



Review

Recent developments in lanthanide-based luminescent probes



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ABSTRACT

Lanthanide-based luminescent probes have attracted increasing attention due to their unique optical properties, such as large Stokes and/or anti-Stokes shifts, long luminescence lifetimes (up to milliseconds), and narrow and compound-independent emission bands, making them widely employed in detection, diagnosis, and bioimaging. This review focuses on the recent developments of lanthanide-based luminescent probes including lanthanide complexes and lanthanide nanoparticles for probing pH, anions, metal ions, reactive oxygen species, and biomolecules (amino acids, proteins, nucleobases, and nucleic acids). The design principles and recognition mechanisms of luminescent probes based on lanthanide ions for various analytes are elaborated in detail. In the end, future research directions with great potentials and the according challenges of lanthanide-based luminescent probes are also discussed.

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1. Introduction

Lanthanide ions, especially Tb^{3+} , Eu^{3+} , Nd^{3+} , and Yb^{3+} , have been widely used as luminescent probes due to their unique spectroscopic properties, such as large Stokes and/or anti-Stokes shifts, long luminescence lifetimes, and narrow emission bands [1–8]. The large Stokes shifts helps to avoid the self-absorption of ligand and reduce the background signals. The long-lived luminescence of lanthanide ions can be collected using time-resolved fluorescence measurement, while the interference of short-lived background fluorescence can be eliminated [9,10]. Furthermore, narrow emission can improve the detection sensitivity of luminescent probes for analytes. Hence, lanthanide-based luminescent probes have favorable signal-to-noise ratios and could serve as sensitive probes for various targets. Due to the large ionic radii and high coordination numbers of trivalent lanthanide center, the coordination configuration of lanthanide complex is complicated, based on which, the relationship between the types of lanthanide complex and luminescence sensing behaviors will provide clues for designing lanthanide complex-based luminescent probes. On the other side, the recognition mechanisms of lanthanide nanoparticle-based luminescent probes are also closely associated with the types of lanthanides employed. Up to now, a great number of lanthanide-based luminescent probes including both lanthanide complexes and lanthanide nanoparticles with multifold applications in biotechnology, nanomedicine, and environment protection have been designed. Some of them have been successfully commercialized within detection systems for immunoassays and DNA assays. For instance, DELFIA and LANCE (PerkinElmer), HTRF and TRACE (CisBio), and LanthaScreen (Life Technologies) technologies based on luminescent Tb^{3+} or Eu^{3+} complexes are used to detect various clinical biomarkers in biomedical diagnostics and imaging [11,12]. Since several valuable reviews concerning the design strategies and applications of such luminescent probes have been published [13–18], this review will focus on the advances in lanthanide-based luminescent probes for the detection of pH, anions, metal ions, reactive oxygen species, and biomacromolecules from the literatures published after 2009. No attempt is carried out to provide the exhaustive coverage of all the publications in this field. Instead, representative examples are described in sufficient details to elaborate the design approaches and recognition mechanisms of lanthanide-based luminescent probes for diverse analytes. We also seek to discuss the effect of the configuration of lanthanide complexes and the types of nanoparticles on the luminescent sensing performances.

2. Luminescent probes based on lanthanide complexes

2.1. Design principles for luminescent lanthanide complexes

Lanthanides are difficult to be directly excited because of their weak f–f transition absorption originated from their low absorption cross sections. Indirect excitation by a sensitive chromophore or “antenna” has proved to be an effective way to solve this problem [19]. After absorption of UV–visible radiation and intersystem crossing, the antenna is excited from singlet to triplet state, the sequential energy transfer from the antenna to the lanthanide ion makes it excited *via* the intramolecular energy transfer (ET) process. Finally the absorbed energy is released *via* radiation and/or non-radiation emission (*i.e.*, luminescence with characteristic peaks) and the lanthanide ion returns to the ground state. For instance, Tb^{3+} and Eu^{3+} exhibit quite intense visible emission, while Er^{3+} , Nd^{3+} , and Yb^{3+} emit in the near-infrared region. On the basis of luminescence mechanism of lanthanide ions, there are four factors influencing their quantum yields [20]. First, the energy gap

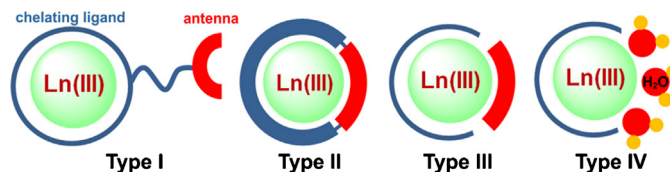


Fig. 1. The schematic structure of the four types of luminescent lanthanide complexes.

between the lowest excited state of the lanthanide ion and the highest sublevel of its ground multiplet. The smaller the energy gap is, the higher the quantum yield of lanthanide luminescence will be. Hence, Tb^{3+} and Eu^{3+} are widely used in luminescent probing due to their appropriate energy gaps [7]. Second, the energy of the triplet excited state of the antenna, which shall be properly higher than the excited ^5D state of the lanthanide ion. Third, the energy transfer efficiency, which follows a distance (r)-dependence between antenna and the lanthanide ions, on the basis of two main energy transfer mechanisms: (i) Dexter's (or exchange) mechanism, which is a short-range mechanism with an exponential distance dependence in $\exp(-\beta r)$, where β is a parameter determined by the strength of electron–lattice coupling, and (ii) Förster's (or dipole–dipole) mechanism, which is a r^{-6} distance dependence and occurs over longer distance [8,20]. Fourth, the coordinated water molecules that quench the luminescence because of the overlap of the O–H vibration with the emission wavelength of the lanthanide ions [21]. Therefore, the design principles for luminescent lanthanide complexes are dependent upon these four factors. In other words, lanthanide ion, antenna, chelating ligand, and the coordination mode are pivotal parameters to consider when designing luminescent lanthanide complexes. The proper combination of the four parameters constitutes the basic design principles of the luminescent probes that will perform precise molecular recognition and luminescence sensing.

Up to date, a great number of luminescent lanthanide complexes have been reported [6,22,23], which can be generally classified into four types (Fig. 1). “Type I” has a pendant chromophore as antenna linked with the chelating ligand of lanthanide complex. For example, polyaminopolycarboxylate and polyaza-macrocyclic are usually selected as chelating ligand due to their strong chelating capability and high water solubility. This type of lanthanide complex can modulate the luminescence *via* the reaction between the antenna and analyte, which affects the energy transfer efficiency. In “Type II”, the antenna is incorporated into the chelating ligand to form chromophoric chelator and involved in the coordination with lanthanide ions. The luminescence change is caused by the modulation of the functional moiety in the ligand with the exterior analyte. Unlike “Type II”, the antenna of “Type III” is not linked with chelating ligand although the antenna also directly coordinates with lanthanide. Generally, the chelating ligand of Type III cannot sensitize lanthanide. In contrast to the three coordinatively saturated types of complexes listed above, “Type IV” is coordinatively unsaturated. The remaining coordination sites are occupied by labile solvent molecules. The solvent molecules are prone to be replaced by analytes, resulting in the changes of luminescence.

There are various mechanisms corresponding to the working principles of the four types of lanthanide complexes. Besides the configuration alterations, the traditional mechanisms such as intramolecular charge transfer (ICT) [24], intramolecular photoinduced electron transfer (PET) [25], and luminescence resonance energy transfer (LRET) [26] also play important roles in modulating the luminescence of lanthanide complexes. ICT and PET often quench the luminescence of lanthanide ions and commonly used as switches in “Type I” and “Type II” lanthanide complexes. The reaction between antenna and analyte can eliminate or induce the

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