Increasing the Efficiency of Photochemical Elementary Steps

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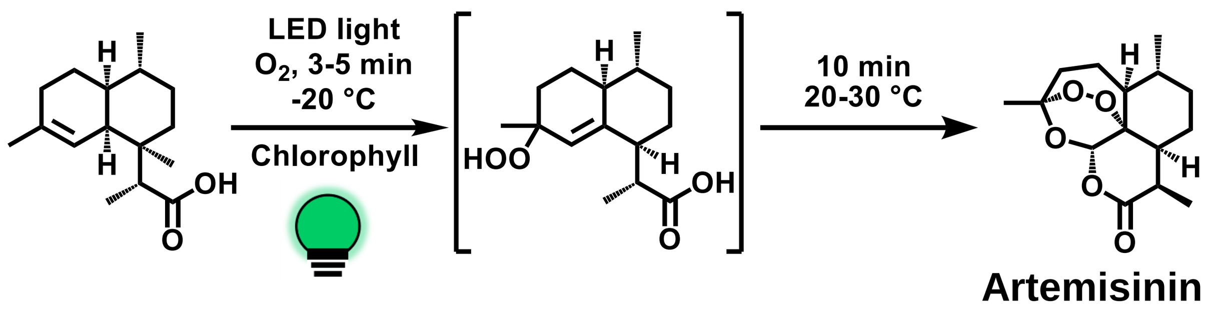
Abstract: Photocatalysis offers great potential for changing the synthesis of value-added molecules, yet many reactions suffer from low efficiencies hindering industrial scalability. Molecular dyads are attractive photocatalysts that enable milder conditions and higher reaction efficiencies for photochemical 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

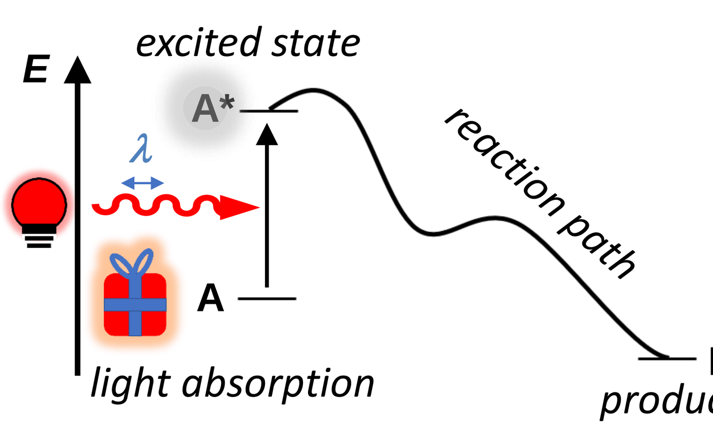


Benefits of photochemical reactions:
- ✓ Mild
- ✓ Controllable
- ✓ Specialized reactions

