Chemistry deals with the properties of substances and the transformations of one substances into others, that is, the chemical reactions. One of the principal tasks of chemical research is to discover and design ways of converting substances easily obtainable from abundant sources, such as oil, minerals, and biomass, into useful compounds, characterized with desired properties. Usually, this cannot be achieved with a single chemical reaction, instead, a series of reactions, gradually changing a raw material into the target substance are carried out, in a process called chemical synthesis. The products of chemical synthesis range from simple ones, such as fertilizers, dyes, fuels, to the most sophisticated – advanced materials and pharmaceuticals. The job of chemists is to improve the existing and to develop novel methods for carrying out the synthesis in a possibly efficient and environmentally benign manner. The latter issue is of a special importance, since the level of sustainability of the current chemical processes is far from satisfactory. An important mean of improving the sustainability of chemical synthesis is the introduction of new reactions that lead to a large increase in the molecular complexity, so that the synthetic sequences can be shorter and, thus, more efficient.

Chemical reactions, i.e. the transformations of matter, are always associated with a concurrent flow of energy. Some of them, such as combustion, release the energy contained in the starting materials, converting them into lower-energy species. Other, conversely, require the supply of energy to progress. In general terms, the reactions that create complexity, for instance, assembling a larger and more complicated molecule out of simpler ones, will usually need the energy to be provided. Most of the synthetic reactions fall into this category. A traditional approach to carry out such reactions is to couple them with other chemical transformations that are downhill in energy. In other words, the general scheme of many synthetic reactions is following: substrates + high-energy compound → product + low-energy compound. This is far from optimal, since, first, the ‘high energy compound’ has to be produced, which costs energy and resources, and, second, the ‘low-energy compound’ constitutes waste side-product, often a toxic chemical, which has to be taken care of.

This research project at its core addresses the issue of the sustainability of chemical synthesis, by employing electric power to drive uphill chemical reactions, instead of using auxiliary high-energy chemicals. This way, it will allow for the elimination of both the need for extra reagents and the generation of attendant waste streams. The electricity has been for long time used for stimulating simple chemical processes, for instance, the splitting of water into hydrogen and oxygen. However, its application in more complex reactions, in particular these involving organic compounds, has been challenged by the sluggish electron transfer rates for many organic molecules and the need to couple the single-electron events that are typical of electrochemistry with the multielectron events required for bond-breaking and -making in organic reactions. In recent years, so-called electrocatalysis has emerged as an effective mean to solve above problems. It employs special compounds (i.e., electrocatalysts) added in small quantity, which convey applied potential from the electrode to the reaction medium, intermediating the energy transfer.

In this project, it is envisioned to use electrocatalysis to effect highly powerful synthetic reactions, that is, ones resulting in a large increase of the molecular complexity. In particular, it is planned to employ compounds called iodoarenes as the electrocatalysts. These species have been used in many valuable synthetic reactions, however, requiring stoichiometric terminal oxidant (i.e., the ‘high-energy compound’) to generate the active form of the iodoarene catalyst. Due to related economic and environmental concerns, it has effectively prevented the widespread application of such reactions, especially on a large scale. The application of electrochemical stimuli to activate iodoarenes will radically, yet elegantly, tackle above issues, removing the burden to translate this chemistry into industrial and semi-industrial setups. Importantly, iodoarenes are non-toxic and environmentally benign, which constitutes a huge advantage, especially in the context of the synthesis of therapeutics.

A highly novel and original aspect of the project is the planned use of chiral iodoarenes to promote asymmetric reactions under electrochemical conditions, which has never been attempted before. The majority of complex compounds may exists as two mirror images (so-called enantiomers). Due to the chirality (‘handedness’) of the molecules of life (peptides, DNA/RNA, carbohydrates, etc.), the opposite enantiomers of a single substance often display quite different biological activities. This results in a need to selectively generate compounds, especially pharmaceuticals, in an enantiopure form. By employing chiral iodoarene electrocatalysts, the developed reactions will not only allow to construct complex organic molecules in a sustainable fashion, but they will also generate predominantly only one of the two enantiomers of the product.