The project goal and reasons for attempting a particular research topic. In living organisms, DNA and RNA nucleic acids play crucial roles in the development and functioning of every cell. DNA serves as the primary storage of genetic information, which is used to produce proteins. RNA, known for its diverse functions, acts primarily as a catalyst in many biomolecular processes. Both DNA and RNA are composed of nucleosides, the fundamental building blocks of these complex biomolecules. One of the most intriguing puzzles in modern science is understanding how these biomolecules naturally formed during the primeval times of Earth.

Over the past decade, scientists from various disciplines have devoted significant effort to investigating the environmental conditions and chemical processes that may have been present on early Earth. These efforts have culminated in the proposal of plausible scenarios for the formation of nucleotides, the building blocks of nucleic acids. One key environmental factor exploited in these studies was UV radiation, which served as a source of energy for triggering high-energy chemical reactions. The application of UV light in prebiotic chemistry often facilitates chemical selectivity in the formation of building blocks. Although many plausible chemical pathways toward RNA nucleotides have been proposed, the corresponding DNA molecules have remained a significant challenge for organic chemistry due to constraints imposed by primordial environmental conditions. Recently, for the first time, canonical DNA building blocks have been successfully synthesized through a new photoredox chemistry that relies on a two-step process. In this new chemistry, the DNA nucleoside precursor must first establish a chemically weak interaction with an inorganic anion, namely hydrogen sulfite (HS^-). Upon UV irradiation, intermolecular electron transfer occurs from the anion to the DNA nucleoside precursor, enabling a selective, high-energy reduction process that yields deoxynucleosides. Despite an initial understanding of how this new class of photoredox chemistry works, much remains unknown about the nature of the complexation between heteroorganic compounds and sulfur-bearing anions via weak interactions, such as chalcogen bonds (S—S). Furthermore, the UV-induced electron transfer process and its molecular mechanisms between molecules still requires experimental and theoretical explanations, particularly concerning its timescales.

Description of research and substantial results expected. In this project, we will focus on studying selected DNA/RNA nucleoside precursors that are prone to forming chemically weak complexes with small inorganic anions (e.g., hydrogen sulfite, bisulfite) through chalcogen-bonding interactions in aqueous solutions. Our first goal is to determine the rules governing the chalcogen-based complexation process and identify functional groups that readily undergo such interactions with anions. Additionally, we aim to explore simple organic molecules with sulfur-bearing functional groups that cannot engage in weak interactions with anions under standard conditions. However, their chemical nature can be altered upon UV irradiation, temporarily enabling these molecules to form chalcogen-bonding interactions. To achieve these objectives, we will employ highly accurate quantum chemical methods to characterize the complexation processes between nucleoside precursors and anions. Moreover, we will assess the feasibility of intermolecular electron transfer within these complexes upon UV excitation. In collaboration with our international partners, our theoretical results will be supplemented by time-resolved absorption measurements to experimentally track photoinduced events and estimate the efficiency of intermolecular electron transfer. Finally, prebiotically relevant complexes will also be studied through UV irradiation experiments to characterize the resulting products and explore their potential for implementation in prebiotically credible chemical pathways. This research will, for the first time, provide an accurate description and establish general rules for a new concept in photoredox chemistry, combining theoretical results supplemented by experiments under broad international collaboration. Potentially, it could become a novel direction in the synthesis strategy of bioorganic molecules. Furthermore, these results may inspire the search for naturally occurring photoredox processes and their impact on nature.