Bio-Inspired, Self-Healing Polymers for Applications in Green Electronics

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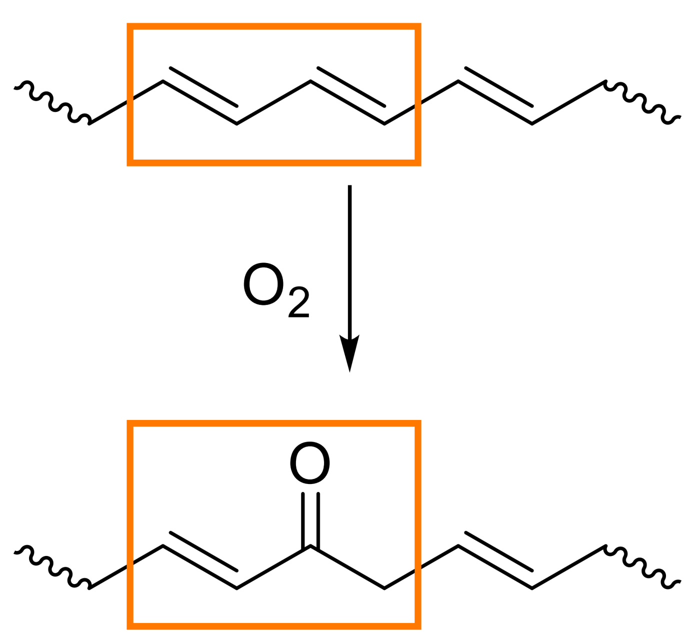
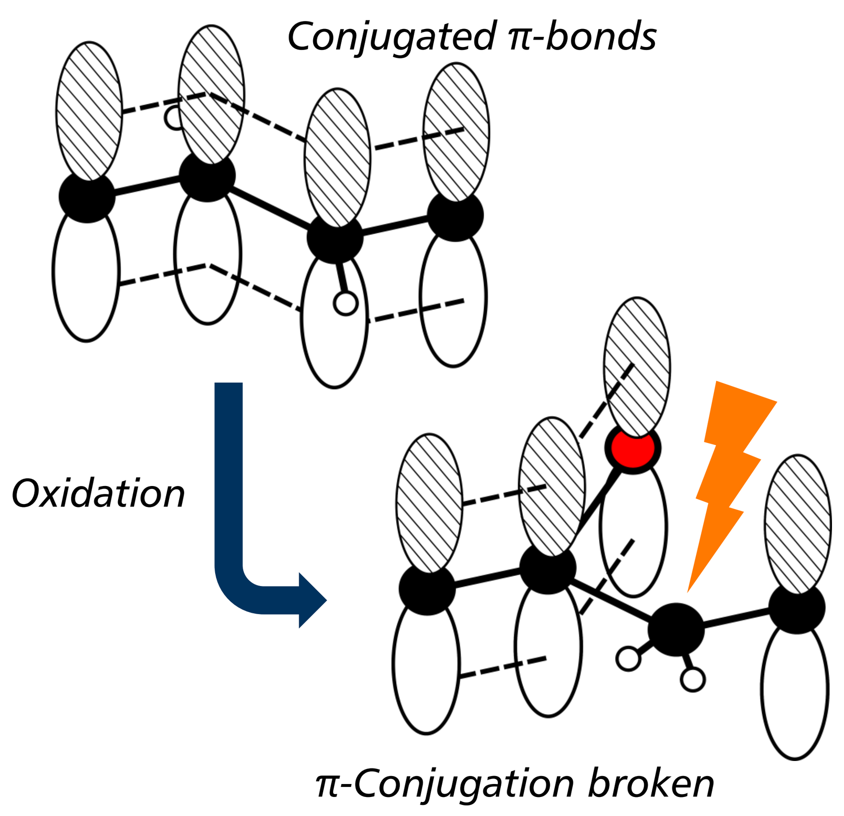
Motivation: Green Electronics

Green electronics involve two fundamental aspects: Sustainable, resource-saving electronic components and energy-efficient algorithms. Currently, electronic components are largely made of silicon with various dopants and metals. Both classes of material are energy-intensive to produce and often cause major environmental damage.

