Description for the general public

Currently, most components for photonic devices are based on inorganic nonlinear optical materials, although organic materials exhibit higher hyperpolarizabilities and very fast nonlinear optical responses. The challenge for organic materials lies in the use of weak noncovalent interactions between the organic molecules to construct suitable and stable organizations for generating efficient nonlinear optical effects. *Ab initio* quantum chemistry is a valuable and efficient toolbox for the bottom-up supramolecular engineering. In fact, high-level *ab initio* calculations contributed substantially to our understanding of the effects of intermolecular interactions on nonlinear optical response of molecular complexes. These effect can be conveniently analyzed in terms of interaction-induced (excess) properties, defined as the difference between a property of the complex and the sum of properties of non-interacting subsystems. Several research groups performed an exploration of the effect of interaction types (exchange, electrostatic, induction, dispersion) on purely electronic excess properties for a large set of molecular complexes. However, it is important to highlight that an insufficient attention was paid to the vibrational contributions to interaction–induced nonlinear optical properties of complexes, although in the case of molecules it is now recognized that vibrational contributions are important for numerous nonlinear optical processes. The primary goal of this project is to perform a pioneering exploration of the physical origins of vibrational contributions to the interaction-induced nonlinear optical properties for a representative set of molecular complexes, including the effects of anharmonicity. In particular, for the first time, a partitioning of anharmonic vibrational contributions into interaction types (exchange, electrostatic, induction, dispersion) shall be performed for two most common structural motifs, i.e. stacking and hydrogen bonding. The partitioning will also be performed for electronic (hyper)polarizabilities in a similar vein, thus allowing for a comparative analysis of intermolecular interactions for both counterparts. The project is intended to be carried out employing *ab initio* quantum chemistry methods. The expected outcome of this project is to extend the understanding of the effects of noncovalent interactions on nonlinear optical response of molecular complexes (including their vibrations). Hopefully, a bottom-up supramolecular engineering can make a benefit of the results expected in this project.