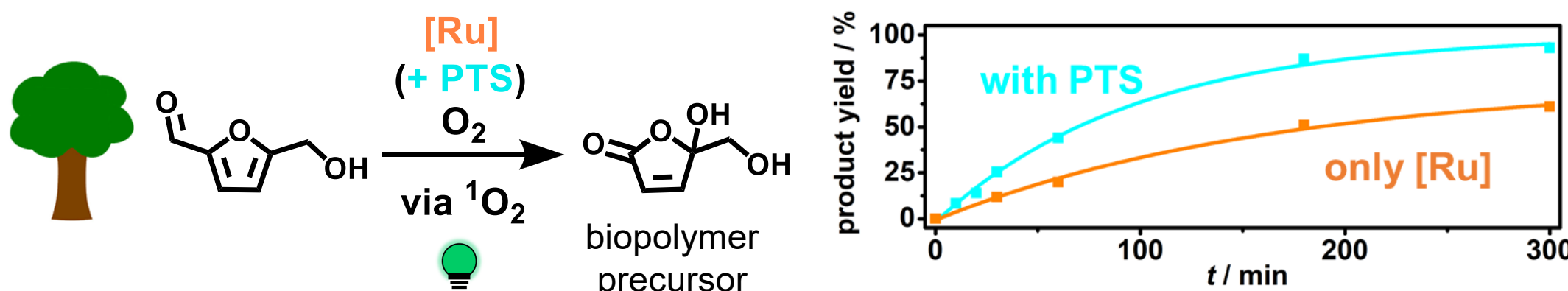
Efficient Electron Transfer Catalysis

HAsc$^-$

$\eta_{ET1} = 21\%$

SOC > SOC
$\Phi_{CE} < \Phi_{CE}$

$\eta_{ET1} \sim 100\%$

HAsc$^\bullet$ HAsc$^-$ ^{3}[Ru] ^{3}PTS   HAsc$^-$ HAsc$^\bullet$

inefficient direct path   [Ru]$^{\bullet -}$ $h\nu$ $\eta \approx 1$ PTS$^{\bullet -}$ **efficient indirect path**

S   [Ru]   PTS   S
S$^{\bullet -}$ S$^{\bullet -}$

S = substrate
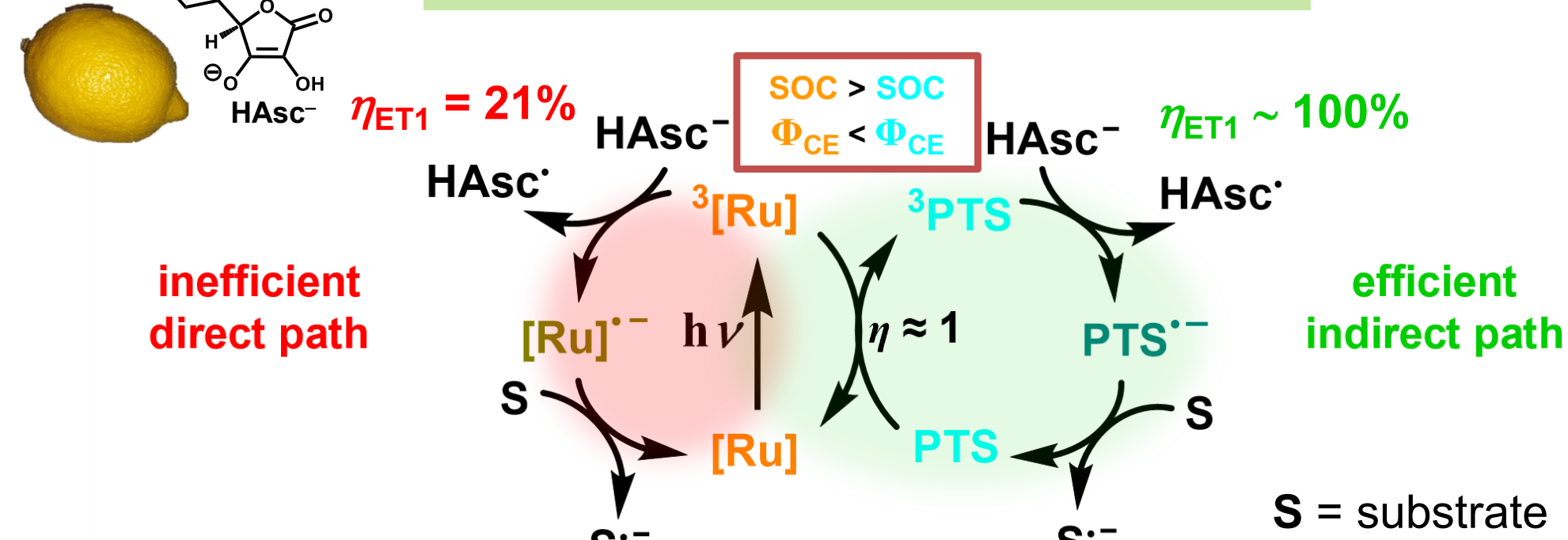
Characteristic TA spectra of all key species

