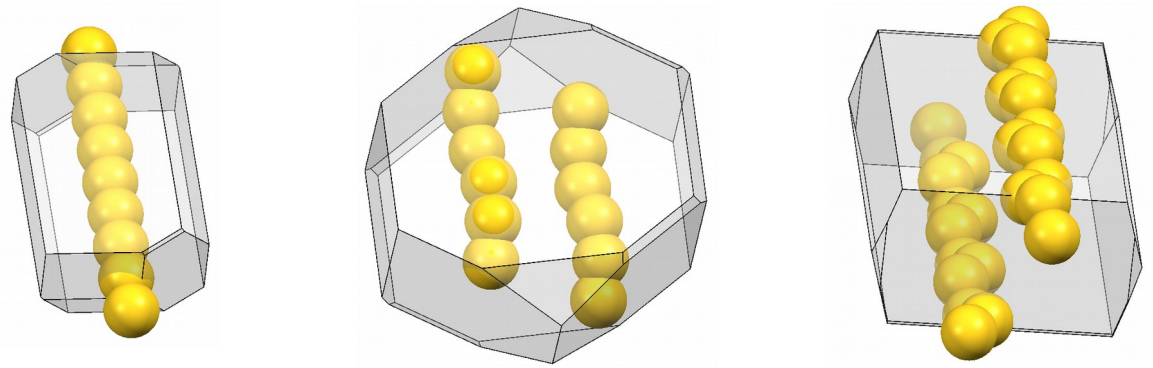
Molecular gold wires - their growth, polymorphism and physicochemical properties

The subject of research will be a class of metal-organic compounds, in which heavy atoms (gold) are bound to organic molecules, in particular *alkinyl gold(I) phosphines*. Compounds of this class can form peculiar crystal structures containing chain-like arrangements of gold atoms — "gold wires" of various shapes, separated by organic molecules (see figure below). Such structures give rise to materials with some very interesting properties, for instance some are strongly fluorescent or piezochromic (changing color with pressure), due to existence of gold-gold interactions (aurophilic). At the same time their properties are distinct from those of metallic gold, gold nanoparticles or organic molecules themselves. For example one may expect that under high pressure conditions "gold wire" structures will become mono-atomic 1D (semi-)conductors. The compounds share another important trait: they exhibit crystallographic polymorphism, which means that the same compound, depending on crystallization conditions, can form crystals of different molecular packing structures, leading to ideally straight or zigzag gold chains, resulting in different physical properties.



Polymorphism is of paramount importance for industrial applications, as pharmaceutical industry has learned when *Ritonavir* drug had to be withdrawn from the market after it transpired that it was prone to undergo an unexpected polymorphic transition that resulted in an insoluble and therefore therapeutically inert form. Polymorphs of the compounds to be studied here may rather find applications as various materials for sensors and optoelectronic devices (including OLEDs). However, such industrial applications will also be contingent on mastering fabrication techniques for particular crystalline forms and on in-depth understanding of their stability, possible phase transitions and other specific properties.

It is the first goal of the project to perform controlled crystallizations of investigated compounds, to obtain various new polymorphs and to identify physical and chemical factors which determine their growth and transformations. The second goal is to study physicochemical properties of newly obtained crystals, with a focus on optical and spectroscopic ones, and ascertain their suitability for practical applications.

Several advanced x-ray diffraction techniques will be used for crystal structure determination including measurements under variable temperature and high pressure (up to 10 GPa, ~10.000 atm.) using diamond anvil cells (DAC) and measurements with synchrotron sources. Properties of crystals such as solid state UV-VIS fluorescence (emission of visible light upon UV irradiation) and Raman spectroscopy will be determined alongside with calorimetric and electronic conductivity measurements.

In order to explain structure-property relationships and to establish a framework for interpretation of experimental results, theoretical calculations will be performed at DFT (density functional) level with periodic boundary conditions, that will provide a quantum-mechanical model for electronic structure including band structure and intermolecular interaction energies.

Systematic comparison of physicochemical properties between several polymorphs of the same compound will provide a unique opportunity to outline the **contribution of crystal packing** to their properties **unbiased by** the influence of **various chemical substituents**.