学 位 論 文 内 容 の 要 旨

博士の専攻分野の名称　博士（工学）　氏名　姜　平宇

学 位 論 文 題 名

Circularly Polarized Luminescence Active Crystalline Materials Based on Chiral NHC Au(I) Complexes and Control by Molecular Dynamics
（不斉 N ヘテロサイクリックカルベン (NHC) 金 (I) 錯体と結晶中の分子運動を利用した新規な円偏光発光性 (CPL) 結晶性材料の開発）

In this Ph.D. thesis, I will introduce several novel CPL-active solid-state materials utilizing N-heterocyclic carbene (NHC) Au(I) complexes. These materials are designed to control chiroptical and photophysical properties, especially CPL, through molecular dynamics.

Chapter 2 is about how the full inhibition of molecular dynamics can “turn on” CPL properties. In this chapter, I introduce a new approach for dynamic chirality stabilization in the conformationally flexible azahelicene species by crystallization-induced intermolecular chirality transfer. By employing shape-tailored chiral NHC ligands, the crystallization of azahelicene Au(I) complexes can lead not only to the suppression of conformational dynamics in the case of the dibenzocarbazole species but also to their homochirality stabilization through the intermolecular conjunction between chiral NHC and dibenzocarbazole ligands. In the case of Au(I) benzocarbazole complexes, the presence of the intermolecular conjunction and chirality transfer in the crystals results in chirality induction of the initially achiral benzocarbazole ligand. Furthermore, the crystallization of the studied complexes also results in the activation of their CPL properties, which were suppressed in solution. Importantly, the presence of chirality transfer within the crystal structure leads to a significant CPL enhancement, with luminescence dissymmetry factors that are 5 to 10 times higher compared to the crystalline complexes without the chirality transfer.

In contrast to full stop of molecular dynamics and active CPL, Chapters 3 and 4 discuss utilization of molecular dynamics to control CPL properties. Chapter 3 presents a new type of crystalline molecular rotor, featuring a neutral para-phenylene rotator enclosed by NHC stators and connected by a C-Au-C rotation axis. By using the chiral NHC ligand, the effect of thermal-induced molecular rotation on CPL was investigated. However, because the rotation in the central para-phenylene rotator does not change the symmetry of the crystal, the rotation could only quench the emission intensity but not change the dissymmetry factor of CPL. Based on these results, Chapter 4 demonstrates how molecular dynamics can alter internal molecular symmetry and further modulate not only CPL intensity but also luminescence dissymmetry factors in the crystalline state. In this chapter, I prepared a pair of chiral binuclear NHC Au(I) complexes that exhibit a distinct axially chiral conformation with C2-symmetry, derived from non-equivalent orientations of phenyl moieties at the chiral centers of NHC ligands. Solid-state NMR studies reveal that these non-equivalent phenyl moieties undergo fast rotational motion, potentially leading to the symmetrization of complexes in the crystal. These complexes display strong CPL in the crystalline state, with emission intensity, lifetime and, most importantly, luminescence dissymmetry factors showing temperature-dependent behavior controlled by molecular rotation.