Major **disadvantage**:
- ➢ Reaction quantum yields typically <<10%

Definition Quantum Yield

Simplyfied photochemical reaction

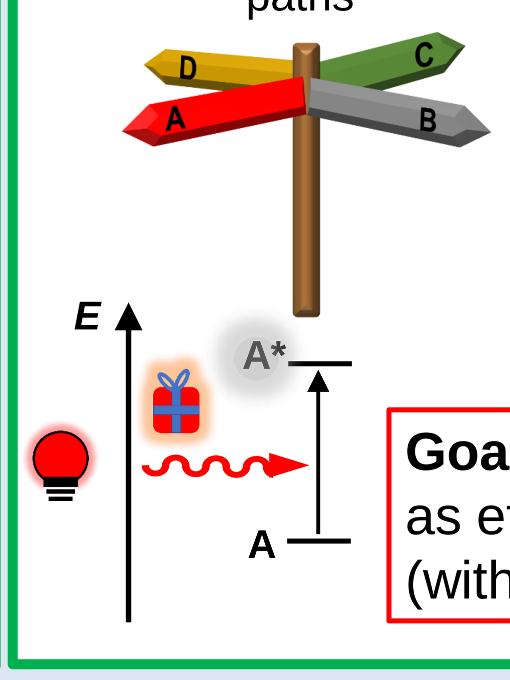


Photon:
- ➢ **Quantum object**
- ➢ **„Energy package"**

$$E(\text{photon}) = h\frac{c}{\lambda}$$

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

Most Important Elementary Steps



1. Energy transfer

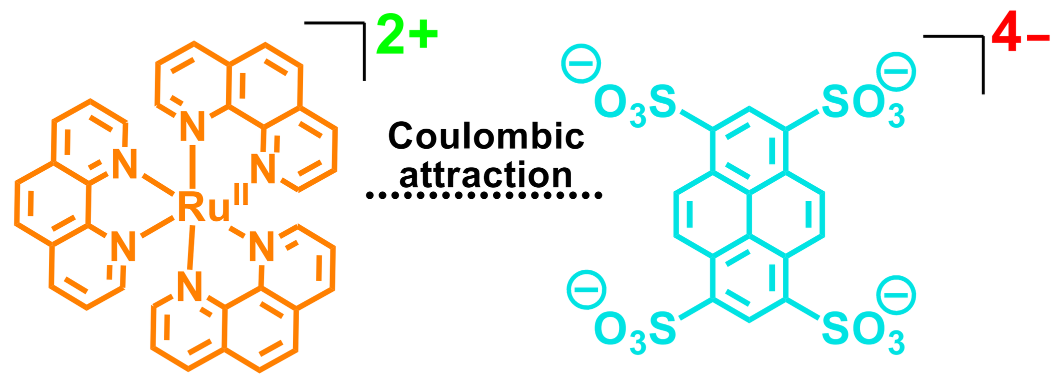
$^3A^* + {}^1X \rightarrow {}^1A + {}^3X^*$

2. Electron transfer

$A^* + Y \rightarrow A^- + Y^+$ (e^-)

