

DOCTORAL THESIS

The study of photophysical properties of organic-lanthanide hybrid materials and their applications

Bao, Guochen

Date of Award:
2020

[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

Designing hybrid materials allows leveraging the properties of different material systems to achieve novel functions. Significant progress has been made in recent years to exploit the physicochemical properties of a new generation of hybrid materials for emerging biomedical applications. In Chapter 1, I review the recent advances in the field of dye-lanthanide hybrid materials, centring on the interface between organic dyes and inorganic lanthanide materials and investigating their photophysical and photochemical properties. Five representative dye-lanthanide hybrid material systems including lanthanide complex, dye-sensitised downshifting nanoparticles (DSNPs), dye-sensitised downconversion nanoparticles (DCNPs), dye-sensitised upconversion nanoparticles (UCNPs), and UCNPs-dye energy transfer systems have been thoroughly discussed. We highlight the key applications of dye-lanthanide hybrid materials in bioimaging, sensing, drug delivery, therapy, and cellular activity studies.

In Chapter 2, I design and synthesize an ytterbium complex-based sensor for the detection of Hg^{2+} ions. The water-soluble ytterbium complex exhibits reversible off-on visible and NIR emission upon the binding with mercury ion. The fast response and 150 nM sensitivity of Hg^{2+} detection are based upon FRET and the lanthanide antenna effect. The reversible Hg^{2+} detection can be performed *in vitro*, and the binding mechanism is studied by NMR employing the motif structure in a La complex and by DFT calculations.

In Chapter 3, I report a pair of stoichiometric terbium-europium dyads as molecular thermometers and study their energy transfer properties. A strategy for synthesizing hetero-dinuclear complexes that contain chemically similar lanthanides is developed. By this strategy, a pair of thermosensitive dinuclear complexes, **cycTb-phEu** and **cycEu-phTb**, was synthesized. Their structures were geometrically optimized with an internuclear distance of approximately 10.6 Å. The dinuclear complexes have sensitive temperature-dependent luminescent intensity ratios of europium and terbium emission, and temporal dimension responses over a wide temperature range (50 - 298 K and 10 - 200 K, respectively). This indicates that both dinuclear complexes are excellent self-referencing thermometers.

In Chapter 4, I investigate spectral structure and intensity changes of a pair of dinuclear complexes with a europium ion on cyclen site and a lanthanum ion on phen site or vice verses (**cycEu-phLa** and **cycLa-phEu**). Though they have the same components and the same energy levels, they present different photophysical properties due to the different coordination environment. The band positions are different in the emission spectra. The emission of **cycEu-phLa** showed a stronger relative intensity of $^5D_0 \rightarrow ^7F_2$ transition whereas the relative intensity of $^5D_0 \rightarrow ^7F_4$ transition was weaker in comparison with **cycLa-phEu**. We found the **cycEu-phLa** have higher internal quantum efficiency while the **cycEu-phLa** have higher sensitizing efficiency, though they have similar external quantum yield. We determined the singlet-triplet intersystem crossing rate with values as $\sim 10^8 \text{ s}^{-1}$.

In Chapter 5, I exploit a dye sensitised upconversion nanoparticle with highly enhanced upconversion emission. I designed and synthesized a new dye by connecting tetraphenylethene (TPE) with the cyanide NIR dye, IR783. The resultant compound (TPEO-IR783) has a quantum yield of 22.46% which is 3 times higher than that of reported UCNP sensitiser (IR806). The TPEO-IR783 exhibits a transparent window in a range of 400 nm to 600 nm, making it suitable sensitiser for upconversion nanoparticles by avoiding reabsorption. The TPEO-IR783 sensitised UCNPs show more than 200-fold upconversion emission than the reported IR806 sensitised UCNPs under the same condition.

In Chapter 6, I develop an ytterbium nanoparticle-mediated upconversion system. The system enables the singlet energy transfer from sensitisers to acceptor triplet states without the requirement of intersystem crossing. I evaluate the hybrid upconversion design by IR808 and rubrene acid. While the mixture of IR808 and rubrene acid does not show any upconversion emission, the introduction of an intermediate ytterbium energy level by adding NaGdF₄:Yb nanoparticles displays strongly enhanced upconversion emissions. This design bypasses the specific requirement of traditional sensitisers in TTA system, providing a wide range of opportunities in deep tissue applications.

Chapter 7 is the experiment sections where details of materials, characterizations, and synthetic procedures in each chapter have been provided.

