Final report from the project

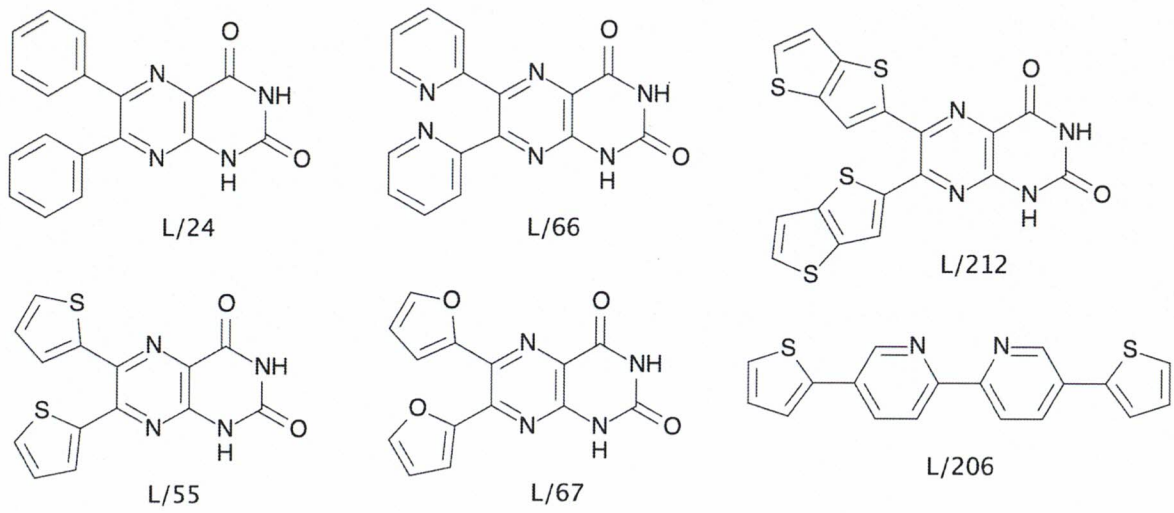
Project number: Aktion 95p3

Project title: Photocatalytic processes for sustainable and green applications

Date of implementation: 1.1.2023 - 31.12.2023

The project started with the work on the synthesis of organic materials based on riboflavin. The syntheses were based on the condensation reaction of selected 1,2-diketones with 1,2-diamines (see *Molecules* 2018 publication) and on expert discussion with Dr. Apaydin. Thus, 5 NH-free flavin derivatives were synthesized in January and February (Scheme 1). This was followed by purification of the materials by crystallization and characterization by spectroscopic and chromatographic methods. In addition, 5,5'-dithienyl-2,2'-bipyridine was prepared by Suzuki reaction with basic optimization of reaction conditions and characterized similarly.

In March, Dr. Richtar's internship took place at TU Vienna in Dr. Apaydin's team, where the above materials were studied. These were first characterized by cyclic voltammetry in $TBAPF_6$ electrolyte solution in acetonitrile. Based on the redox potentials, the parameters for electropolymerization experiments on FTO substrates were determined. Due to the unsatisfactory results (where no layer formation was observed except for L/212), it was proceeded to formulate inks and deposit them on FTO substrates physically so that they could be evaluated at least in the form of small molecules. After drying, the layers of compounds deposited as inks were subjected to LSV experiments followed by electrolysis to evaluate their performance in CO_2RR. However, delamination of the layers was observed during electrolysis in aqueous basic media. For the thiophene derivative L/55, chemical polymerization using $FeCl_3$ was proceeded. The prepared polymer purified from iron using EDTA and subsequently tested deposited as an ink (FTO substrate - no ideal layers formed, carbon paper - relatively stable layers). The polymer PL/55 thus prepared was repeatedly tested on a carbon electrode for HER (hydrogen production) and CO_2RR (carbon dioxide reduction). It showed the ability to accelerate HER, whereas CO_2RR was comparable to the blank experiment. After lowering the pH, the PL/55 electrode was shown to produce hydrogen approximately 5 times faster than the blank experiment. Another polymer PL/212 prepared by electropolymerization on FTO showed 3 times higher rate in HER and 1.7 times in CO_2RR (to form CO) than the blank experiment. In contrast, the polymerization on carbon electrode showed 5x higher CO formation rate. Evaluation of photoelectrocatalysis by LSV in darkness and illumination did not provide promising results. The furan derivative L/67 showed approximately 10 times higher rate in homogeneous HER than the blank experiment. In the case of the bipyridine derivative L/206, it was proceeded to its polymerization on FTO glass to produce PL/206 as a thin film. The latter was investigated on HER and CO_2RR, and 3 times faster HER and 4 times faster CO production were observed. SEM experiments with electrodes were not performed due to the primary nature of the experiments. Thus, of the series investigated, polymer PL/206 offers the best potential for carbon dioxide reduction so far and will be pursued for its synthetic modification to achieve easier polymerization (conjugated chain extension) and subsequent complexation with transition metals. In the case of flavins, the ability to catalyse mainly the electrolysis of water to produce hydrogen has been demonstrated.