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

Novel Catalyst System

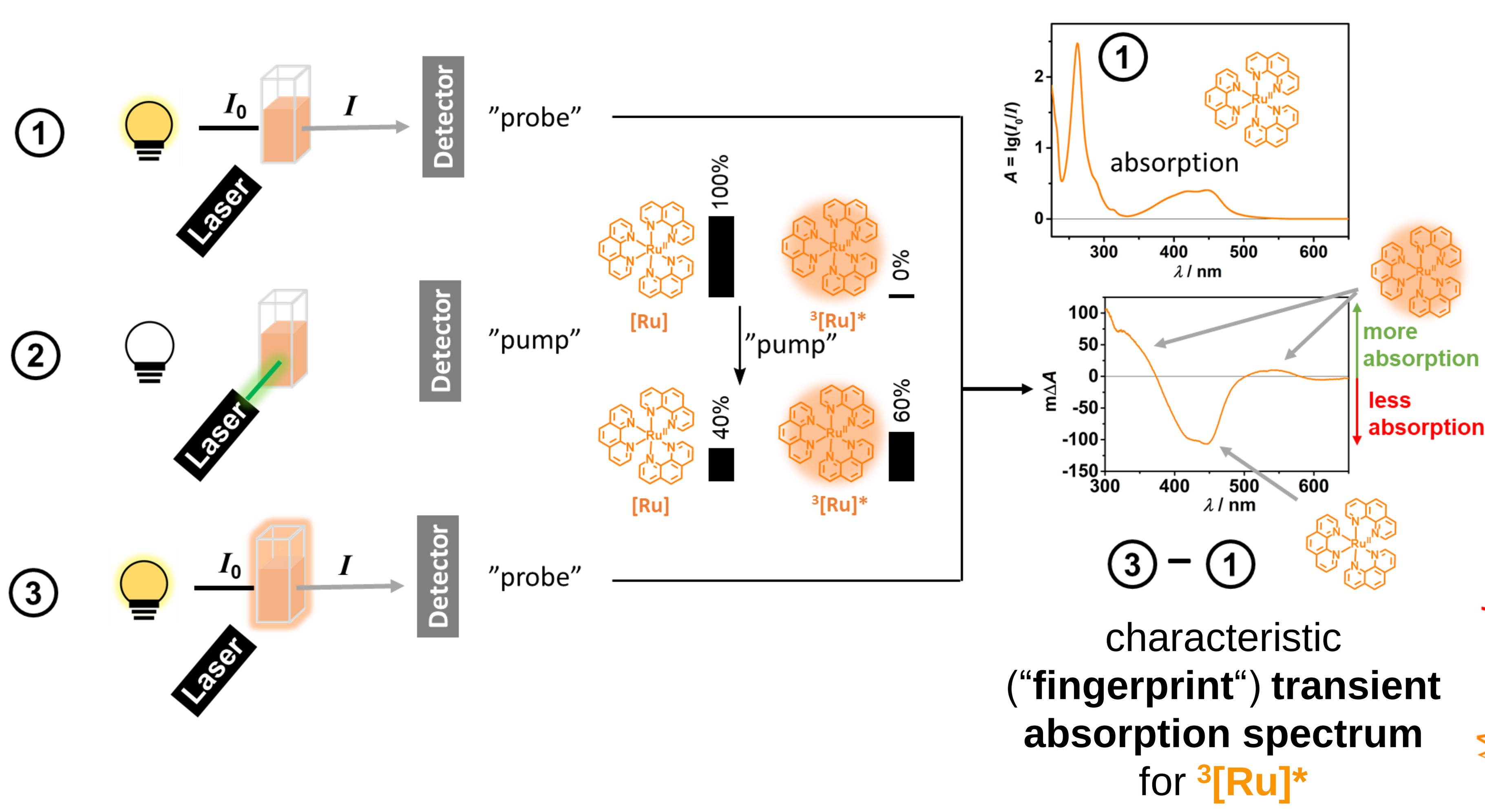


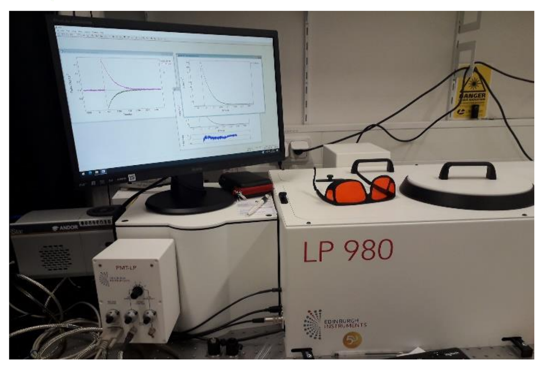
Tris(1,10-phenanthroline) ruthenium(II) **[Ru]**

1,3,6,8-Pyrenetetrasulfonate **PTS**

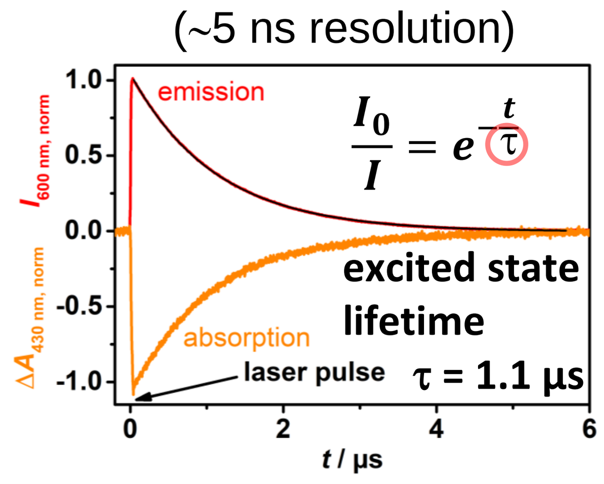
- ✓ Commercially available compounds
- ✓ Strong attraction between **[Ru]** and **PTS** → forms "**one unit**"
- ✓ **[Ru]** absorbs visible light (absorbs light energy)
- ✓ Efficient triplet formation through **[Ru]** (important for energy transfer catalysis)
- ✓ **Key step:** Energy transfer from **^{3}[Ru]**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

