Metallocomplexes in MOFs and COFs for Visible-Light-Driven CO_2 Conversion to Solar Fuels

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The global reliance on fossil fuels has led to unprecedented energy and environmental challenges, driven by rising energy demand and excessive carbon dioxide (CO_2) emissions. Because of this, the urgent need to develop alternative ways to produce substitutes to fuel from other resources has been under research and consideration for many years. Harnessing sunlight, an abundant and renewable energy source, to drive the conversion of CO_2 and water into energy-rich fuels represents a compelling strategy toward a sustainable, fossil fuel-free future. Although natural photosynthesis achieves this transformation efficiently in plants, the development of synthetic material systems capable of converting CO_2 into storable and transportable solar fuels with high efficiency, selectivity, stability, and scalability remains a scientific challenge. This project aims to address this challenge through the rational design of advanced porous photocatalysts based on metallocomplexes, with a particular focus on bipyridine and terpyridine metallocomplexes, integrated within metal-organic frameworks (MOFs) and covalent organic frameworks (COFs). These materials uniquely interlink organic and inorganic components, offering precise control over light absorption, charge separation, catalytic activity, and CO_2 adsorption. Incorporating photoactive metal complexes into ordered porous frameworks enables visible-light-driven CO_2 conversion into solar fuels, including formate, methanol, and methane. The research is structured around complementary material design strategies. First, MOFs incorporating photoactive metal nodes and metalloligands including Ru, Cu, Os, or Fe-based complexes will be synthesized to function directly as heterogeneous photocatalysts under visible light. Rational linker design, including nitrogen-rich and π-extended ligands, will be employed to enhance light harvesting, charge transfer, and excited-state lifetimes. Second, selected MOFs will serve as host that will be post-metalated with metallocenters that will serve as active sites for the generation of heterostructures by a controlled coordination, enabling systematic investigation of structure-activity relationships. Third, COFs will be assembled by linking metallocomplex-based subunits through covalent bonds to form photoactive conjugated systems aiming to improve charge separation and catalytic efficiency for CO_2 photoreduction. Comprehensive characterization using PXRD, HR-TEM, spectroscopic methods, gas sorption analysis, and density functional theory (DFT) calculations will elucidate structure-property relationships. Photocatalytic CO_2 reduction will be evaluated under visible light using both liquid-phase and gas-phase reactors, the latter developed in collaboration with the Chemical Engineering Department. Key performance metrics including activity, selectivity, efficiency, and long-term stability will be systematically assessed. By integrating metallocomplex chemistry with framework engineering, this

project aims to establish robust design principles for multifunctional MOF- and COF- photocatalysts. The predicted outcomes will contribute to scalable, efficient solar fuel production and provide a viable pathway for CO_2 recycling, offering a sustainable solution to the intertwined energy and climate challenges facing modern society.