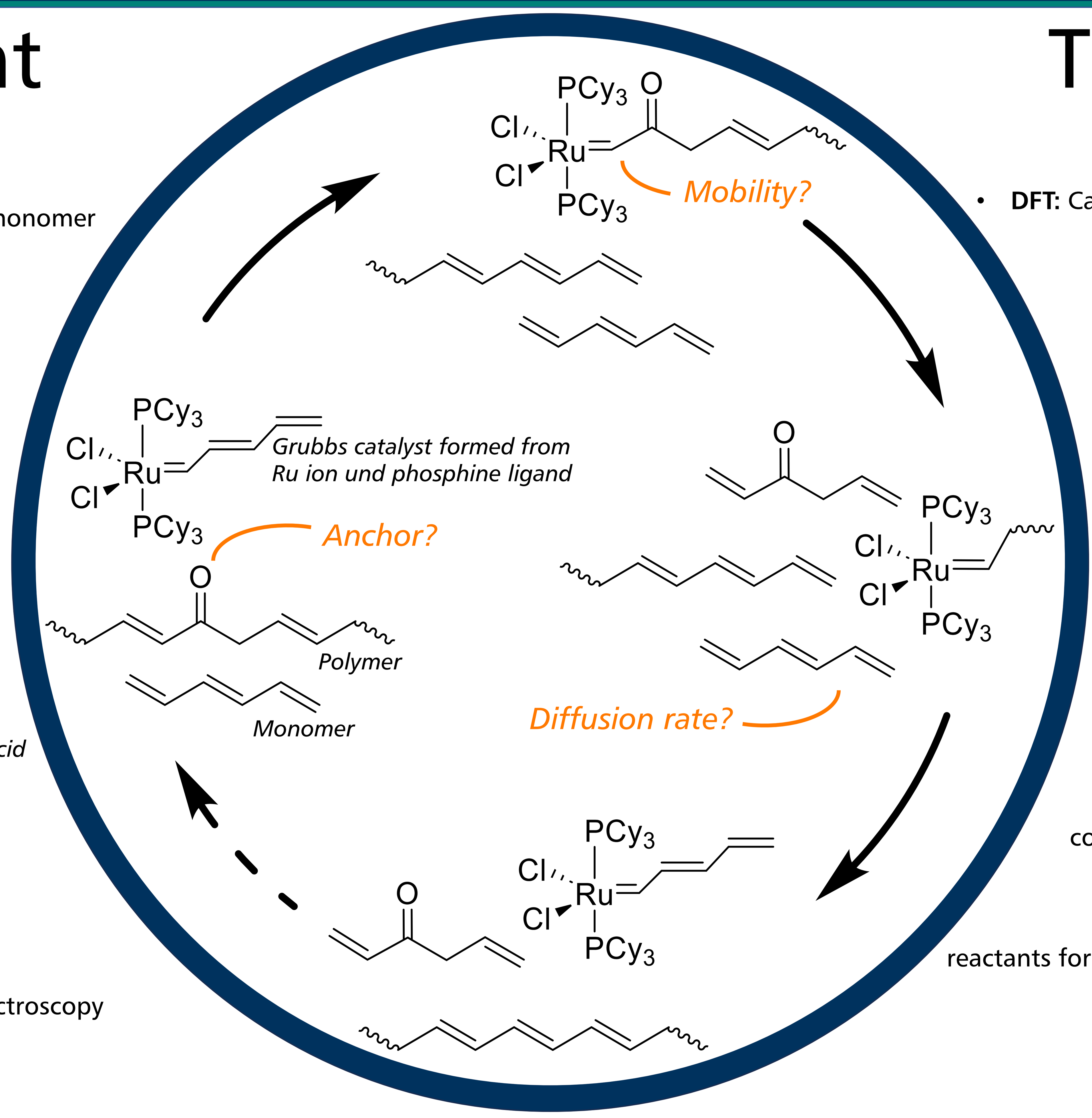
Electrically conductive polymers are available as an alternative, the discovery of which was awarded the Nobel Prize in 2000. Despite all efforts, these materials, which are made up of organic elements such as carbon, hydrogen, nitrogen and oxygen, were not yet technically established. One reason for this is their sensitivity to atmospheric oxygen, which oxidizes and thus destroys the system of conjugated π-bonds.

As a solution, the bio-inspired, functional self-healing of electrically conductive polymers[1] is being investigated in this project. In self-healing, the intelligent material system is able to repair damages independently, similar to biological systems, and thus restore its original properties. This is based on dynamic bonds within the polymer system.





