INTERFACIAL PHOTOELECTROCHEMISTRY FOR MODERN ORGANIC SYNTHESIS

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Climate change is the defining crisis of our time, and it is happening even more quickly than we feared. But we are far from powerless in the face of this global threat. As António Guterres, Secretary General of the United Nations, pointed out, 'the climate emergency is a race we are losing, but it is a race we can win'.

The worldwide news of dramatic natural disasters (only this year extreme fires in Greece, Italy, and Hawaii) has led to discussions about climate change and the urgent need for action. As if the climate crisis was not enough, at this exact moment humanity is also struggling with economical aspects of the energy crisis – in the past year the price of natural gas reached record highs, and as a result so did electricity in some markets. *However, the global crisis, together with the energy crisis, can be a historic turning point* in the development of novel green methods for fine chemical production by developing alternative methods that increase energy efficiency, atom economy, and eliminate toxic chemicals.

With respect to sustainable organic chemistry, one of the *greenest* ways for driving chemical transformations is electrochemistry and photochemistry. Although a number of efforts have brought both of these methods to the forefront in organic chemistry, the focus is mostly on optimizing the efficacy of atom usage: *however, by maximizing the atom economy, we are forgetting about maximizing energy efficiency*. One way to change that is to take inspiration from biological systems; Nature itself offers sustainability that may and should be an inspiration for us. For decades, natural systems, and in particular photosynthesis, have provided the principal model for solar energy science and engineering. The scientific basis of the photosynthesis process is used, among others, as a model for the development of photovoltaic cells, in which solar energy is converted into electricity. However, such *photoelectrochemical cells* can work not only for the production of electrical energy but also for the light-powered production of fuels. One can think of it as of a system similar to artificial photosynthesis that could be the way of storage of solar energy for fuel production (hydrogen). Therefore, I postulate that photo-supported electrochemical synthesis is a solution to the problem of energy loss by allowing for dramatic decreases in applied potential as a result of light energy assistance. In typical electrochemical cell each redox process can be constructed as a combination of two half-reactions (cathodic reduction and anodic oxidation) and over the past decade, electrolysis allowed for numerous organic transformations. In regard to sustainability, electrochemistry shows obvious environmental benefits: it allows relatively mild conditions with the elimination of the use of hazardous, toxic, and wasteful oxidants and reductants. However, in electrochemical methods, a high applied potential and a large amount of electrical power are required to achieve the conversion of some organic compounds, sometimes leading to unselective reactions and energy losses. Photo-supported electrochemical synthesis is a solution to these problems allowing for dramatic decreases in applied potentials as a result of light energy assistance. In *interfacial photoelectrochemistry* (*i*PEC) a reaction occurs at a semiconducting photoelectrode surface, which under visible-light irradiation generates an electron-hole pair that is used to drive a redox reaction. With the use of the photoelectrode, the use of external power can be avoided or the applied voltage can be decreased to the minimum. As a consequence, the current can be used as a crucial reagent in the catalytic amount, which means that chemical transformation is performed under incredibly mild conditions without energy loss.

The main objective of this research proposal is to set a general paradigm for the design and application of *interfacial photoelectrochemical systems* (*i*PECs) for the synthesis of fine organic chemicals and pharmaceutics, where the use of external electric power can be avoided or the applied voltage can be reduced to the minimum (Figure 1). While the utility of this approach is well-known with solar energy conversion (e.g. solar cells), the benefits of its application in organic synthesis are still underexplored. Our efforts will establish new photo-supported electrochemically driven methodologies that will expand the synthetic toolbox for organic chemists providing fine chemicals in a mild, energy-efficient, green, and less-expensive way. In the future, some of the developed systems may share the history of photovoltaics and be widely applied in the industry, increasing the atom economy and energy efficiency.

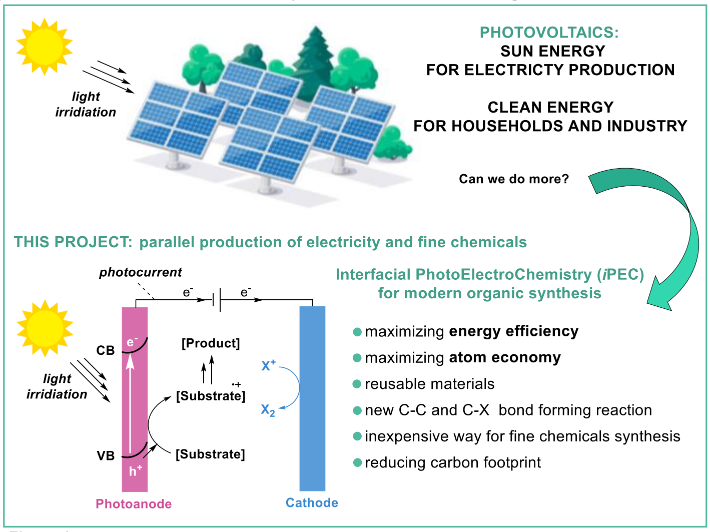

Figure 1. General idea for the proposal