ABSTRACT

Thesis Title: Cyclic and Acyclic Rhenium(I)-based Complexes

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Chapter I

Design and synthesis of metal-directed supramolecules have received considerable attention because of their aesthetic structures and potentials in several fields of chemistry and materials sciences. The \( \text{fac-Re} (\text{CO})_3 \)-corner directed neutral metallomacrocycles are highly interested because of their important functions and potential its valuable applications in host-guest chemistry, catalysis, probes for photoluminescence quenching, anticancer agents, and photo- and electro-chemical sensing. Examples of the different sizes and shapes of the \( \text{fac-Re} (\text{CO})_3 \)-based metallacycles are mononuclear cycles, dinuclear cyclic compounds, trinuclear cages, squares, rectangles, gondolas, trigonal prisms and tetragonal rectangular prisms. Re(I)-polypyridyl complexes are known to be highly emissive and have been used as emitting dopants in a variety of OLED structures. Due to their interesting materials properties, efforts are still being expanded on synthesis of either new type of cyclic and acyclic complexes or existing type with improved properties using new organic building blocks.

Chapter II

Neutral \( \pi \)-stacked octanuclear metallomacrocycles were prepared using \( \text{Re}_2 (\text{CO})_{10} \), and linear tetratopic \( \pi \)-conjugated nitrogen donors with/without bischelating ligands in toluene under solvothermal condition. The metallacycles were characterized by elemental analysis, FT-IR, and NMR spectroscopy. The structure of alkoxy bridged prism and bisimidazolate prism were characterized via X-ray crystallography. They adopt \( \pi-\pi \)
stacked structure using two planar nitrogen donors. Four ethylene units in the cycle are parallel to each other with a distance of less than 4.1 Å. Disorder of two ethylene units among the four units in the tetratopic donors was observed after photoirradiation of bisimidazolate prism 5. The absorption and emission nature of these metallacycles were studied using UV-Vis and fluorescence spectrophotometry.

Chapter III

Two new flexible bis-chelating ligands, 1,4-bis(2-(2-hydroxyphenyl)benzimidazol–1-ylmethyl)benzene (p-XyHpbi), and 1,3-bis(2-(2-hydroxyphenyl)benzimidazol–1-ylmethyl)-2,4,6-trimethylbenzene (m-TXyHpbi), possessing two N\∩OH units were designed and synthesized. Reaction of the flexible dianionic ligand with Re₂(CO)₁₀ in the presence of flexible neutral ditopic nitrogen donors in a one-step solvothermal method or reflux condition yields a neutral dinuclear heteroleptic metallomacrocycle. Ligands (p-XyHpbi), (m-TXyHpbi), and metallomacrocycles (6 and 7) were characterized by elemental analysis, FT–IR, \(^1\)H–NMR, and UV–Vis spectroscopic methods, cyclic voltammetry, IR and EPR spectroelectrochemistry and single-crystal X-ray diffraction analysis. The molecular structure of 6 is an unsaturated dinuclear heterostranded helicate, while the structure of 7 is a non-helicate metallomacrocycle.

Chapter IV

Series of neutral heteroleptic trinuclear M₃L₃L’-type supramolecular cage was synthesized in a one step process using partially protected tritopic fac-Re(CO)₃ acceptor, anionic rigid angular ditopic bridging nitrogen donors, and neutral flexible tri(monodentate) tripodal nitrogen donors in toluene. Three benzimidazolyl/imidazolyl units and three fac-Re(CO)₃ cores make up the metallacalix[3]arene-shaped trinuclear cycle which was capped by tritopic nitrogen donors. Metallacyclic cage 8-10 and 12 was characterized by elemental analysis, FT-IR, IH NMR methods. The molecular structure of 8 and 12 further characterized by single crystal X-ray diffraction method.
Chapter V

Neutral heteroleptic tetranuclear complex [(fac-Re(CO)$_3$)$_4$(BOP)$_4$(Tkpvb)] (13) was synthesized in a one step process using Re$_2$(CO)$_{10}$, benzoxazol-2-ylphenol (BOPH), and 1,2,4,5-tetrakis{2-(4-pyridyl)vinyl}benzene (Tkpvb) in toluene. Four mononuclear complex [(fac-Re(CO)$_3$)(BOP)(pyridyl)] units are arranged spatially at the corner of 13. Complex 13 was characterized by elemental analysis, FT-IR, $^1$H NMR methods and single crystal X-ray diffraction study. The absorption and emission nature of 13 was studied using UV-visible and fluorescence spectroscopic techniques.