M:M-PROP: metallophilic interactions - allies or enemies?

One of the currently most important areas in chemistry is developing new materials that would display a rapid and reliable response to changes in local environment, and send out signals indicating the phenomena taking place. Therefore, chemical compounds exhibiting specific photoactive properties, either in solution or, even more importantly, in the solid state, are among the most desired materials nowadays. Especially interesting here are coordination complexes of transition metals which have versatile applications in solar-energy conversion and other fields ranging from molecular electronics and photocatalysts to light-emitting devices (LEDs) and biolabels. It is, thus, of high importance to sensibly control optical properties of such materials at the molecular level, so as to apply this knowledge to generate materials with particular properties across all the size scales from molecules to bulk materials, relevant for the specific applications. Despite numerous efforts, this very challenging target remains far from being achieved.

In view of the above, the current project is dedicated (but not restricted) to a family of complexes containing Rh^{I}, Pt^{II} or Au^{III} centres. Such systems are often luminescent (including bright phosphorescence and thermally-activated delayed fluorescence), display dichroism, or exhibit different colour dependent on molecular aggregation in the solid state. The studied systems shall cover discrete monocentre complexes, as well as structures stabilised by different types of intra- and/or intermolecular metal···metal interactions. The aim of this project is to deeply investigate the effect of formation of metallophilic contacts, their type, character and impact on light-induced charge-transfer processes and, in consequence, on the spectroscopic properties of the examined materials. We are interested in relationships between structural and electronic features, and the macroscopic properties of substances. We would like to explain the observed phenomena and trends, find clear answers when specific interactions enhance the desired properties and when not, and to verify whether (and if so – when) it is possible to sensibly control the spectroscopic properties via temperature and pressure.

The studies will be conducted in the most comprehensive and systematic way, starting from synthesis, through crystallisation, spectroscopy of solution and single crystals, diffraction studies (including high-resolution, multi-temperature and high-pressure measurements), to advanced time-resolved ultrafast spectroscopic and photocrystallographic methods. The experimental work shall be supplemented with theoretical computations, as well as with standard material characterisation methods.

The outcomes of the project shall help to elucidate the nature of interactions in the studied systems in their crystalline state and in solution, and their role in light-induced charge transfer processes. The obtained results shall provide information on dynamics of phenomena related to charge transfer, light-induced structural changes, and electron density distribution in the examined complexes. Furthermore, the high-pressure and multi-temperature X-ray diffraction studies shall enable correlation between structural features and spectroscopic properties and give an insight into the controllability of spectroscopic properties of a given material. The gained knowledge may contribute significantly to future conscious and intelligent design of new complexes/materials with carefully tuned properties appropriate for LEDs, solar cells, biomarkers, *etc.*