Scheme 1: Target flavin and bipyridine derivatives

After the internship at TUW, an online discussion between the project investigators was organized to evaluate the results and suggestions for further work. The synthesis of a larger number of materials with promising performance in HER and CO_2RR was started.

Project activities included an intensive workshop held between 1st and 2nd August 2023 at BUT. In frame of this workshop, Dr. Apaydin and his Ph. D. students - Hannah Rabl, Jakob Blaschke visited BUT. The first day of the workshop included a lecture by Prof. Krajčovič, Dr. Apaydin (Artificial Photosynthesis - What can we learn from nature to help nature?), Dr. Richtar (paper Photoelectrocatalytic processes for sustainable and green applications. On the second day of the workshop, a brainstorming session was held with the participation of both teams to discuss the possibilities of deepening the collaboration also using the results of the internship within the Aktion project. Within the team at FCH BUT a plethora of organic functional materials with structurally different motifs are synthesized. The TUW team has a wide knowledge and background in post-processing (electrode fabrication, electrochemical methods, evaluation in hydrogen production and CO2 reduction, work with inorganic and hybrid materials). After a joint discussion, suggestions for further work were made both in the rational design of new organic materials and suggestions for modifications of the hybrid materials studied. Afterwards, the work-in-progress manuscript with the working title "Polymerised flavins are efficient metal-free electrocatalysts for hydrogen production" was discussed. During the discussion, the draft of the paper was fine-tuned and experimental priorities were set to successfully complete all necessary measurements for a relevant publication. The further measurements were performed by Ing. Ivanová who was participating in frame of Erasmus traineeship program at TU Wien. Beforehand, she participated on experiments at BUT under mentorship of dr. Richtár.

In November, a two-day common workshop at TU Wien was held where members of both partner teams (and a wider audience) presented topics of their research (day 1), and a complex laboratory tour with a detailed presentation of the instrumental background was taken (day 2).

In December, a 3-day stay in Vienna was held by members of the team from BUT (prof. Krajčovič, dr. Richtár, Ing. Arkhiptsava). The stay involved multiple activities. The experimental activities concerning a draft of the prepared manuscripts were evaluated and a preliminary plan for experimental work and bilateral exchanges in the next year was suggested. Moreover,

novel alkoxythiophene-based polymers were investigated electrochemically and novel bio-inspired dopamine and L-DOPA derivatives were discussed. Electrochemical and FTIR experiments with novel promising bipyridine derivatives and pioneer experiments with complexation (Pt, Ni) were investigated as well. Further discussions about the broader project platform were undertaken concluding a need for further experimental data as preliminary results.
In the continuing project, further experiments will be performed to obtain additional data for the successful preparation of the manuscript. Moreover, novel materials derived from already studied structures will be investigated.

At the end of the project, the BUT returned a substantial amount of the CZK grant due to the fact that experiments at Austrian side has branched into various characterizations as well as catalytic performance evaluation of the samples prepared by BUT. Here the team at TUW had to make a strategic decision to investigate the bipyridine samples further in terms of electrochemistry. PhD students Hannah Rabl and Jakob Blaschke were involved in the characterization of the newly-synthesized bipyridine derivatives, namely the as synthesized bipyridine and metal incorporated ones. As the results of photoelectrochemical measurements were promising it was necessary to focus on the experiments than visiting BUT. Furthermore, as the samples required several characterization techniques such as FTIR, UV-Vis, cyclic voltammetry, chopped-light chronoamperometry and gas chromatography, currently there was no need for further sample production at BUT by the members of TUW.

Both TUW and BUT decided to submit an extension of the project as the collaboration seems fruitful so far. The next project will involve the further characterization of polymeric bypridine structures with various metal centers in both electrochemistry and photoelectrochemistry. The synthetic capabilities of BUT creates a great synergy with the catalytic expertise of TUW.

People involved from BUT: prof. Jozef Krajčovič, dr. Jan Richtár, Ing. Lucia Ivanová, Ing. Katsiaryna Arkhiptsava

People involved from TUW: dr. Dogukan H. Apaydin, Jakob Blaschke, MSc., Hannah Rabl, MSc.

Ongoing articles related with project:

N. Kleinbruckner, E. Leeb, D. Wielend, C. Schimanofsky, M. Cobet, F. Mayr, A. Kerschbaumer, C. Yumusak, J. Richtar, M. C. Scharber, H. Neugebauer, M. Irimia-Vladu, J. Krajcovic, N. S. Sariciftci, Polymerized Riboflavin and Anthraquinone Derivatives for Oxygen Reduction Reaction. *Adv. Sustainable Syst.* 2023, 2300352. https://doi.org/10.1002/adsu.202300352 ACS: *J. Org. Chem.*

D. Yordanov, R. Smolka, K. Nakashima, SI Hirashima, Y. Matsushima, M. Vala, K. Krajčovič, M. Weiter, T. Miura, A. Georgiev. Fluorescent Rotary Switches: Four- vs Three-Substituted Phthalimide Boron Difluoride Schiff Base Complexes. *J. Org. Chem.* 2023, *88*, 17206. doi: 10.1021/acs.joc.3c02056.

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