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

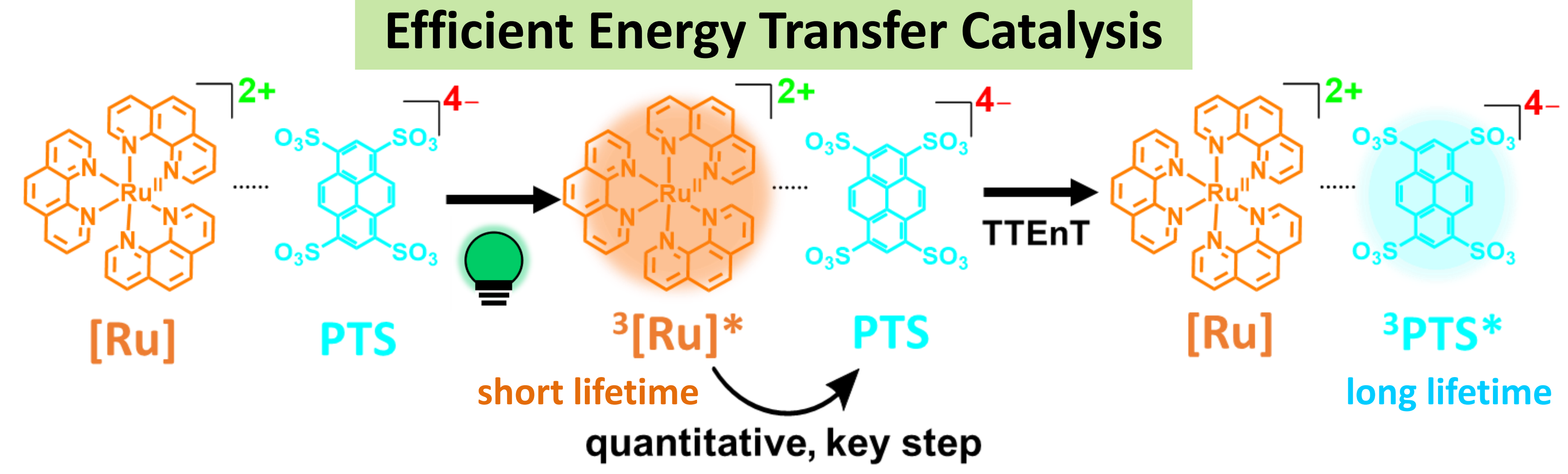




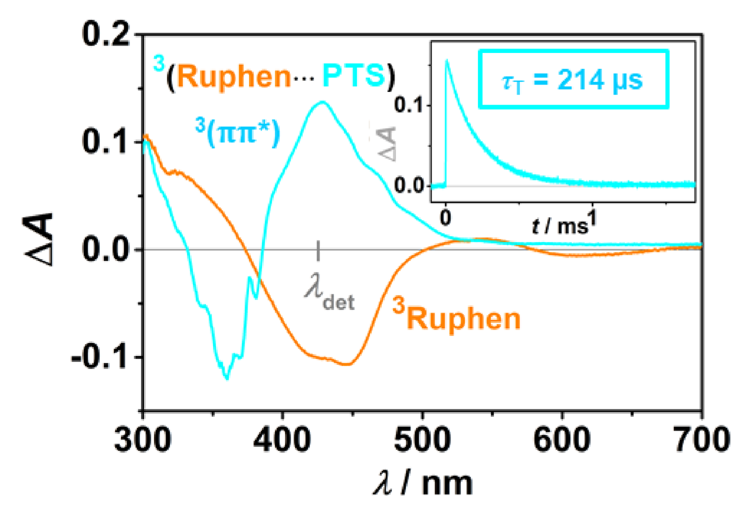
Time-resolved (~5 ns resolution)



