DOCTORAL THESIS

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

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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 ~10^8 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 $NaGdF_4$: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.

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