Abstract

In the last couple of decades, the frontiers in synthetic inorganic chemistry have been pushed in a new direction, aiming to reduce the utilization of Earth's less abundant or noble metal resources. Such a path toward the environment's sustainability began with the innovative approach of identifying base metal ions that can be strategically combined with redox-interesting ligand systems. The coordination of a redox-active ligand helps the coordinated base metal ions to survive unfavorable oxidation states and retain overall stability during the chemical reactions. The introduction of redox-active ligands facilitates the uninterrupted multielectron transfer, stabilizes the electron-deficient transition states, and can successfully tune the single electron metal-centered redox changes. Therefore, the molecules with superior redox activity are important charge carriers and can be implied as active materials or catalysts for various applications. In this regard, we have carefully functionalized the phenalenyl-based ligands for a variety of sustainable applications. Phenalenyl (PLY) refers to an odd alternant polycyclic hydrocarbon that has shown the potential to exist in three energetically favorable redox states, i.e. cation, anion, and radical. The cationic form of PLY can be readily generated via metal coordination, which can accept electrons to form stable PLY-based radical and anionic species. The work in this thesis highlights the coordination chemistry approach for the synthesis of PLY-based metal complexes, their extensive characterization and the applications varying from resistive memory device to (electro)catalysis. In Chapter 3, we discuss a square planar [Co^{II}L] complex, which was prepared from a PLY-based ligand, LH_2 = *9,9'-(ethane-1,2-diylbis(azanediyl))bis(1H-phenalen-1-one)*. The interesting solid-state packing analogous to the charge transfer salts present in this complex motivated us to explore its application in solid-state resistive memory device. Chapter 4 covers the synthesis of square planar [Cu^{II}L] complex, which is employed as a catalyst for the oxidation of polycyclic aromatic hydrocarbons. The Chapter 5 of the thesis highlights the synthetic modifications of PLY architecture to design ligands that can give rise to dinuclearity in the resulting metal complexes. We prepared two dinuclear Fe(III) complexes, [Fe^{III}_2(hmbh-PLY)$_3$] and [Fe^{III}_2(hnmh-PLY)$_3$] from hmbh-$PLYH_2$ = *9-(2-(2-hydroxy-3-methoxybenzylidene)hydrazineyl)-1H-phenalen-1-one* and hnmh-$PLYH_2$ = *9-(2-((2-hydroxynaphthalen-1-yl)methylene)hydrazineyl)-1H-phenalen-1-one* ligands, respectively. Both complexes are explored for the electrochemical H_2O_2 reduction and employed as cathode material in one-compartment H_2O_2 fuel cell. In Chapter 6, we discuss the synthesis of a dinuclear Ni(II) complex, [Ni^{II}_2(dtbh-PLY)$_2$] from *9-(2-(3,6-di-tert-butyl-2-hydroxybenzylidene)hydrazineyl)-1H-phenalen-1-one,* dtbh-$PLYH_2$ ligand and its electrocatalytic behaviour in the oxygen evolution reaction (OER).

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