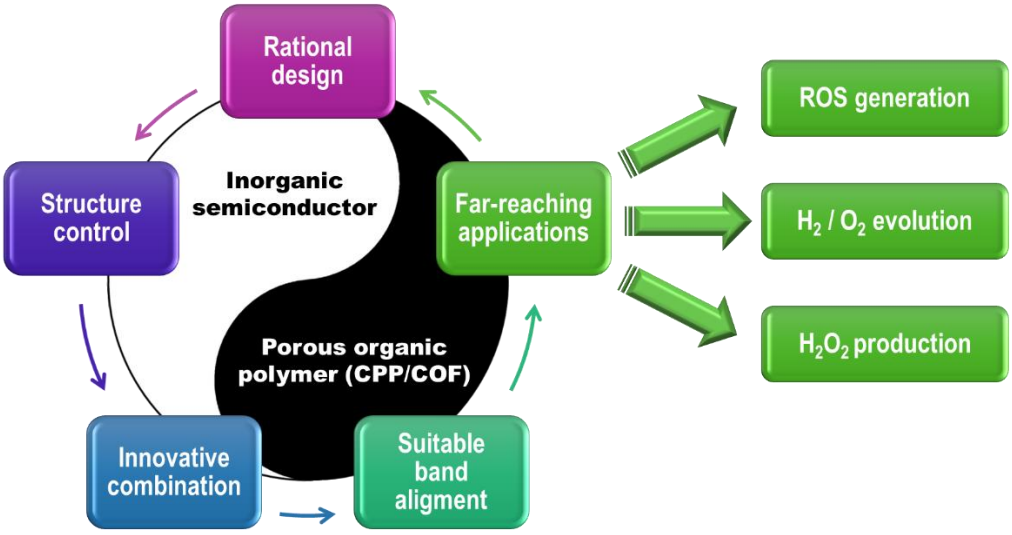
Toward critical raw material-free photocatalysis: insight into charge carrier dynamics and transfer mechanisms in hybrid photocatalysts based on porous organic polymers



Schematic illustration of the proposed approach.

Today's society, regardless of the latitude in which it is located, faces two major challenges: the energy crisis and environmental pollution. In this regard, heterogeneous photocatalysis is considered as a sustainable technology based on solar energy which can be applied for overcoming global problems. It takes advantage of photoactive semiconductors, which are able to generate charge carriers under illumination, necessary to initiate chemical reactions.

Currently, the most commonly studied materials for photocatalytic applications are inorganic semiconductor oxides (e.g. TiO_2, $BiVO_4$, WO_3, BiOCl, $SrTiO_3$) and sulfides (e.g. CdS, CuS, $ZnIn_2S_4$). However, numerous elements used for photocatalyst preparation, such as graphite, platinium, ruthenium, cobalt, galium, and vanadium, are listed as critical raw materials for the European Union. These materials, often rare or geographically concentrated, are of critical importance for industry, and the management of their resources has become a key factor in shaping economic policy and innovation. Therefore, to reduce the strategic dependence of our country, studies on metal-free photocatalysts, are of particular interest. Recently, **porous organic polymers (POPs)**, including **conjugated porous polymers (CPPs)** and **covalent organic frameworks (COFs)**, have received considerable research attention. Unlike inorganic photocatalysts, organic photocatalysts can absorb visible light without modification, and their photoredox properties can be adjusted by rational design and synthesis. Their porous structure in combination with high photochemical stability, make them ideal for photocatalytic applications. Moreover, the diversity of possible organic π-systems allows to obtain rationally designed materials with tuned light absorption and electronic structure to match the specific requirements of the target reaction.

Despite the promising properties of POPs for photocatalytic applications, the study of single-component organic photocatalysts may be insufficient to realize their full potential. Therefore, at present, the most suitable approach to enhance photocatalytic activity is the design of **organic–inorganic hybrids**, in which the polymer is an organic counterpart in the binary photocatalyst with inorganic semiconductors, for example, metal oxides or sulfides. This combination can be beneficial for photocatalytic activity due to the possibility of heterojunction formation or sensitization mechanisms. However, principles of cooperation between the organic and inorganic components are still unknown, due to the lack of the reported information. As a result, there is still a need to discover highly efficient and durable hybrid photocatalysts for various photocatalytic applications, such as H_2 evolution (HER), O_2 evolution reaction (OER), and O_2 reduction to H_2O_2 (ORR).

The main goals of the POPcat project are: **(1)** synthesis and characterization of new class of hybrid photocatalysts based on inorganic photocatalysts and organic component (CPPs or CPFs), possessing enhanced photocatalytic activity, **(2)** unveiling the role of organic structure (amorphous/crystalline) on the morphology and electronic structure of the photocatalyst, **(3)** detailed insight into the mechanisms of excitation and transport of the photogenerated charge carriers together with the ability to produce reactive oxygen species. It is expected that coupling CPPs/COFs with selected inorganic photocatalysts and the comprehensive characterization using advanced techniques (XRD, NMR, spectroscopy techniques: XPS, UPS, UV-vis, TRPL, ESR, TAS) allow to obtain efficient photocatalysts with high quantum yield and decreased amount of critical raw materials.