Abstract

Drawing inspiration from nature, the concept of redox-active ligands explores the catalytic potential of earth-abundant metals like iron and copper despite their preference for one-electron redox reactions. Unlike traditional spectator ligands, redox-active ligands offer energetically accessible levels for reduction or oxidation, enabling oxidation state changes to occur either exclusively at the ligand or synergistically at both the ligand and metal. The incorporation of redox-active ligands presents numerous benefits, such as facilitating continuous multielectron transfer, regulating electron-deficient transition states, and enabling single-electron changes in the redox state of the metal center. In this context, we have meticulously adapted redox-active formazan-based ligands to explore a broad spectrum of applications, encompassing resistive switching memory, antibacterial properties, and electrocatalysis. Formazans boast a rich history in chemistry, where deprotonation generates monoanionic chelating N-donor ligands called "formazanates." The synthesis of formazan ligands provides a straightforward route to formazanate-based complexes with tunable electronic and steric characteristics. Complexes featuring a formazanate ligand typically exhibit a narrow HOMO–LUMO gap, resulting in energetically accessible π*-orbitals. This property renders formazanate complexes redox-active, enabling reversible storage of electrons in a ligand-based manner within these compounds. The utilization of formazanate-based ligands in coordination with base metal ions has initiated a novel research domain, expanding the range of applications in the design of magnetic, optical, and intriguing electrical materials. This is achieved by leveraging the distinctive optoelectronic properties and adaptable electrochemistry offered by formazanate ligands. The primary focus of this thesis lies in the synthesis of formazanate-based ligands, their corresponding metal complexes, and their diverse applications, ranging from resistive switching memory to antibacterial activity and electrocatalysis. An ionic organotin complex was prepared using a 2-pyridine substituted formazan ligand and investigated for its application in solid-state non-volatile write once read many (WORM) memory devices, demonstrating a high switching on-off ratio. Furthermore, distorted octahedral bis(formazanate) zinc complexes were used in the fabrication of a memory device that intriguingly exhibited non-volatile resistive switching memory behavior. The bis(formazanate) iron complexes displayed extensive redox behavior during the cathodic sweep in cyclic voltammetry analysis and were realized as electroactive cathode materials for the electrocatalytic H_2O_2 reduction in one-compartment H_2O_2 fuel cell. Later, a mono(formazanate) mercury complex was prepared and was further studied as an antimicrobial agent.

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