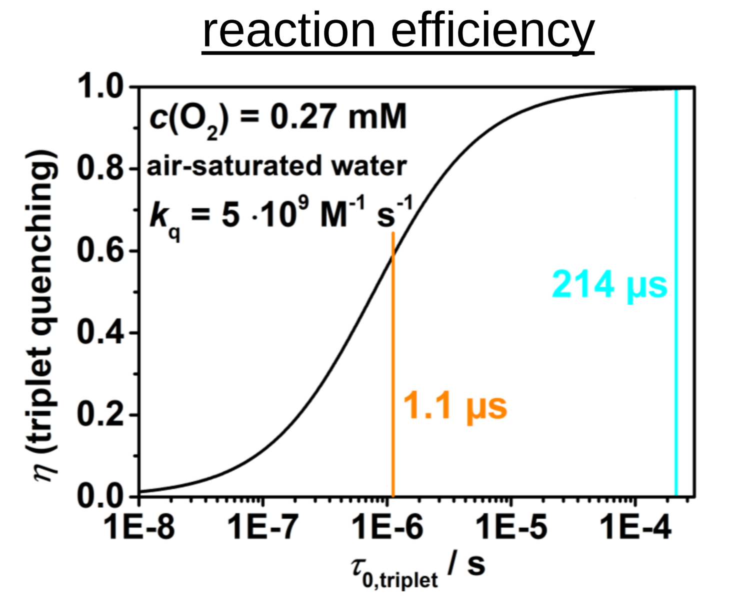
Efficient Energy Transfer Catalysis



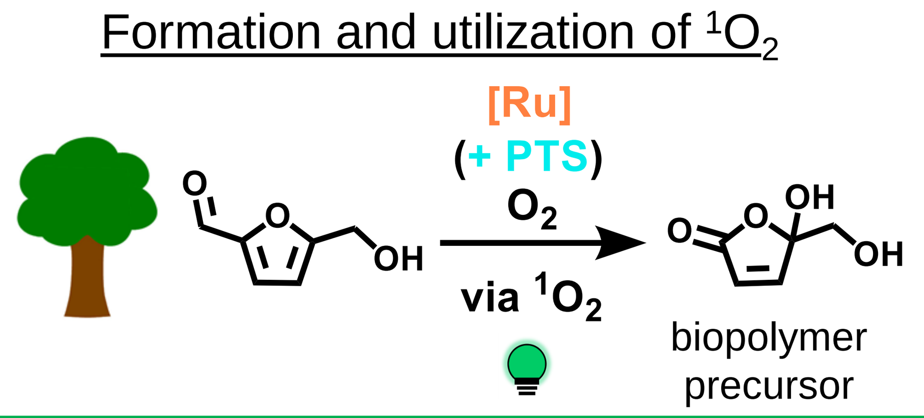
Proof that ^{3}**PTS** is the key species

