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Novel antennae for the sensitization of near infrared luminescent lanthanide cations

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ABSTRACT

Near Infrared (NIR) luminescence is useful for many applications ranging from lasers, telecommunication to biological imaging. We have a special interest for applications in biological media since NIR photons have less interference with such samples. NIR photons can penetrate relatively deeply in tissues and cause less damage to biological samples. The use of NIR luminescence also results in improved detection sensitivity due to low background emission. The lower scattering of NIR photons results in improved image resolution. NIR emitting lanthanide compounds are promising for imaging because of their unique properties such as sharp emission bands, long luminescence lifetimes and photostability. Here, we review our efforts to develop novel sensitizers for NIR emitting lanthanides. We have employed two global strategies: (1) monometallic lanthanide complexes based on derivatives of salophen, tropolonate, azulene and pyridine; and (2) polymetallic lanthanide compounds based on nanocrystals, metal-organic frameworks and dendrimers complexes.

RÉSUMÉ

La luminescence proche-infrarouge est utile pour un grand nombre d'applications pratiques qui s'étendent de la technologie des lasers, de la télécommunication à l'imagerie biologique. Nous avons développé un intérêt tout particulier pour les applications liées à l'étude des milieux biologiques étant donné que les photons proche-infrarouge interférent très peu avec de tels échantillons. Les photons proche-infrarouge peuvent pénétrer relativement profondément dans les tissus et induisent moins de dommages aux échantillons biologiques. Par ailleurs, l'utilisation des photons proche-infrarouge offre l'avantage d'une détection plus sensible en raison du faible bruit de fond dans ce domaine d'énergie. Enfin, la diffraction plus faible des photons proche-infrarouge induit une meilleure résolution des images obtenues. Les composés de lanthanide émettant dans le proche-infrarouge sont donc prometteurs pour l'imagerie en raison de leurs propriétés uniques comme leurs bandes d'émission étroites, les temps de luminescence longs et leur photostabilité. Nous décrivons ici nos efforts de développement de nouveaux sensibilisateurs de cations lanthanide émettant dans le proche-infrarouge. Nous avons pour cela adopté deux stratégies distinctes : (1) les complexes de lanthanide monométalliques basés sur des dérivés de salophène, de tropolonate, d'azulène et de pyridine et (2) des composés polymétalliques de lanthanide basés sur des nanocristaux, des architectures metallo-organique et des complexes de dendrimère.

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1. Introduction

In electromagnetic radiation, near-infrared (NIR) region ranges approximately from 650 to 1500 nm. There is constantly growing interest in NIR luminescence in the last decade because of its potential for bioanalytical applications and biological imaging, as well as for technological applications. The use of NIR luminescence is a promising approach for biological imaging and bioanalytical applications for three main reasons: (1) NIR photons have less interference with biological materials as they are mostly not absorbed by biological tissues [1]. Therefore, photons can penetrate deeply into tissues allowing noninvasive detection of biological molecules or events. (2) Since the autofluorescence arising from biological tissue is mainly located in the violet–blue region [2], imaging in the NIR region also provides the advantage of detection sensitivity due to improved signal to noise ratio, the background emission (‘‘autofluorescence’’) of biological material in the NIR being almost inexistent [1]. (3) An additional advantage of NIR photons for biological imaging is the limited scattering of such photons in comparison to visible photons that results in improved image resolution. As the intensity of scattered light is proportional to $1/\lambda^{SP}$ (SP = scattering power), the longer wavelength of NIR light has reduced scattering, which results in the higher resolution of the obtained image [3].

Beside the biological imaging, NIR luminescence is useful for NIR organic light-emitting diode technology [4], telecommunication where the electronic structure of lanthanide ions such as Er^{3+}, Nd^{3+} and Ho^{3+} can be used as the active material for optical amplification of the NIR signal [5], and encrypted tags (‘‘barcodes’’) to recognize the identity of chemical or biological entity or of an object [6].