Work Plan: From Theory to Application



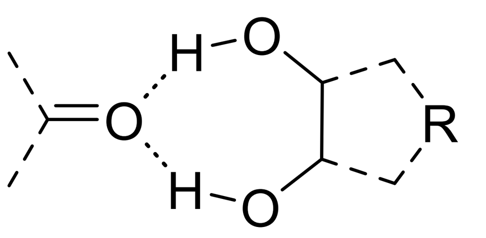
Experiment

WP1: System Formulation

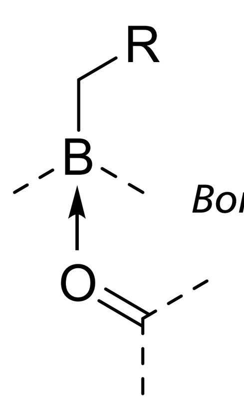
- System from **3 components**: Polymer, catalyst & monomer
- Dynamic π-bonds via **alkene metathesis**
- **Grubbs catalysts** open and close C=C bonds

WP3: Synthesis of Modified Catalysts

- Oxo group as **anchor point**
- Oxophil ligands lead **pre-coordination**
- Hydrogen bonds and Lewis acids



Diol as hydrogen bond donor



Boron as Lewis acid

WP5: Conductivity and Self-Healing

- Four point measurement
- Determination of **self-healing rate** via Raman spectroscopy
- Validation of theoretical calculations

Theory

WP2: Catalyst Design

- **DFT:** Calculation of the **binding energy** of the catalyst system at the oxidized anchor point
- Variation in ligand structures
- Calculation of **activation Energies** for alkene metathesis
- Coordinated binding and activation energies are central to the success of the project

WP4: Molecular Dynamics

- **Complex dynamics** in the mixture of catalyst, monomer and polymer
- **MD: Mobility** of the components involved components in the polymer matrix
- **Optimized provision** of the reactants for self-healing at the oxidized sites

Challenges, tasks and research questions

This project does not extend an existing project, we want to develop a new approach for the self-healing of oxidative degraded conductive polymers. Therefore, the project starts with a challenging **preparative** proof-of-concept study to show that a self-healing system can be constructed by combining (oxidized) polymer, monomers and Grubbs catalyst. The specific parameters and educts are your responsibility. **Spectroscopic methods** are used to characterize the self-healing system and evaluate its performance. An efficient self-healing system requires a balanced interplay between the formation energy for covalent bonds between different ligands, the metal atom and the energy profile for the metathesis reaction. On the one hand, the catalyst should simultaneously form strong coordinative bonds to both the oxidized anchor points of the polymer and monomers. On the other hand, the catalyst should only bind weakly to oxidized products of the metathesis. Several possible products can also be obtained as a result of the metathesis reaction, but only the desired one (the recovered polymer) should be pronounced by the catalyst. The PhD student will perform DFT/MD simulations to calculate the binding energies of the ligands and the free energy profiles for the metathesis reaction. These calculations will lead to suggestions for better ligands to be synthesized as part of the PhD work, and the resulting catalysts will be tested for their self-healing potential. **To summarize, we propose a challenging project that will pave the way to new mechanisms of self-healing for conductive polymers.**

Therefore, we are primarily looking for an experimental chemist with a strong interest in theory rather than an expert in simulations who has no experience in spectroscopy and synthesis.

Important Remark

In addition to the work packages described above, other projects can be initiated according to candidates' own ideas and wishes. In particular, collaboration with other ISGE projects is highly appreciated, even if this leads to deviations from the original project structure.

1. Li, Yang, et al. "Recent Progress on Self-Healable Conducting Polymers." Advanced Materials 34.24 (2022): 2108932.
2. Adlhart, Christian, and Peter Chen. "Mechanism and activity of ruthenium olefin metathesis catalysts: the role of ligands and substrates from a theoretical perspective." *Journal of the American Chemical Society* 126.11 (2004): 3496-3510.
3. Remya, Premaja R., and Cherumuttathu H. Suresh. "Grubbs and Hoveyda-Grubbs catalysts for pyridine derivative synthesis: Probing the mechanistic pathways using DFT." Molecular Catalysis 450 (2018): 29-38.