THE STUDY OF PHOTOPHYSICAL PROPERTIES OF ORGANIC-LANTHANIDE HYBRID MATERIALS AND THEIR APPLICATIONS

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CERTIFICATE OF ORIGINAL AUTHORSHIP

I, Guochen Bao, declare that this thesis, is submitted in fulfilment of the requirements for the award of Doctor of Philosophy, in the School of Mathematical and Physical Sciences, Faculty of Science, at the University of Technology Sydney.

This thesis is wholly my own work unless otherwise reference or acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of the requirements for a degree at any other academic institution except as fully acknowledged within the text. This thesis is the result of a Collaborative Doctoral Research Degree program with Hong Kong Baptist University as part of a Collaborative Doctoral Research Training Program.

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List of Publications

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LIST OF ABBREVIATIONS

a.u.	arbitrary unit
$CDCl_3$	deuterated chloform
CD_3OD	deuterated methanol
d	doublet
DCM	dichloromethane
DCNP	downconversion nanoparticle
DET	Dexter energy transfer
DFT	density functional theory
DIPEA	N, N‘‘-diisopropylethylamine
DMSO	dimethylsulphoxide
DSNP	downshifting nanoparticle
EA	ethyl acetate
EtOH	ethanol
FRET	Förster resonance energy transfer
HOMO	highest occupied molecular orbital
HPLC	high performance liquid chromatography
Hz	hertz
ICG	indocyanine green
ISC	intersystem crossing
J	coupling constant
K	degree Kelvin
Ln	lanthanide
LOD	limit of detection
LUMO	lowest unoccupied molecular orbital
m	multiplet
M^+	molecular ion
MeCN	acetonitrile

MeOH	methanol
MOF	metal-organic framework
MS	mass spectroscopy
m/z	mass to charge ratio
MTT	3-(4,5-dimethyl-2-thiazolyl)-2,5-diphenyl -2-H-tetrazolium bromide
NIR	near infrared
NMR	nuclear magnetic resonance
ppm	parts per million
PDT	photodynamic therapy
PTT	photothermal therapy
r.t.	room temperature
s	singlet
t	triplet
TTA	triplet triplet annihilation
TEA	triethylamine
TFA	trifluoroacetic acid
THF	tetrahydrofuran
UCNP	upconversion nanoparticle
UV	ultraviolet
Vis	visible
δ	chemical shift (in ppm)
℃	degree Celsius
λ_{ex}	excitation wavelength (in nm)
λ_{em}	emission wavelength (in nm)

ABSTRACT

Significant progress has been made in recent years to produce a new generation of dye-lanthanide hybrid materials with physicochemical properties for various applications. The lanthanide complexes, where organic ligands are engineered to chelate individual lanthanide ions, are broadly used in analytical, biological, and clinical applications. However, the visible emission suffers from low penetration depth in biological tissues, the synthesis of hetero-dinuclear complexes remains challenging because lanthanide ions are chemically similar, and there is a lack of systems for comprehensive study of ligand-lanthanide energy transfer. To this end, the primary focus of my thesis is to develop near-infrared probes, hetero-dinuclear compounds and energy transfer platforms based on lanthanide complexes for energy transfer study and sensing applications (Chapter 2, 3, & 4). In Chapter 2, I design and synthesize an ytterbium complex-based sensor for the detection of Hg^{2+} ions. In Chapter 3, I report a pair of stoichiometric terbium-europium complexes as molecular thermometers and study their energy transfer properties. In Chapter 4, I investigate the spectral structure and intensity changes of a pair of dinuclear complexes.

Learning from lanthanide complexes, considerable progress has recently been made to exploit the hybrid structure of lanthanide-doped inorganic nanoparticles "coated" with organic dyes. This has resulted in hybrid materials that have many benefits, for example, large absorption cross-section, easy modification, tuneable spectral bands, long lifetimes, and large (anti)-Stokes shift. To improve the performance of upconversion process, near-infrared dyes with high quantum yields are required for efficient sensitisation of lanthanide nanoparticles, and diverse energy transfer systems are required for brighter upconversion emissions. Therefore, the parallel program of my thesis is to develop brighter dye-lanthanide nanoparticle upconversion systems, including dye-sensitised upconversion nanoparticles (Chapter 5) and ytterbium-mediated upconversion system (Chapter 6). In Chapter 5, I exploit a dye sensitised upconversion nanoparticle with highly enhanced upconversion emission by developing a NIR dye (TPEO-IR783) with a quantum yield of 22.46% which is 3 times higher than that of reported UCNP sensitiser, IR806. In Chapter 6, I develop an ytterbium nanoparticle-mediated upconversion system and the design bypasses the specific requirement of traditional sensitisers in TTA system, providing a wide range of opportunities for deep light penetration applications.

Overall, this thesis has eight chapters, including the introduction of dye-lanthanide hybrid materials (Chapter 1), three lanthanide complex-based projects (Chapter 2, 3, & 4), two dye-lanthanide nanoparticle-based projects (Chapter 5 & 6), experimental details (Chapter 7) and conclusions and perspectives (Chapter 8).