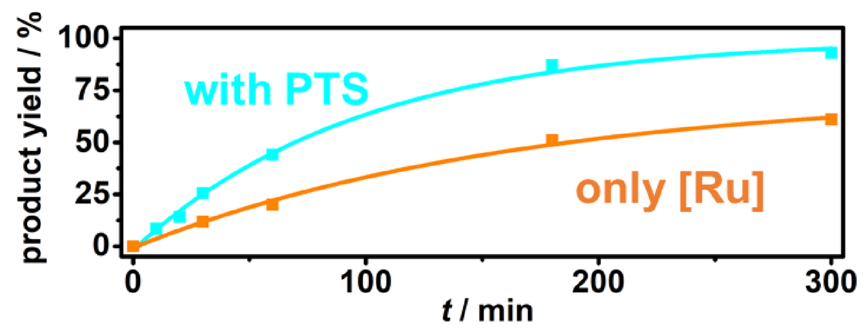


Connection between lifetime and reaction efficiency

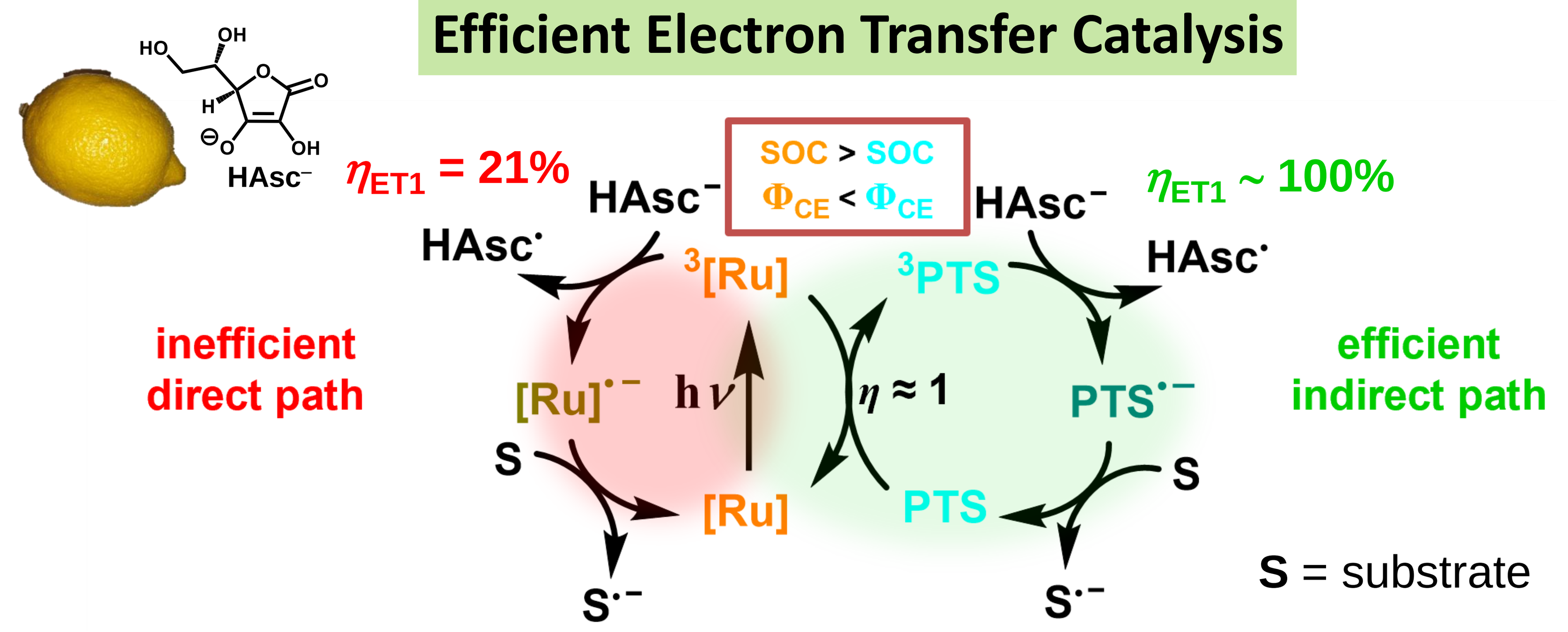


Formation and utilization of $^1O_2$

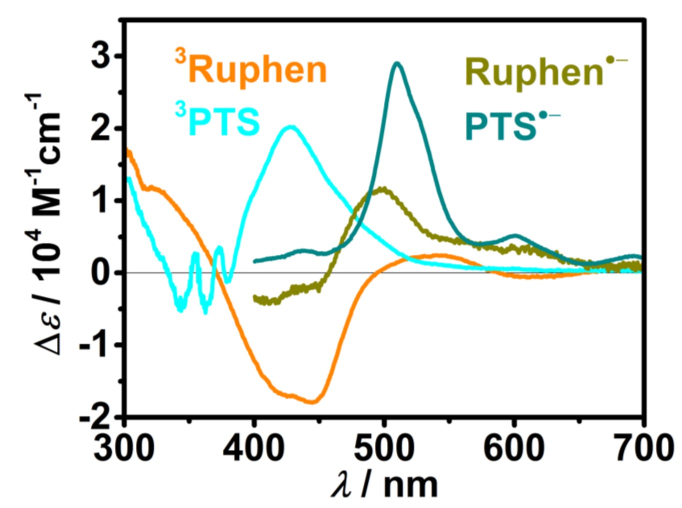




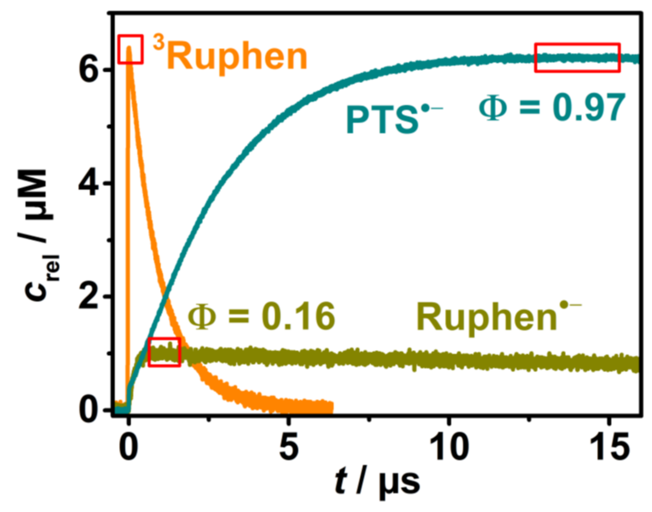
Efficient Electron Transfer Catalysis



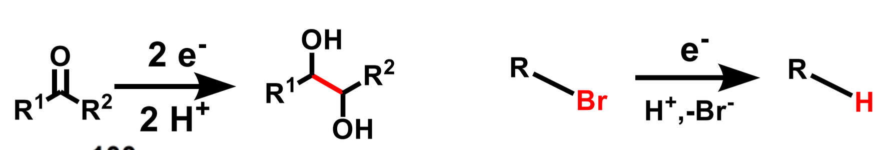
