Development of new pathways for CO_2 utilization: From a common waste to a valuable chemical feedstock

Design and development of the novel synthetic pathways as well as synthesis of the functional materials of desired functionality are one of the most important issues in the modern chemistry. In this regard, CO_2 seems to be very interesting reagent, which can be easily extracted directly from the air or obtained during the industrial processes and its transformation can occur according to well-known from Nature bioinspired reaction pathways. Simultaneously, the carbon dioxide is one of the most spreading greenhouse gas in the atmosphere and decreasing of its concentration is now a very important issue in the point of view the fight with global warming. Nowadays, extremely high investments are dedicated to projects concerning capture, storage and conversion of CO_2 into value-added products. The main goal of the proposed project is the development of new pathways for rational transformation of CO_2 into valuable products and materials of desired functionality. This strategy changes the role of CO_2 from an unwonted waste to a commonly available chemical feedstock and, as such, it is a fast developing area of research with potentially far-reaching technological applications. The project is a highly multidisciplinary platform, drawing from a number of fields such as organic, organometallic and bioinorganic chemistry, catalysis and materials science.

The proposed project aims at more in-depth understanding of CO_2 activation as well as the development of novel non-covalent porous materials and catalytic systems for the photocatalytic conversion of CO_2 into energetic carbon fuels. The initial stage of the project will include synthesis of the chosen main-group and transition metal hydroxide compounds supported by various 8-hydroxyquinolinate ligands, which in the next will react with CO_2 leading to new, luminescent metal carbonates. These carbonate species may self-assemble into a unique non-covalent porous material, and their self-organization processes will be also a subject of our investigation. We believe that the acquired experimental and theoretical knowledge on the CO_2 activation open new perspectives in the design and synthesis of novel metal carbonate building blocks for functional materials. The next part of this project focuses on development of new hydrogen-bonded organic frameworks (HOFs) based on carbonate organic systems. Based on our experience in crystal engineering and working with nitrogen organic ligands, we plan to develop new organic systems for CO_2 transformation to carbonate species which will be self-organize *via* complementary hydrogen bonds into novel supramolecular architectures. The last part of our project focuses on the development of novel catalytic systems for CO_2 photoreduction based on ZnO nanocrystals (NCs) derived from organometallic approaches. This process can mimic the natural photosynthesis system by converting the solar light energy into valuable, unconventional carbon fuels (e.g., CO and CH_3OH) without requiring other high-energy input. The need to find alternative renewable and sustainable fuels for transportation is triggering an increasing interest in the photocatalytic reduction of CO_2.ZnO-based nanostructures represent a highly desired alternative for heavy-metal based systems due to their biocompability and intrinsic physicochemical properties. However, a number of significant impediments of ZnO NCs derived from the commonly used sol-gel method extremely limit their applications. Conversely, the ZnO NCs derived by our organometallic approaches possess many advantages over materials synthesized using standard sol-gel technique and seem to be very good alternative for widely used TiO_2 nanoparticles in CO_2 photoreduction processes.

The proposed research project fits squarely into this current technological trend. The results should allow not only to significantly broaden the current state of knowledge of CO_2 activation, by metal hydroxide complexes, but also make an outstanding contribution to both the area of hybrid organic-inorganic supramolecular systems and novel quantum dots-based catalytic systems for CO_2 conversion into value-added products.