TABLE OF CONTENTS

DECLARATION.....	i
ABSTRACT.....	ii
ACKNOWLEDGEMENTS.....	v
TABLE OF CONTENTS.....	vii
LIST OF SCHEMES, TABLES AND FIGURES.....	x
LIST OF ABBREVIATIONS.....	xviii
Chapter 1 Introduction.....	1
1.1 Introduction of dye-lanthanide hybrid materials.....	1
1.2 Photophysical properties of organic dyes and lanthanide materials.....	3
1.2.1 Basis of energy levels of organic dyes.....	3
1.2.2 Basis of energy levels of lanthanide materials.....	7
1.2.3 Optical properties of organic dyes and lanthanide materials.....	10
1.3 Dye-lanthanide hybrid materials.....	13
1.3.1 Lanthanide complex.....	13
1.3.2 Dye-sensitised downshifting and downconversion nanoparticles.....	17
1.3.3 Dye-sensitised upconversion nanoparticles.....	21
1.3.4 UCNP-Dye system.....	28
1.4 Biomedical applications of dye-lanthanide hybrid materials.....	33
1.4.1 Bioimaging.....	34
1.4.2 Biosensing.....	40
1.4.3 Drug delivery.....	47
1.4.4 Therapy.....	53
1.4.5 Control and monitoring cellular activities.....	59
1.5 The scope of this thesis.....	61
1.6 References.....	64
Chapter 2 Reversible and sensitive Hg ²⁺ detection by visible and NIR emission from ytterbium complex.....	74
2.1 Introduction.....	74
2.2 Results and discussion.....	77
2.2.1 Synthesis of GBYb001, GBLa001 and GBYb002.....	77
2.2.2 Photophysical properties.....	78
2.2.3 Titration with Hg ²⁺	82
2.2.4 Selectivity.....	89
2.2.5 Reversibility.....	90
2.2.6 Mechanism study.....	91
2.2.7 Confocal microscopic images, MTT and cellular uptake.....	94

2.3 Conclusions	96
Chapter 3 A Stoichiometric Terbium-Europium Dyad Molecular Thermometer: Energy Transfer Properties	98
3.1 Introduction	98
3.2 Results and discussion	100
3.2.1 Structure	100
3.2.2 Synthesis	102
3.2.3 Singlet and triplet states	103
3.2.4 Lanthanide luminescence at low temperature	106
3.2.5 Emission decay lifetimes of Tb ³⁺ and Eu ³⁺ and temperature dependence	108
3.2.6 Energy transfer from Tb ³⁺ to Eu ³⁺	110
3.2.7 Energy transfer from antenna to Eu ³⁺ ion	117
3.2.8 Thermometric properties	121
3.3 Conclusion	123
3.4 References	124
Chapter 4 Effects of Europium Spectral Probe Interchange in Ln-dyads with Cyclen and Phen Moieties	127
4.1 Introduction	127
4.2 Results and discussion	129
4.2.1 Synthesis	129
4.2.2 Singlet and triplet properties: intersystem crossing	131
4.2.3 Excitation spectra of Eu ³⁺ complexes	136
4.2.4 Room temperature emission spectra of Eu ³⁺ complexes	139
4.2.5 Low-temperature emission of the Eu ³⁺ complexes	143
4.2.6 Room temperature solution spectra of the Eu ³⁺ complexes	146
4.3 Conclusion	149
4.4 References	150
Chapter 5 Luminescent enhancement of dye sensitised upconversion nanoparticles	154
5.1 Introduction	154
5.2 Results and discussion	155
5.2.1 Synthesis	155
5.2.2 Photophysical properties	156
5.2.3 Sensitisation of UCNPs	160
5.3 Conclusion	161
5.4 References	162
Chapter 6 Ytterbium nanoparticle-mediated upconversion system	164
6.1 Introduction	164

6.2 Result and discussion	166
6.2.1 Synthesis.....	166
6.2.2 Photophysical properties.....	167
6.3 Conclusion.....	171
6.4 Reference	171
Chapter 7 Experimental Section	174
7.1 Experimental section of Chapter 2.....	174
7.2 Experimental section of Chapter 3.....	185
7.3 Experimental section of Chapter 4.....	194
7.4 Experimental section of Chapter 5.....	198
7.5 Experimental section of Chapter 6.....	202
7.5 Appendix.....	204
7.6 References	247
LIST OF PUBLICATIONS	248
CURRICULUM VITAE.....	250