A Study on Luminescent Heteropolynuclear Complexes Having NHC-based Chelate Ligands

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Generally, mononuclear Pt(II) complexes having *α*-diimine (N^N chelate) or phenylpyridine derivatives (C^N chelate) exhibit emission attributed to the emissive states derived from metal-to-ligand charge transfer (MLCT) transitions or intra-ligand (IL) transitions depending on the nature of chelate ligands. In addition, when the Pt···Pt interaction increases due to the formation of dinuclear complex or the stacking of mononuclear complexes in the solid state, the MLCT emission bands shift to lower energy. These lower energy bands are particularly called metal-metal-to-ligand charge transfer (MMLCT) bands.

The metal-metal interactions can also be observed for heteropolynuclear metal complexes. When metal-metal interactions are observed in the ground state, the Pt•••M distances become shorter than the sum of the van der Waals radius of each atom. On the other hand, the metal-metal interactions in the excited state are observed as the change of the emission energies corresponding to the difference of incorporated heterometal atoms. It is thus very interesting to study the photophysical properties arising from the metal-metal interactions between heterometal atoms. Furthermore, it is also possible to make strong metal-metal interactions between heterometal atoms, leading to the formation of dative bond. This bond can be formed by the donation of electron pair in the filled d_{z^2} orbital of Pt atom to the vacant s orbital of group 11 metal atoms.

Although various properties of heteropolynuclear complexes have been investigated by using a variety C^N chelate ligands, those of heteropolynuclear complexes involving N-heterocyclic carbene (NHC) ligands have not been fully explored. The NHC-based ligands have unique electron donating character on the carbene moiety. The strong σ-donor properties of the NHC-based ligands are expected to increase the d-d transition energy effectively, resulting in a higher energy emission from the complexes.

In this thesis, synthesis of heteronuclear metal complexes having NHC-based chelate ligand, and elucidation of structural and photophysical properties of heteropolynuclear metal complexes are described.

In chapter 1, the background and aim of this research are described.

In chapter 2, synthesis and photophysical properties of butterfly-shaped dinuclear Pt(II) complex having pyridyl-NHC chelate ligand are described. The crystal structure of the Pt_2 complex showed short intramolecular Pt···Pt distance (3.129 Å) and unique packing structure containing one-dimensional infinite pore that was filled with solvent molecules. The Pt_2 complex showed bluish-green emission (λ_{max} = 459 nm) in the solid state at 25 °C (λ_{ex} = 330 nm). TD-DFT calculation revealed that the lowest-energy absorption bands are mainly as- signed to the combination of metal-to-ligand charge transfer (MLCT) and ligand-to-ligand charge transfer (LLCT) transitions.

In chapter 3, synthesis, structure, isomerization and photophysical properties of heteropolynuclear Pt_2Ag_2 complex having pyridyl-NHC chelate ligand are described. The Pt_2Ag_2 complex could take two geometrical isomers possessing a twisted U-shaped structure and a Z-shaped structure. The rate of the isomerization reaction depended on the concentration of the solution, implying that the reaction took place through an intermolecular process. The Pt_2Ag_2 complex having pyridyl-NHC chelating ligands showed higher emission energy than the Pt_2Ag_2 analogues having other aromatic C^N chelate ligands like 2-phenylpyridine derivatives.

Chapter 4 describes the synthesis, structures and photophysical properties of heteropolynuclear Pt_2Ag_2 and Pt_2Ag_3 complexes having phenyl-NHC chelate ligand. These heteropolynuclear complexes can be recognized as sandwich complexes, in which Ag clusters are sandwiched by Pt complex units. ^{1}H NMR studies revealed that the Ag sandwiched complexes showed fluxional behaviour in solution. The Pt_2Ag_3 complex showed rapid bridging ligand slippage on the Ag_3 core and a reversible demetalation–metalation reaction by the treatment with Cl^- and Ag^+ ions, respectively. Similarly to the Pt_2Ag_2 complex having pyridyl-NHC chelate ligand described in chapter 3, the Pt_2Ag_2 complex obtained by demetalation reaction from the Pt_2Ag_3 complex also displayed U to Z transformation of huge complex cation intermolecularly. These sandwich complexes showed strong photoluminescence originated from MMLCT transition. Theoretical calculations supported the understanding for the structural features and physical properties of the sandwich complexes.

In chapter 5, a summary and significance of the results and future perspectives are described.