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Review

Lanthanide complexes for luminescence-based sensing of low molecular weight analytes

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A R T I C L E I N F O

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Dedicated to the memory of our friend and colleague, Professor Leone Spiccia, an Australian coordination chemist of the highest calibre.

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A B S T R A C T

Recent developments (2012 and onwards) in the design and application of luminescent lanthanide-based complexes for chemical sensing are reviewed. Sensors for a variety of metal cations, anions and neutral small molecules are highlighted, including several developed by Australian researchers. Emphasis is placed on describing the general design features and range of mechanisms by which such sensors are able to elicit a luminescent response upon exposure to an analyte.

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1. Introduction

According to the IUPAC, a chemical sensor is regarded as "a device that transforms chemical information into an analytically useful signal" [1]. A chemical sensor, commonly referred to as a chemosensor, consists of a recognition unit that binds to or reacts with an analyte, and a transduction unit responsible for generation of a signal correlating to concentration of analyte [2–6]. Chemosensors have become an integral part of science and technology, and have found applications in a diverse range of areas, including medical, biological and environmental fields [7–17].

The field of chemosensors is vast but, broadly speaking, chemosensors can be categorised according to their physical mode of detection: electrical, thermal and optical [18]. Of these, optical chemosensors are particularly attractive because of their combination of high sensitivity, rapid response and ease of use. Several extensive reviews highlight recent advances in the field of colourimetric/absorption- and fluorescent-based optical chemosensors [19–31], and efforts continue to develop sensors of this type displaying improved selectivity for particular analytes, higher dynamic ranges, lower limits-of-detection (LoD) and permitting real-time monitoring of analyte levels. Alongside this work, the past decade has witnessed increasing interest in the application of luminescent lanthanide ions, particularly the green- and red-emitting terbium (Tb^{3+}) and europium (Eu^{3+}) ions, in optical chemosensor design. As outlined below, the photophysical properties of these ions lend themselves to the development of chemosensors possessing a number of distinct advantages over more traditional organic-based fluorescent designs.

The lanthanides/lanthanoids are a series of elements that have long intrigued scientists. A common misconception is that they are rare since they are also commonly referred to as "rare earth elements" [32]. The rarest of the lanthanide elements are in fact two orders of magnitude more abundant than gold [33]. The lanthanide elements span the top row of the "*f*-block" of the periodic table. They have found widespread use in everyday technology, with major applications including catalysis, metallurgy, lasers and permanent magnets to name a few [34–41]. This wide range

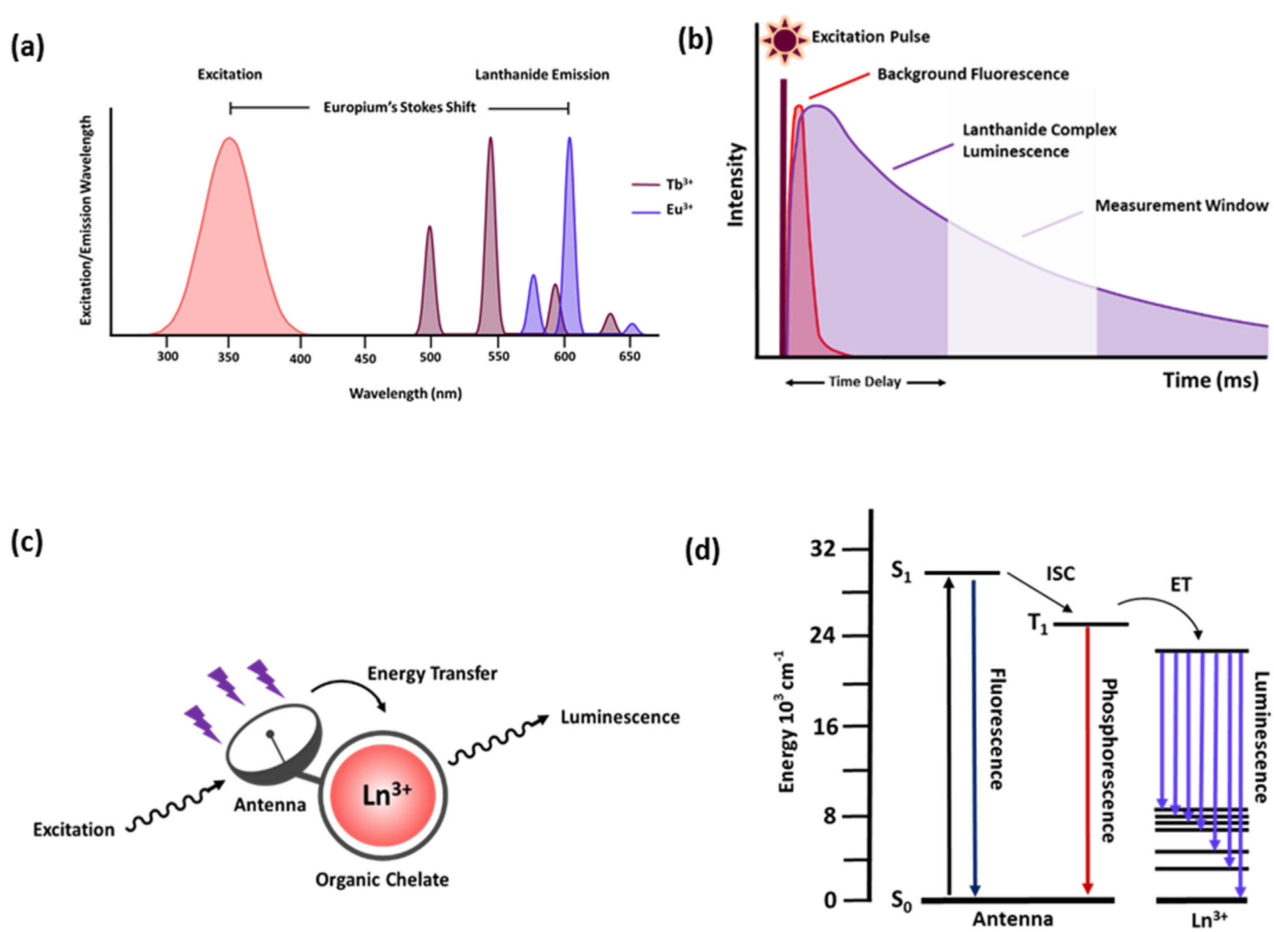

Fig. 1. (a) Typical absorption and emission bands of Tb(III) and Eu(III) complexes; with the representative Stokes shift between the absorption band of the antenna (pink) and emission of Eu^{3+} ion (blue) shown. (b) Principle of time-gated detection. (c) Schematic representation of the antenna effect (indirect excitation of the lanthanide ion). (d) Simplified Jablonski diagram showing the pathway leading to lanthanide sensitisation.

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