^{3}Ruphen   Ruphen$^+$
^{3}PTS   PTS$^{\bullet -}$
$\Delta\varepsilon$ / $10^4\ M^{-1}cm^{-1}$
λ / nm
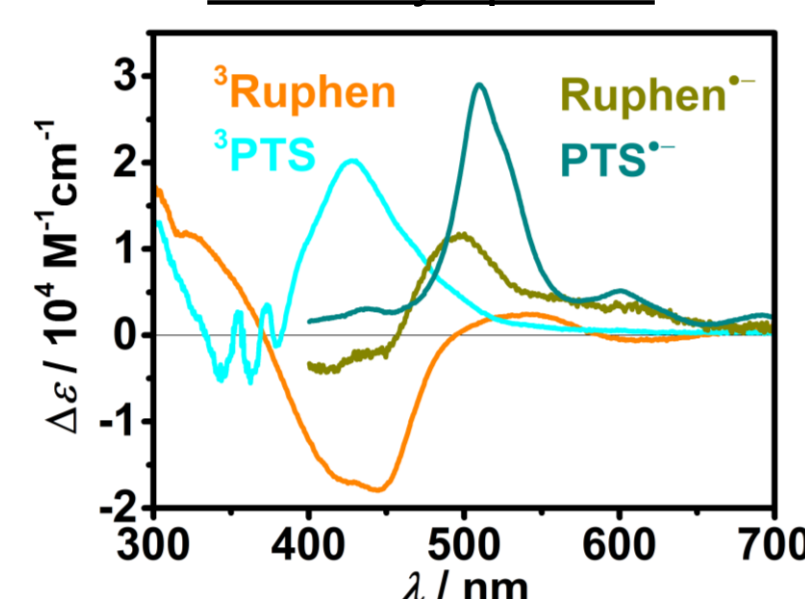
Quantification of the key species

^{3}Ruphen
PTS$^{\bullet -}$ $\Phi = 0.97$
$\Phi = 0.16$ Ruphen$^{\bullet -}$
c_{rel} / μM
t / μs
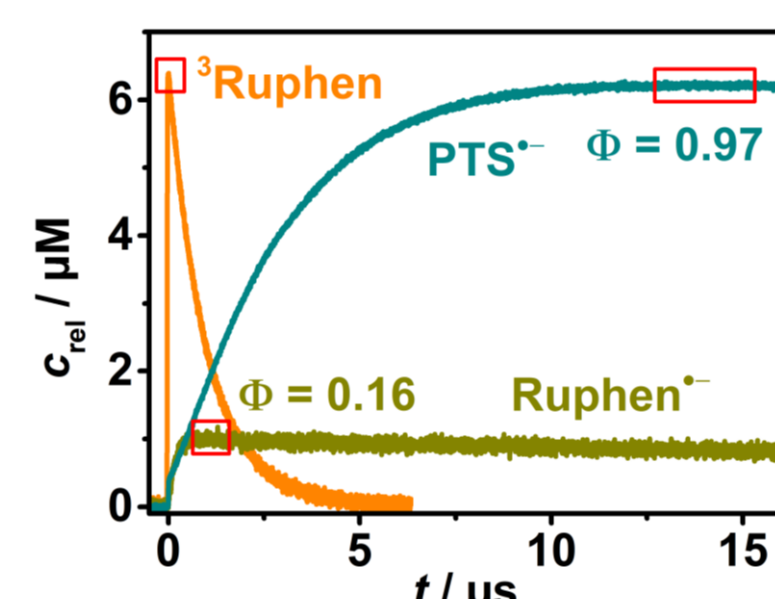
Bond formation and bond clevage

