



## Review

## On the design of highly luminescent lanthanide complexes

Jean-Claude G. Bünzli<sup>a,b,\*</sup><sup>a</sup> École Polytechnique Fédérale de Lausanne, Institut des Sciences Chimiques et Ingénierie, BCH 1402, CH-1015 Lausanne, Switzerland<sup>b</sup> Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, People's Republic of China

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## ABSTRACT

Presently, phosphors and luminescent materials for lighting, telecommunications, displays, security inks and marking, as well as for probes in biosciences represent one third of the total value of the lanthanides used worldwide. If optical glasses and laser materials are added, this figure is close to 40%, explaining the large interest that the scientific community is devoting to such materials. The present review focuses on the design of highly luminescent lanthanide complexes and discusses all aspects needing optimization. Reference is made to the mastering of the various energy migration processes in luminescence sensitization by organic ligands, to minimizing non-radiative deactivation mechanisms, as well as to other parameters such as the radiative lifetime, the refractive index, and the benefit of inserting luminescent

\* Correspondence to: École Polytechnique Fédérale de Lausanne, Institut des Sciences Chimiques et Ingénierie, BCH 1402, CH-1015 Lausanne, Switzerland.

E-mail address: [jean-claude.bunzli@epfl.ch](mailto:jean-claude.bunzli@epfl.ch)

Design  
Energy transfer  
Radiationless transitions  
Quantum yield  
Lifetime  
Radiative lifetime  
Luminescent complexes  
Model calculations

complexes into inorganic-hybrid structures. Comparative tables list the most luminescent complexes emitting in the visible and near-infrared ranges and the best chromophores are pointed out.

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## 1. Lanthanide luminescence

A search for lanthanide luminescence and associated terms in any bibliographic database or web search engine will typically return tens of thousands of articles, pointing to the popularity of the field. Indeed, applications as diverse as lighting, telecommunications, road marking, or immunoassays rely on lanthanide luminescence. In this review article, we intend to highlight salient features of the emission of light by lanthanide coordination compounds, with special emphasis on the requirements needed to design highly emissive materials. It is noteworthy that detection of lanthanide-containing single particle or molecule is at hand, using relatively simple instrumentation; in particular, it has been demonstrated for Ln-doped oxide nanoparticles [1], upconverting nanocrystals [2,3], and, quite recently, for an europium chelate [4]. This is useful for multicolour barcoding [5,6] and in biological sensing and imaging: for instance, a single nanoparticle can be used to monitor the production of reactive oxygen species inside live cells [7].

Emission of light by chemical compounds or materials stems from two different mechanisms: incandescence, or black-body emission, which does not depend on the chemical nature of the material but only on its temperature, and luminescence or “cold light emission” [8] that involves quantified energy levels in the sample. Luminescence can be excited in different ways and specific terms are used accordingly; to name but a few: thermoluminescence is consecutive to heating of the sample, liberating energy trapped in defects; photoluminescence results when the sample is irradiated with photons; electroluminescence is produced upon excitation of the sample in an electric discharge or in an electric field; chemiluminescence (bioluminescence) arises from the energy released by a chemical (biological) reaction. In the following, however, we exclusively concentrate on photoluminescence, abbreviated luminescence, and on f–f transitions. Depending on the emission mechanism, luminescence can be divided into two processes: fluorescence is defined as a fast, spin-allowed phenomenon while phosphorescence is a slow, spin-forbidden emission. Lanthanide ions display fluorescence, phosphorescence or, often, both types of luminescence [9].

### 1.1. Historical landmarks

As for many other elements, spectroscopy, particularly atomic spectroscopy but, also, luminescence of salts and oxides, has played a major role in the discovery and precise identification of the series of elements named lanthanoids or lanthanides (Ln,  $Z = 57–71$ ) between 1803 (cerium) and 1907 (lutetium; promethium was artificially synthesized in 1947) [10]. The spectroscopic properties of lanthanide ions are unique due to the radial extension of the 4f orbitals being smaller than the expansion of filled 5s<sup>2</sup> and 5p<sup>6</sup> sub-shells. This feature confers Ln ions a special status in photonics with respect to light generation, amplification, and conversion [11]. In our opinion, the field has been shaped by eight important discoveries that are briefly described in this section.

(i) *The Auer light*. The first industrial application of lanthanides has taken advantage of cerium emission when Carl Auer von

Welsbach demonstrated in 1891 that addition of 1% CeO<sub>2</sub> to ThO<sub>2</sub> leads to much brighter white light emission upon heating; he therefore created the incandescent gas mantle, also known as the Auer light. In fact since visible emission is larger than expected from the black body curve in these mantles, while infrared emission is minimized, it seems that thermoluminescence is operating in addition to incandescence, so that the resulting complex phenomenon is termed candoluminescence. Modern versions of these mantles are still in use today.

(ii) *The red phosphor*. Another important discovery was made at the turn of the 20th century when Georges Urbain studied the luminescence of Eu<sup>III</sup> ions diluted in various matrices [12]. This eventually led to the discovery of the extraordinary bright, orange-red emitting phosphor Y<sub>2</sub>O<sub>3</sub>:Eu (4–6 mol%) that is close to the ideal prime-colour red-emitter. This phosphor, with quantum yield close to 1 [13], is a real nature's gift. It has been used in fluorescent lamps and cathode-ray tubes since the early 1960s and is still providing brilliant red colour for light-emitting diodes, displays of all kind, including flat-panel televisions, despite the large variety of potential substitute materials tested so far, but with limited success.

(iii) *Solving the puzzle of lanthanide optical spectra*. In 1937, J.H. Van Vleck deciphered the long intriguing and obscure nature of the sharp optical transitions observed for most of the trivalent lanthanide ions [14]. He stated that these transitions are forbidden and postulated that the most intense ones are electric dipole in nature and caused by a “distortion of the electronic motion by crystalline fields”. He also established that this “distortion” arises only if the ligand field does not have an inversion centre, otherwise orbital mixing cannot occur. Probabilities for quadrupolar, magnetic dipole, and electric dipole transitions were estimated. Finally, Van Vleck pointed out that interaction between vibrations and electron motion results in additional vibronic lines in the spectra and/or in broadening of some lines. In a way, this contribution can be compared with the order brought in the forest of elements by the Periodic Table and it paved the way for Diecke's diagram, ligand-field modelling, and Judd–Ofelt theory.

(iv) *The antenna effect*. Molar absorption coefficients ( $\epsilon$ ) of trivalent lanthanide ions are small, usually in the range 0.1–10 M<sup>-1</sup> cm<sup>-1</sup> so that even if quantum yields ( $Q$ ) reach sizeable values, the overall luminosity ( $L = \epsilon \times Q$ ) of Ln<sup>III</sup>-containing luminescent compounds remains small (typically  $\ll 10$  M<sup>-1</sup> cm<sup>-1</sup>) if samples are excited into the f–f transitions. In 1942, S.I. Weissman [15] discovered that light emission in lanthanide complexes with organic ligands can also be triggered when excitation is performed into the ligand electronic levels. Energy is then funnelled onto the metal ion excited states by intramolecular energy transfer. The energy transfer mechanism is highly complex and will be dealt with in details in Section 2. This finding, usually referred to as the antenna effect or luminescence sensitization, proved to have a major impact on the design of Ln-containing luminescent compounds and materials since luminosity can now easily reach 10<sup>4</sup>–10<sup>5</sup> M<sup>-1</sup> cm<sup>-1</sup>, being essentially determined by the molar absorption coefficients of the surrounding ligands.

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