Molecular chirality is a common property of biomolecules. Yet, there are various fundamental questions regarding our chiral world, still unanswered, including how key biomolecules gained enantiopurity, i.e. property to occur naturally only as single optical isomer. Chirality controls activity of living organisms to a large extent. For example, chiral receptors interact differently with stereoisomers of substrates, what is called chiral recognition. For drugs, most often only one enantiomer exerts the therapeutic effect while the other one is non-active or harmful (drug enantioselectivity). The driving force in chiroptical research to a large extend is, therefore, potential in practical applications, also due to the fact that chirality is very often used in designing new catalysis, functional materials or drug delivery systems.

There are several spectroscopic (i.e. based on interaction of light and matter) methods that enable to study chiral compounds. The youngest among them are techniques called vibrational circular dichroism (VCD) and Raman optical activity (ROA) that provide local and detailed information about the molecular structures of chiral compounds by studying vibrations of molecules. Rich information about the structure, however, is paid for with the relatively low sensitivity of these methods. Therefore, special modifications of these techniques that enable signal enhancement are intensively developed. Among various interesting approaches recently investigated in the context of chiroptical signal enhancement, one of yet highly unexplored potential is plasmon enhancement. This type of enhancement is related to formation of the intense electromagnetic field around metal nanoparticles (surface plasmons) or some molecules (quantum plasmons). Recently it was demonstrated that plasmon enhancement enabled chiral information to “jump” through-space to achiral molecules and then, the achiral molecules manifest in the chiroptical spectra. While is seems really surprising and exciting, the mechanism behind these new observations is not well understood.

In our recent chiroptical studies of a specific supramolecular unit, built from oxo-vanadium(V) aminotriphenolate complex and a enantiopure chiral co-ligand, we have observed serendipitously that the obtained ROA signal is derived solely from achiral solvents and not the chiral supramolecular unit. Therefore, the obtained supramolecular cage can be treated as a nano-size antenna that is able to efficiently transfer chirality to the environment. The fundamental objective of this project is systematic tuning of properties of this nanoantenna to determine conditions dictating efficiency of the through-space chirality transfer. Hence, the aim of the project is to understand how the chirality is transferred to achiral molecules (mechanism) and fine-tuning of the properties of the supramolecular unit to yield a superefficient molecular nanoantenna for chirality transfer to achiral solvents and, in a broader context, the environment.

To understand how various structural modifications impact on the observed intensity transfer to solvents, a systematic analysis of influence of various factors (different chiral co-ligands, metal ions, side groups in the supramolecular unit, temperature, solvent, competing equilibria as well as testing other supramolecular systems) on the ability to transfer chirality from studied supramolecular systems to solvents will be undertaken. A multiparameter approach is going to be applied to analyze chiroptical properties of investigated supramolecular units based on key chiroptical methods, i.e. VCD, ROA and ECD (electronic circular dichroism) supported by quantum-chemical computations. Achieved results will enable linking molecular properties with efficiency of chirality transfer and magnitude of signal enhancement. The obtained nanoantenna for superefficient chiral transfer should create a “superchiral”, very confined in space, resonant field that can be transmitted to the environment and illuminate the surrounding achiral molecules to enable their registration.

Of the 200 most commonly used drugs, over 110 are compounds in which active pharmaceutical ingredients are chiral. Although generally only one enantiomer has therapeutic properties, racemic mixtures of active pharmaceutical ingredients are still very commonly used, due to high costs of obtaining and testing enantiopure compounds. A practical aspect of the project is formation of a tailored supramolecular unit of high ability for a resonant chiroptical response. This unit should be capable to produce the enhanced signal enabling measurement of an attached chiral ligand at low concentrations and in a short time for determining of its absolute configuration. Hopefully, in the broader context, the results of the project may contribute to development of chiroptical methods, their application in the biochemical and medical fields, enantioselective synthesis or designing of new range of molecular switches and chiral plasmonic nanomaterials.