In general, the luminescence of lanthanides possesses several advantages over organic fluorophores [7], semiconductor nanocrystals [8] and carbon nanotubes [9], such as sharp emission band, photostability and long luminescent lifetimes.

Luminescent lanthanides can have emission bands ranging from UV to NIR regions, controlled by the nature of lanthanide cations. As shown in Fig. 1, Nd^{3+}, Er^{3+}, Ho^{3+}, Tm^{3+} and Yb^{3+} have NIR emission, while Tb^{3+} and Dy^{3+} have visible emission. The emission bands from Sm^{3+} and Eu^{3+} are located in both the visible and NIR regions. Since interactions between lanthanide cations and ligands are predominately electrostatic [10], the emission of lanthanide complexes appear as atom-like, sharp emission bands [11,12], and the wavelength position of these bands does not vary significantly with change of ligand or experimental conditions such as temperature, pressure, pH or biological environment. The bandwidths are significantly narrower than those of organic fluorophores and luminescent semiconductor nanocrystals (quantum dots) [13]. As these emission bands do not overlap significantly, it is possible to monitor the emission of several different lanthanide cations during the same experiment for multiplex detection.

Since the energy is absorbed by a chromophore (or ‘‘antenna’’, see below) and the emission originates from the lanthanide cations, there is a large energy gap between the absorption and emission bands of lanthanide complexes, minimizing luminescence reabsorption and corresponding quantification artifacts. Due to their electronic properties, the luminescence of the lanthanide cations can be spectrally discriminated from other signals, allowing enhanced detection sensitivity in complex mixtures such as biological media.

Most lanthanide compounds are photostable [14]. Trivalent electron-deficient lanthanide cations stabilize the excited states of bound organic sensitizers, preventing irreversible photoreactions when the complex is irradiated. Therefore, protection from light is not required, yielding a long shelf life and easy manipulation in ambient laboratory conditions. Most importantly, this photostability allows for long exposure times and repeated experiments.

The luminescence lifetimes of lanthanide cations are in the range of micro- to milliseconds [15], which is much longer than the pico- to nanosecond lifetimes that are typical for fluorescent organic molecules and proteins. The long luminescence lifetimes allow simple and accurate discrimination of the lanthanide complex signal from autofluorescence (background fluorescence) through time-resolved measurements, providing enhanced detection sensitivity [16].

Since f → f transitions are forbidden by the Laporte rule, free lanthanide cations have low extinction coefficients

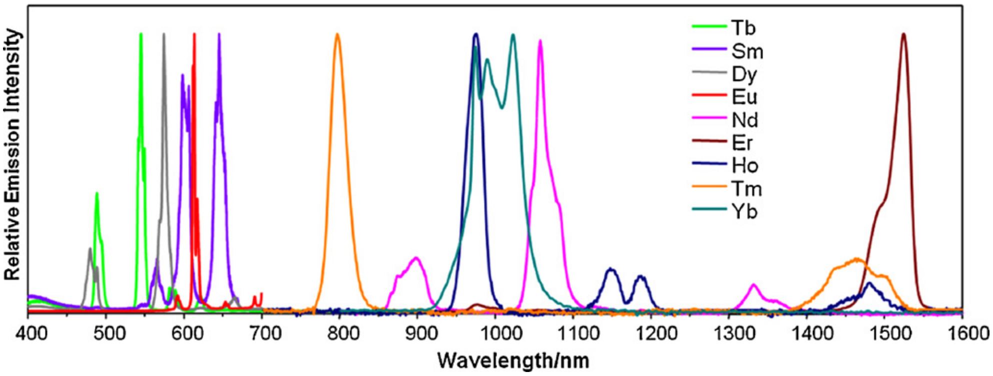

Fig. 1. Normalized emission spectra of luminescent lanthanide complexes in solution, illustrating the sharp emission bands and minimal overlap of lanthanide luminescence. Adapted from [11] and [12].