Characteristic TA spectra of all key species

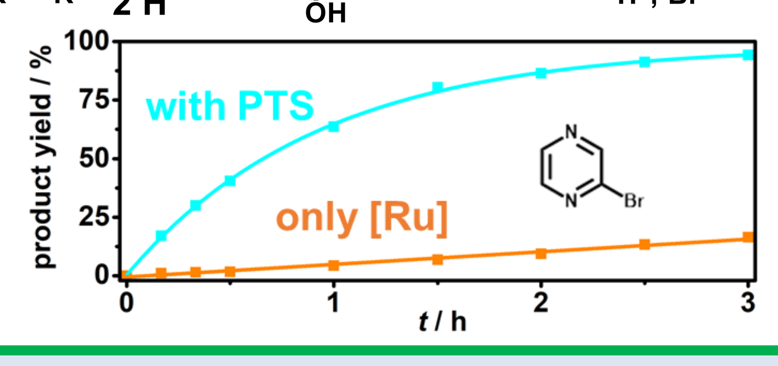


Quantification of the key species

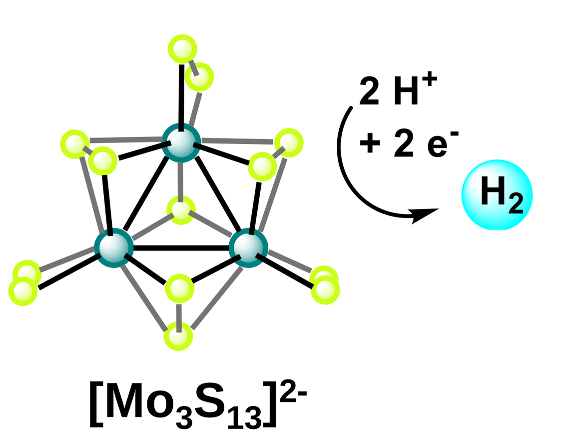


Bond formation and bond clevage





Hydrogen evolution



$[Mo_3S_{13}]^{2-}$

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.

FCI Fonds der Chemischen Industrie