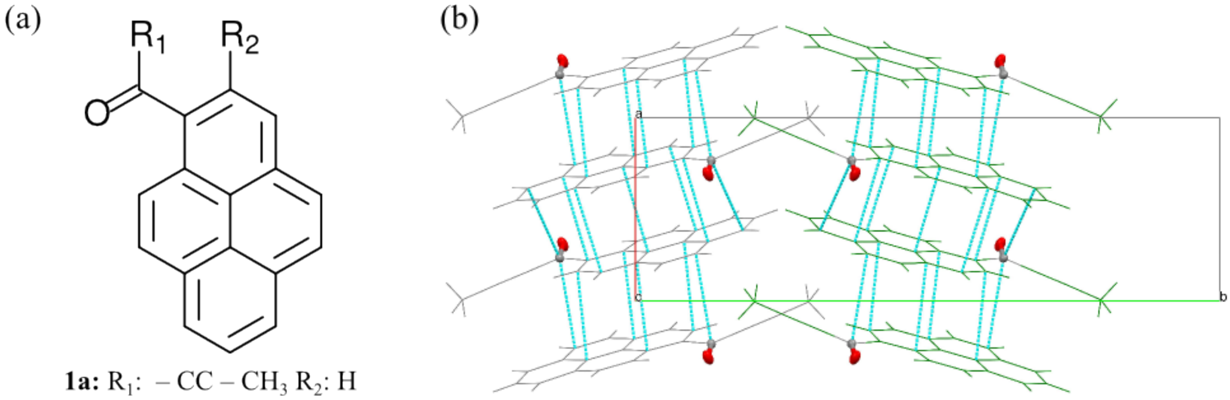
We aim to describe the interplay between the structural changes effected by high pressure and fluorescence (i.e.: emission of light, resulting from sample's excitation by, for instance, exposition to UVor visible light) of a family of pyrene derivatives in the crystalline state. We intend to investigate the mechanisms responsible for their efficient fluorescence in the solid state.

The results of the project can help to explain fluorescent propensities of a much wider family of fluorophores (i.e. chemical compounds capable of fluorescence). Understanding the mechanisms of the fluorescence is an essential step in designing new, more efficient light-sensitive materials, utilized in various sensors, diodes and photovoltaics, and optimizing properties of already existing ones.

The compounds selected for our project, simple pyrene derivatives (Fig. 1a), are special representatives of the pyrene-based fluorophores. They share a common packing motif in crystalline state (Fig. 1b) and tendency to enhanced (in some cases over 2-fold) fluorescence upon transition from solution to that state.



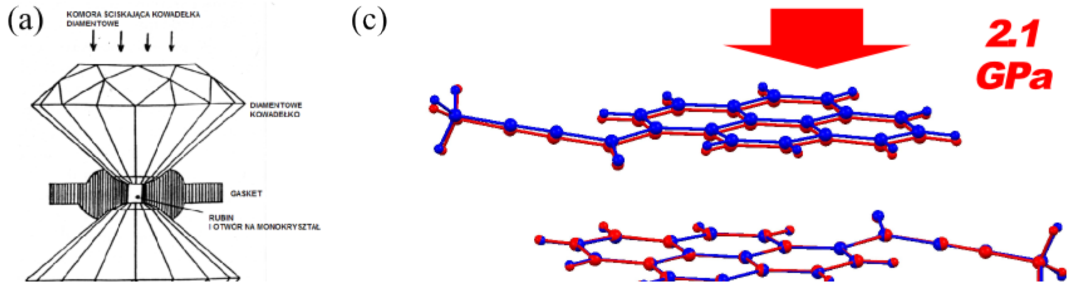
1a: R_1: $-CC-CH_3$ R_2: H

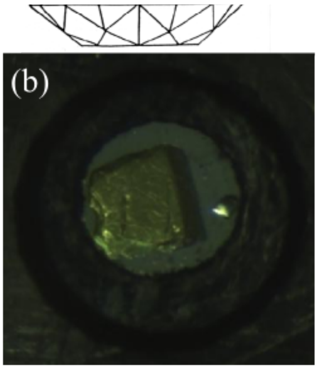
Figure 1. (a) The scheme of the compounds to be investigated in the project (b) molecules of the selected compound **1a** stacked in crystal lattice; the shortest intermolecular contacts marked in cyan.

Another interesting property of these compounds is the variability of their photophysical properties (e.g. sample color, fluorescence) under mechanical stress (grinding, pressing), in other word: piezochromism. For instance, applying high pressure to a crystal of one of our compounds, **1a**, induced a color changeof the crystal from yellow to orange and red-shifted the fluorescence spectra. The same physical stress resulted in negligible changes in the molecular structure and very significant decrease in distances between the planes of the aromatic rings in the crystal structure (Fig. 2c). Similar changes are associated with ultra-fast formation of groups of excited molecules (excimers), directly preceding fluorescence emission. Investigation of the changes induced in the crystal by applying high-pressure may be therefore considered as a model of excited multimer formation process. Using such model, we want to investigate the process step-by-step, by controlling the pressure applied to our samples.

The project will combine the experimental and theoretical investigation of the selected samples. The X-ray diffraction studies at different pressures will provide detailed experimental description of the structure of the compounds in the crystalline state and structural changes resulting from high pressure application. The spectroscopic studies, conducted on the same samples at the same pressures, will provide confirmation of the structural changes (Raman spectroscopy) and will document the changes in fluorescence properties (UV-VIS spectroscopy), such as wavelength, efficiency, electronic excited state lifetime. Quantum-mechanical calculations, combined with the experimental data, taking into account the crystalline environment and the effects of high pressure, will provide description of the electronic structure of each compound and will allow description of the observed changes on deep, electronic level. The calculations will also provide information on the importance and strength of various intermolecular interactions in the crystalline state.

X-ray structure analysis under high pressure will be performed in dedicated diamond anvil cells (DAC) (Fig 2a). We will place single crystals of chosen pyrene derivatives (Fig 2b) inside separate DACs in hydrostatic medium (e.g.: oil) and perform a sequence of X-ray diffraction experiments, at different pressures. A sample already enclosed in DAC can also be analyzed by means of UV-VIS and Raman spectroscopy, yielding results for the exact same sample and structure with all techniques.





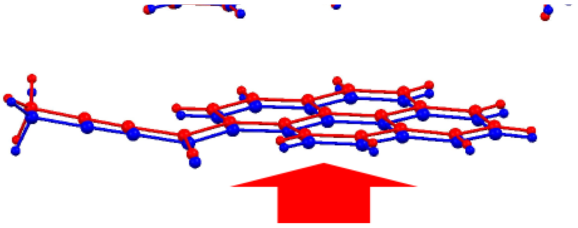


Figure 2. (a) Schematics of the high-pressure cell
(b) single crystal of compound **1a** in the cell
(c) The overlay of the fragments of the crystal lattice of **1a** under ambient pressure (blue) and under the pressure of 2.1 GPa (red).