



Title	Studies on Dinuclear Iridium(III) Complexes Bridged with Salicylaldimine Ligand Bearing Flexible Polymethylene Spacers
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## Abstract of Thesis

Name (AHADITO BIJAK RIYANDI)	
Title	<p>Studies on Dinuclear Iridium(III) Complexes Bridged with Salicylaldimine Ligand Bearing Flexible Polymethylene Spacers</p> <p>(柔軟なポリメチレン鎖で架橋されたサリチルアルジミン配位子を有するイリジウム(III)二核錯体に関する研究)</p>
<p><b>Abstract of Thesis</b></p> <p>Iridium complexes have been widely studied for their photophysical properties. However, previous studies mostly focused on mononuclear or dinuclear complexes with rigid platform, due to the generally accepted view that these type of complexes have better emission quantum efficiency. This established consensus made the research on dinuclear iridium complexes incorporating flexible linkers becoming scarce despite the potential for structural control that they have. Our research group focuses on the study to develop functional organometallic materials with three-dimensional superstructures. In our previous researches, we demonstrated the strength of flexible linkers in terms of structural tuning to achieve distinct aggregation/association properties, molecular mobility, and also unique emission properties owing to the intermolecular interactions in the platinum or palladium complexes. In this dissertation, I studied the synthesis, structure, and photophysical properties of dinuclear iridium complexes containing phenylpyridine cyclometalating ligand and bridged with salicylaldimine-derived ligand bearing flexible polymethylene spacers (<b>1</b>, <math>n = 2</math>; <b>2</b>, <math>n = 5</math>; <b>3</b>, <math>n = 8</math>). Although iridium may not be able to have extended intermolecular interactions like palladium or platinum, I expect the flexible linker to invoke unique photophysical characteristics that correlate to the spacer's length, by means of intramolecular interactions. Experimental and computational results revealed an undeniable effect of spacer length towards the molecular structure, intra- and intermolecular interactions, and emission properties of the complexes, as a remarkable redshift of emission from green in complexes <b>2–3</b> to yellow in complex <b>1</b> at 77 K was observed. It was also found that these complexes exhibit aggregation-induced emission enhancement.</p> <p>In Chapter 1, the background of phosphorescence in organometallic complex, specifically in iridium complexes, was discussed. Previous studies on dinuclear and mononuclear iridium complexes were compiled and the discrepancy between the two classes of compound was analyzed. The concept of fine-tuning of emission properties by structural alteration, especially in the aspect of emission quantum yield and emission wavelength maxima, was also explored in this chapter along with the philosophy behind this study.</p> <p>In Chapter 2, synthesis of the aforementioned iridium complex was described. Structure, intramolecular, and intermolecular interaction of the complexes were established by X-ray crystallographic analyses, <math>^1\text{H}</math> nuclear magnetic resonance (NMR) spectroscopy, correlation spectroscopy (COSY), and nuclear Overhauser effect spectroscopy (NOESY). Photophysical properties of the complexes were measured by ultraviolet-visible (UV-Vis) absorption and emission spectroscopy. Theoretical study was conducted with time-dependent density functional theory (TD-DFT) calculations to gauge the orbital energy of the complexes. The analyses revealed that the proximity between the two iridium cores causes the stabilization of orbital energies that are involved in the <math>T_1 \rightarrow S_0</math> transition by the virtue of through-space interactions.</p> <p>In Chapter 3, the comparison between various kinds of spacers – i.e. rigid, flexible, or imbued with heteroatom – was thoroughly explored by using time-dependent density functional theory (TD-DFT) calculations. The theoretical studies revealed that alteration to the properties of the spacers have a direct impact on the through-space interaction and subsequently modifies the emission properties.</p> <p>Aggregation-induced emission enhancement (AIEE) of complexes <b>1–3</b> was investigated in Chapter 4. The emission of <b>1–3</b> in solution state at room temperature was found to be weak in Chapter 1, and it is clearly demonstrated in this Chapter that these complexes undergoes an increase in emission intensity in aggregated state, created by a mixture of tetrahydrofuran and water.</p>	

論文審査の結果の要旨及び担当者

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論文審査の結果の要旨

本博士論文は柔軟なポリメチレン鎖で架橋されたサリチルアルジミン配位子を有するイリジウム(III)についての研究成果をまとめたものである。

第一章では、序論として金属錯体、特にイリジウム錯体にしぼり発光特性と構造の関係をまとめたものである。過去の研究における 2 核金属錯体の発光性制御の概要として、発光強度や発光波長が多核錯体の分子設計とどのように関係するのかについて、広くまとめた。

第二章では、本論文が議論するポリメチレン鎖で架橋されたサリチルアルジミナトイリジウム二核錯体の合成と、構造解析の詳細について各種分光学的手法および、単結晶X線回折法をもとに述べている。さらに得られた錯体の光物性として、溶液状態における吸収、および発光スペクトルを測定し、鎖長依存性をみいだしている。鎖長に依存した光物性の変化はDFT計算による量子化学シミュレーションによっても解析し、イリジウム核同士の近接効果がもたらす分子軌道の相互作用について議論している。

第三章では、イリジウム二核錯体における柔軟および剛直な架橋部位の効果について、DFT計算を行うことで調査し、さまざまな構造を有するイリジウム二核錯体において、発光性変化の近接効果を議論している。

第四章では、第二章で合成したイリジウム錯体の凝集有機発光増大現象 (AIEE)について検討し、イリジウム溶液に対して水を添加した場合、凝集体の形成により発光強度が増大する現象について見出している。

以上のように、本博士論文はポリメチレン鎖で架橋したイリジウム二核錯体の発光性における近接効果および、架橋部位の柔軟性についてまとめたものであり、博士 (工学) の学位論文として価値のあるものと認める。