

Efficient Noble-Metal-Free photosensitizers based on BODIPY, perylene monoimide and ketocoumarine dyes

Benedikt Callies¹, Konrad Hotzel¹, Daniel Costabel, Gergely Knorr, Kalina Peneva¹

¹Institute for Organic Chemistry and Macromolecular Chemistry, Friedrich-Schiller University Jena, Germany

Our research is centered on innovating the design and application of noble-metal-free photosensitizers such as BODIPYs, perylene monoimides, and ketocoumarins for light driven hydrogen evolution.^[1-4] Ketocoumarins provide a simple and straightforward route for synthesis, while exhibiting high extinction coefficients, excellent ISC rates from singlet to triplet state, small singlet-triplet gaps and long triplet lifetimes.^[5] In HER experiments with cobaloxime catalyst TONs of up to 3955 were measured with the noble-metal-free system over 20 hours.^[4] Close spatial proximity between the catalyst and photosensitizer was achieved with the synthesis of two unimolecular photocatalysts consisting of bipyridine-annulated perylene tetracarboxylic ester bearing platinum or palladium as a metal center. Both complexes exhibited significant catalytic activity in hydrogen evolution catalysis, with the platinum complex achieving TONs of 186 over 48 hours.^[1] Additional mercury poisoning experiments revealed the stability of the Pt-photocatalyst during the catalysis, as no reduction in activity was observed, while the palladium complex decomposed during catalysis, forming Pd⁰ nanoparticles. Furthermore, we will illustrate how the utilization of different macromolecular templates influences the photocatalytic activity of our systems, exemplified by the immobilization of various BODIPY photosensitizers and [Mo₃S₁₃]²⁻ as the HER catalyst within a soft-matter matrix.^[3]

[1] D. Costabel, *et al.*, *ACS Catal.* **2023**, *13*, 7159, DOI: 10.1021/acscatal.3c01201.

[2] D. Costabel, *et al.*, *Chemistry* **2021**, *27*, 4081, DOI: 10.1002/chem.202004326.

[3] D. Costabel, *et al.*, *ACS applied materials & interfaces* **2023**, *15*, 20833, DOI: 10.1021/acscami.2c18529.

[4] G. Knorr, *et al.*, *J. Mater. Chem. A* **2023**, *11*, 23260, DOI: 10.1039/D3TA04450E.

[5] D. Huang, *et al.*, *Photochem Photobiol Sci* **2013**, *12*, 872, DOI: 10.1039/c3pp25416j.