

## DOCTORAL THESIS

### Structural modifications to optimise lanthanide luminescence

Dai, Lixiong

*Date of Award:*  
2017

[Link to publication](#)

#### **General rights**

Copyright and intellectual property rights for the publications made accessible in HKBU Scholars are retained by the authors and/or other copyright owners. In addition to the restrictions prescribed by the Copyright Ordinance of Hong Kong, all users and readers must also observe the following terms of use:

- Users may download and print one copy of any publication from HKBU Scholars for the purpose of private study or research
- Users cannot further distribute the material or use it for any profit-making activity or commercial gain
- To share publications in HKBU Scholars with others, users are welcome to freely distribute the permanent URL assigned to the publication

## Abstract:

Luminescent lanthanide coordination complexes have attracted significant attention due to their unique optical properties. The poor absorption of a lanthanide ion can be resolved by so-called antenna effect and improve the intensity of its luminescence. Three bidentate chromophores: phosphate-pyridine chromophore, 1,2-Hydroxy pyridone (1,2-HOPO) and 2-thenoyltrifluoroacetone (TTA), functioned as both chelator and sensitizer, their energy levels are well matched with the excited state energy levels of the Eu(III) and Sm(III).

To get highly luminescent and stable lanthanide complex, we designed and synthesized various Eu(III) complexes with different backbones to compare different parameters that will affect the sensitizing efficiency of the chromophores, such as rigidity, geometry and coordination saturation.

In chapter two we combined the phosphate-pyridine chromophore with the well-studied cyclen-based chelator to fulfil the requirement of high stability and brightness. We designed a nine-coordinate europium(III) complex as platform, through coupling reactions to realise fast screen of the chromophores energy transfer efficiency.

Chapter three focuses on the structure modifications based on the chromophore of 1,2-HOPO, different chelators and backbones were compared, a europium complex **EuL4** with the highest quantum yield with this chromophore was obtained and it could go into cells and localized on lysosome very fast. Two-phonon *in vitro* imaging was done which showed its high potential bioapplications.

Chapter four focuses on the structure modification based on the chromophore of TTA. Different backbone directly determined the europium complexes saturation number and sensitization efficiency, therefore, their quantum yields.

## Table of Content

<b>Abstract:</b>	<b>ii</b>
<b>Acknowledgement</b>	<b>iv</b>
<b>List of Tables:</b>	<b>ix</b>
<b>List of Figures:</b>	<b>ix</b>
<b>List of Schemes:</b>	<b>xiii</b>
<b>List of Symbols:</b>	<b>xiv</b>
<b>List of Abbreviation:</b>	<b>xiv</b>
<b>Structural Modifications to Optimise Lanthanide Luminescence</b>	<b>1</b>
<b>Chapter One</b>	<b>1</b>
<i>Introduction to the Lanthanides and Their Photophysical Properties</i>	1
1.1 <i>General Introduction to Lanthanides</i>	1
1.2 <i>Lanthanide Chemistry</i>	2
1.2.1 Oxidation States and Electronic Properties	2
1.2.2 Ionic Radii and Coordination Properties	3
1.3 <i>Lanthanide Luminescence</i>	5
1.3.1 Important Terms and Properties	7
1) Energy Levels in the Lanthanide Ions	7
2) The Antenna Effect	8
3) Hypersensitivity	10
4) Lifetime and Quantum Yield	10
1.3.2 Energy Transfer Mechanism	13
1.3.3 Optimisation of Energy Transfer	14
1.3.4 Quenching, Nonradiative Decay of Lanthanide Ions	17
1.4 <i>Parameters for Luminescent Lanthanide Complexes as Probes for Bioapplications</i>	19
1.4.1 Stability	20
1.4.2 Chromophore	24
1.4.2.1 Small Organic Molecules as Lanthanide Chromophores	25
1.4.2.2 Organic Dyes as Lanthanide Chromophores	25
1.4.2.3 Metal-Organic Complexes as Lanthanide Chromophores	26
1.5 <i>Two-photon Absorption of Lanthanide Complexes</i>	30
1.5.1 The Theory of Two-photon Absorption and Two-photon Excitation	31
1.5.2 Typical Two-photon Absorption Lanthanide Complexes	33
1.6 <i>Conclusion</i>	34
<b>Chapter Two</b>	<b>36</b>
<i>Synthesis of Europium Complexes with Phosphate-Pyridine Chromophores</i>	36
2.1 <i>Outline and Direction of Work</i>	36
2.2 <i>Design and Synthesis of DO3A-based Phosphate-Pyridine Europium Complexes</i>	38
2.2.1 Chromophore Synthetic Scheme	38
2.2.2 Synthesis of LnP1 Complexes	40
2.2.3 Photophysical Properties of LnP1	41
2.2.3.1 Absorption Properties	42