$R^1 R^2$ 2 e$^-$, 2 H$^+$ R^1 OH R^2 OH

R—Br   e$^-$, H$^+$, -Br$^-$ R—H

product yield / %
with PTS
only [Ru]
t / h
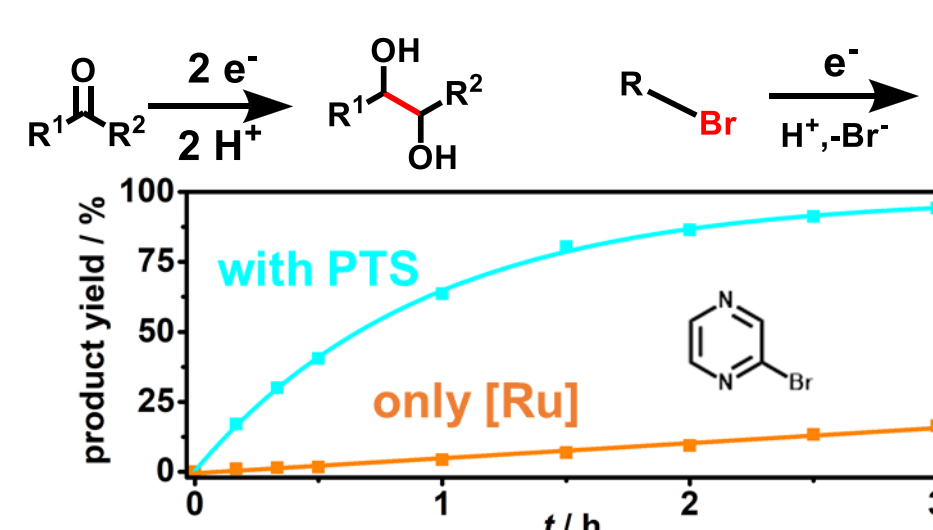
Hydrogen evolution

2 H$^+$ + 2 e$^-$ → H$_2$

[Mo$_3$S$_{13}$]$^{2-}$
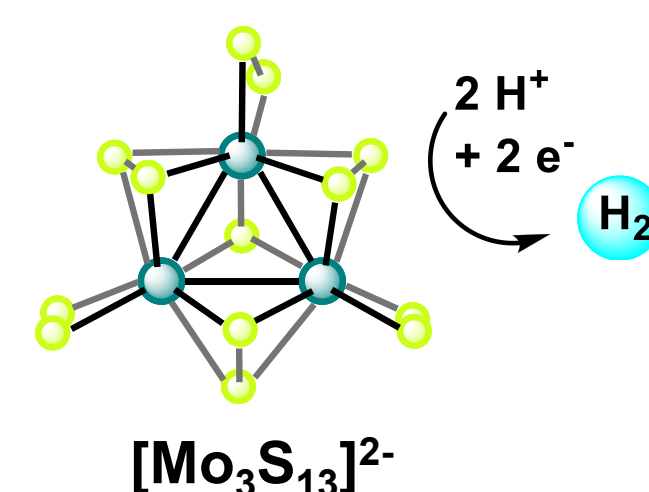
References
[1] A. C. Sell, M. Schmitz, C. Kerzig, et al., *Dalton Trans.* **2022**, *51*, 10799–10808.
[2] S. Neumann, O. S. Wenger, C. Kerzig, *Chem. Eur. J.* **2021**, *27*, 4115–4123.
[3] M.-S. Bertrams, C. Kerzig, et al., *Chem. Sci.* **2023**, *14*, 8583–8591.

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