



Title	Development of Thermal Process Methodology and Mechanochemical Synthesis for Luminescent Copper(I)-halide Complexes [an abstract of dissertation and a summary of dissertation review]
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学位論文内容の要旨

博士の専攻分野の名称 博士 (理学) 氏名 梁 磐儀

学位論文題名

Development of Thermal Process Methodology and Mechanochemical Synthesis for Luminescent Copper(I)-halide Complexes

(発光性銅(I)-ハライド錯体のメカノケミカル合成および熱プロセス法の開発)

Monovalent copper complexes have been widely studied in the field of luminescent materials, because these complexes are promising candidates for solar energy conversion, OLEDs (organic light emitting diodes), biosensors, and LEECs (light emitting electro-chemical cells). Highly luminescent materials have been obtained by conventional solution method, however, more environmental-friendly and efficient synthetic methods are highly required to reduce the potential risk of environment pollution by these harmful organic solvents. Recently, mechanochemical synthesis has attracted considerable attention as the alternative synthesis method of traditionally-used solution reactions. Minimal amount of solvent was required in the case of all ligands are solid state at room temperature and without crystalized solvent. Under the consideration of phase transition from solid to liquid phase obtained at melting point of solids, the seldom applied thermal method was introduced in this study.

In chapter 1, the general introduction of the luminescence of metal complexes was presented, as well as the synthetic method of metal-organic luminescent materials, including the widely accepted mechanochemical method with typical examples of solvent-free or minimal amount of solvent was required; and seldom used solvent-free thermal synthesis.

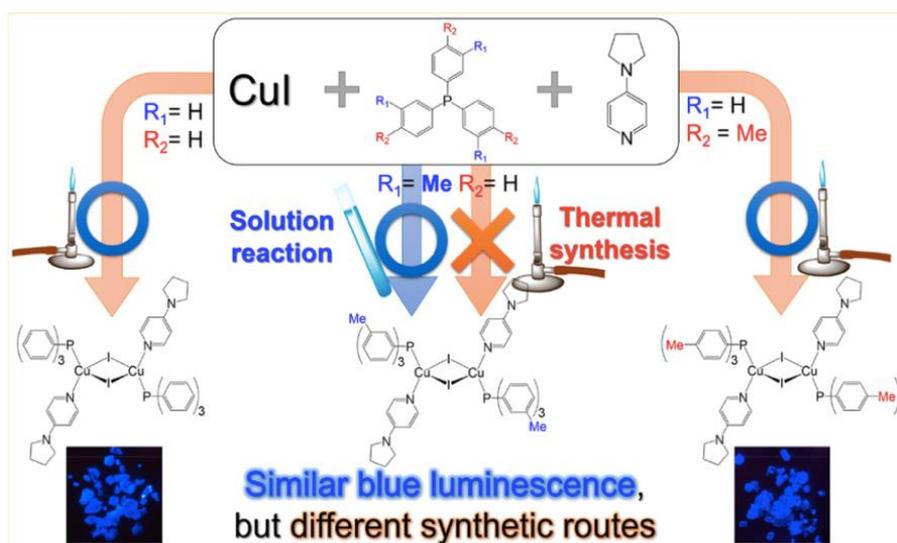
In chapter 2, mononuclear Cu(I) iodide complexes [CuI(PPh₃)₂L] {PPh₃ = triphenylphosphine; L = 4-aminoisoquinoline (4-aiq) (2), 5-aminoisoquinoline (5-aiq) (3), and 5-nitroisoquinoline (niq) (4)} were prepared. The relation between melting point of ligands and heating temperature of thermal synthesis was investigated by gradual increasing of melting point of ligands. For the mononuclear complexes 2-4, normally used reactions in the solution state, mechanochemical synthesis, and newly developed solvent-free thermal synthesis were applied. Although, no solvent was required for the mechanochemical synthesis of the parent complex [Cu(PPh₃)₂(iq)] (1); iq = isoquinoline), a minimal amount of assisting solvent (PhCN) was required for the mechanochemical synthesis of the three functional isoquinoline complexes. The amino-functionalized isoquinoline complexes were successfully synthesized by heating the ground mixture of three types of



starting materials at ca. 100 °C, where the PPh₃ ligand melted to promote complex formation by acting as the ligand and the solvent. The emission properties of complexes **2–4** strongly depend on the ligand: complexes **2** and **3** showed vibronic emission spectra originating from the ³MLCT* excited state localized on the L ligand, whereas complex **4** did not show any emission in the visible region. Emission-lifetime measurements of complexes **2** and **3** shows ms-range decay lifetimes, and time-dependent density functional theory (TD-DFT) calculations suggested the introduction of electron-donating amino group to the isoquinoline ligand stabilized the ¹MLCT* excited state localized on the isoquinoline ligand, as for complex **4**, the electron withdrawing nitro group has remarkably stabilized the MLCT excited state of isoquinoline ligands.

In chapter 3, the luminescent dinuclear complexes [Cu₂L₂(pyrpy)₂(PR₃)₂] {pyrpy = 4-pyrrolidinopyridine; PR₃ = triphenylphosphine (**5**), tri-*m*-tolylphosphine (**6**), tri-*p*-tolylphosphine (**7**)} were prepared by solution

reactions and rarely reported solvent-free thermal method. X-ray structure analyses revealed that complexes composed of dinuclear {Cu₂L₂} cores surrounded by two PR₃ and pyrpy ligands were formed. Although the melting point of pyrpy is the lowest among the organic units used in



this study, the temperature required to form the luminescent dinuclear complex, prepared by the thermal synthesis method, depended strongly on the PR₃ moiety. Two of the three complexes (**5** and **7**) were successfully prepared by the solvent-free thermal method. Complexes **5–7** exhibited blue emissions at around 450 nm with moderately high quantum yields (Φ) of 0.24, 0.31 and 0.51, respectively. Emission-lifetime measurements and time-dependent density functional theory (TD-DFT) calculations suggested thermally activated delayed fluorescence (TADF) of complexes **5–7**.

Chapter 4 gave a summary of this thesis. According to the above studies, solvent-free thermal synthesis of luminescent materials represents a promising method for the preparation of luminescent materials directly onto substrates of thin-layer electronic devices, such as organic light-emitting diodes. The temperature required to promote the reactions mainly depend on the melting point of ligands.