2.2.3.2	Excitation and Emission Properties	43
2.2.3.3	Lifetimes (Emission Decay)	44
2.2.3.4	Summary of Photophysical Properties	45
2.2.3.5	Low-Temperature Studies of GdP1	46
2.2.4	Stability Studies for LnP1	47
2.2.5	Discussion for the Photophysical Properties	48
2.3	<i>Chromophore Structure Modification</i>	49
2.3.1	Photophysical Properties of EuP2 - EuP7	51
2.3.1.1	Absorption, Excitation and Emission Spectra of EuP2 - EuP7	51
2.3.1.2	Lifetimes (Emission Decay)	54
2.3.1.3	Summary of Photophysical Properties of EuP2 - EuP7	59
2.3.2	Summary of the Chromophore Modification	60
<b>Chapter Three</b>		<b>61</b>
<b>Synthesis of Cyclen-based Lanthanide Complexes with 1,2-HOPO</b>		<b>61</b>
3.1	<i>Introduction to the 1,2-HOPO</i>	61
3.2	<i>Outline and Direction of Work</i>	64
3.3	<i>Synthesis of Ln-DO3A-1,2-HOPO Complexes</i>	65
3.3.1	Chromophore Synthetic Scheme	66
3.3.2	Ligand and Complex Synthetic Scheme	67
3.3.2.1	The Synthesis of LnL1	67
3.3.2.2	Synthesis of LnL2	68
3.3.2.3	The Synthesis of LnL3	70
3.3.3	Photophysical Properties of Synthesised Complexes (LnL1 – LnL3)	73
3.3.3.1	Absorption Properties	74
3.3.3.2	Excitation and Emission Properties	75
3.3.3.3	Lifetimes (Emission Decay)	77
3.3.4	Summary of Photophysical Properties	83
3.3.5	Conclusion for the Complexes EuL1 – EuL3	83
3.4	<i>New Direction (Octadentate Ligation)</i>	85
3.4.1	Synthesis of Octadentate Ligation of LnL4	86
3.4.2	Photophysical Properties of LnL4	87
3.4.2.1	Absorption, Excitation and Emission Spectra of EuL4 and SmL4	88
3.4.2.2	Lifetimes (Emission Decay)	89
3.4.2.3	Photophysical Properties of GdL4	91
3.4.3	Summary of Photophysical Properties of LnL4	93
3.5	<i>Cell Imaging</i>	94
3.6	<i>Conclusion</i>	96
<b>Chapter Four</b>		<b>97</b>
<b>Synthesis of Lanthanide Complexes with TTA Chelator</b>		<b>97</b>
4.1	<i>Overview of <math>\beta</math>-Diketone Ligands and Types of Complexes</i>	97
4.2	<i>Bioapplication of Lanthanide <math>\beta</math>-Diketonate Complexes</i>	100
4.3	<i>Lanthanide Complexes with TTA Chelator</i>	102
4.4	<i>Outline and Direction of Work</i>	103
4.5	<i>Synthesis of Ln-Cyclen-TTA Complexes</i>	104
4.5.1	Screening of Synthetic Route	105
4.5.2	Synthesis of LnL5	107
4.5.3	Photophysical Properties of LnL5	110

4.5.3.1 Absorption, Excitation and Emission Spectra of EuL5	111
4.5.3.2 Lifetime (Emission Decay) of EuL5	113
4.5.3.3 Summary of Photophysical Properties	115
4.6 <i>The Design and Synthesis of Ln-H(2,2)-TTA and Ln-(3,4,3)-TTA</i>	115
4.6.1 The Synthesis of LnL6	117
4.6.2 The Synthesis of LnL7	121
4.7 <i>Photophysical Properties of LnL6 and LnL7</i>	122
4.7.1 Absorption, Excitation, Emission Properties	123
4.7.2 Lifetime (Emission Decay)	130
4.8 <i>Cell Imaging</i>	143
<b>Chapter Five</b>	<b>145</b>
<b>Experimental</b>	<b>145</b>
5.1 <i>Materials and General Methods</i>	145
5.2 <i>Spectroscopic and photophysical measurements</i>	146
5.2.1 Lifetime Measurement	146
5.2.2 Inner Sphere Solvent Number ( <i>q</i> value)	146
5.2.3 Molar Absorption Coefficient Measurement	147
5.2.4 Triplet Energy Measurements	148
5.2.5 Quantum Yield Determination	148
5.3 <i>Synthetic Procedure and Characterization</i>	149
<b>Appendix:</b>	<b>169</b>
<sup>1</sup> H and <sup>13</sup> C NMR Spectra	169
HRMS:	188
Charts for Measurement of the Extinction Coefficient:	192
<b>References:</b>	<b>195</b>