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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（工学）　氏名　フェレイラ　ダ　ローサ　ペドロ　パウロ

学 位 論 文 題 名

Study on Control of Electronic and Structural Parameters in Luminescent Seven-coordinate Lanthanide Complexes
（発光性七配位希土類錯体の電子および立体構造の制御に関する研究）

Luminescent lanthanide (Ln(III)) complexes have been widely studied because of their distinctive photophysical properties derived from the metal centered 4f-4f transitions. The 4f-4f emission is based on the electric-dipole Laporte-forbidden transition with small offset (non-stoke shifts), which leads to characteristic emission with high color purity and long emission lifetime. According to crystal-field theories, enhancement of the luminescence can be achieved by the introduction of unsymmetric structures, such as eight-coordinated square anti-prism (8-SAP), dodecahedron (8-TDH: D2d) and nine-coordinate monocapped square-antiprism (9-SAP: C4v). Recently, seven-coordinate Ln(III) complexes have been synthesized and show even more unsymmetric structures. Seven-coordinate Ln(III) complexes using tmh ligand show great potential in lanthanide chemistry, for their enhanced luminescent possibilities and geometrical structural control through ancillary ligands.

For this thesis, the appropriate design of novel ancillary ligands for tmh-based Ln(III) complexes makes it possible to control the electronic and structural parameters, necessary to provide new insights into their photophysical properties and provide novel photofunctional materials, such as highly efficient thermo-sensors and photonic crystals. In particular, the author reports on 1) the enhancement of quantum yields in seven-coordinate Tb(III) thermo-sensors; 2) the dynamic structural control of seven- and eight-coordinated structures in Eu(III) complexes with LMCT states; and 3) dynamic polymerization of dinuclear seven-coordinate Ln(III) complex in crystal media.

In Chapter 1, the overall lanthanide chemistry background is overviewed. It is paid particular attention to the electronic and structural control of Ln(III) complexes in previous works and the challenges remaining. The objective and purpose of this study is described.

In Chapter 2, highly luminescent green thermo-sensors are proposed by the ligand electronic control with the introduction of ethynyl groups in phosphine oxide ligands. The introduction of large π-conjugated groups allowed the formation of novel ligand-to-ligand charge transfer (LLCT) bands, which created the necessary quenching conditions for temperature-depended emission lifetimes. Remarkably, this seven-coordinate Tb(III) complex showed reliable thermo-sensitivity while keeping high emission quantum yields.

In Chapter 3, the molecule design for dynamic structural control is demonstrated using bulky and flat ligands. The structural control using same ligands provided the necessary conditions to investigate exclusively the structural effects in the LMCT states of seven- and eight-coordinate Eu(III) complexes. The energy transfer dynamics of LMCT-present Eu(III) complexes is elucidated according to time-resolved spectroscopy and quantum calculations. In eight-coordinate Eu(III) complexes, which show longer distances between the ligands and center Eu(III) ion, the LMCT energy level was found to be higher and enhance the total energy transfer efficiency.

Based on the strategy suggested in Chapter 2 and Chapter 3, simultaneous structural and electronic control is described in Chapter 4. The dynamic polymerization of a dinuclear seven-coordinate Ln(III) complex is observed for the first time. By careful structural transformation, seven-coordinate Ln(III) complex is changed to eight-coordinate Ln(III) coordination polymer in crystal media with the assistance of pyridine vapor. This dynamic polymerization allows the connection of different crystals of Tb(III) and Dy(III) complexes at the molecular level. The ligand electronic states are greatly influenced by the polymerization process and contribute for long-range energy migration observed from Dy(III) to Tb(III) crystals.

Finally in Chapter 5, summary and outlook of the research are described.