



Luminescence as a tool to study lanthanide-catalyzed formation of carbon–carbon bonds



Zhijin Lin, Matthew J. Allen*

Department of Chemistry, Wayne State University, 5101 Cass Avenue, Detroit, MI 48202, USA

ARTICLE INFO

Article history:

Received 28 January 2014

Received in revised form

10 March 2014

Accepted 11 March 2014

Available online 27 March 2014

Keywords:

Lanthanides

Luminescence

Luminescence lifetime

Catalysis

Water-coordination number

Aldol

ABSTRACT

Lanthanide ions have been widely studied in imaging and sensing applications, and they are also strong Lewis acids that have the ability to catalyze organic reactions. Here, we review the spectroscopic properties of lanthanides that enable the calculation of water-coordination numbers. Additionally, the application of these calculations to study the mechanism of lanthanide-catalyzed organic reactions is reviewed.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

The lanthanides include the 14 elements from cerium to lutetium that most often exist in the tripositive oxidation state where they exhibit interesting luminescence properties. These properties have inspired the study of lanthanide ions in anion-sensing [1], cation-sensing [2], biomolecule-sensing [3], medical imaging [4], and light amplification [5]. A number of reviews of the luminescence properties of lanthanides have been published including the use of luminescent lanthanides to sense anions, pH, and oxygen [6]; applications of luminescent lanthanides in biomedical imaging [7]; lanthanide-based materials in light-emitting diodes [8]; and the use of lanthanides in ionic liquids including their spectroscopic properties [9].

In addition to having useful luminescence properties, lanthanide ions are strong Lewis acids. Unlike other Lewis acids—such as AlCl_3 , TiCl_4 , and SnCl_4 that readily hydrolyze in water—lanthanide trifluoromethanesulfonates or triflates $[\text{Ln}(\text{OTf})_3]$ are water-tolerant. The use of these salts as water-tolerant precatalysts for organic reactions has received a great deal of attention over the last few decades [10–17], and the use of coordination complexes of

these salts as aqueous-phase pre-catalysts and asymmetric pre-catalysts has been reviewed [18,19].

In this article, we summarize a combination of these two seemingly disparate areas of lanthanide chemistry. We begin with a review of the principles of lanthanide luminescence with a focus on the use of luminescence-decay measurements to study the water-coordination numbers of lanthanide ions. We then describe how these measurements have been used to study lanthanide-catalyzed carbon–carbon bond-forming reactions.

2. Lanthanide spectroscopy

Interest in the spectroscopic properties of the lanthanides is due in part to their uniquely narrow absorption and emission peaks, large Stokes shifts, and long luminescence lifetimes. These properties are determined by the electronic structures of the ions. Trivalent lanthanide ions have electronic configurations of $[\text{Xe}]4f^n$ ($n = 1–14$). Because the 4f orbitals are shielded from the environment by the filled $5s^2$ and $5p^6$ subshells, the spectroscopic properties of these ions are largely independent from their environment and ligands. This section details the relationships between electronic structure and absorption and emission.

There are three types of electronic transitions that govern absorption and emission in trivalent lanthanide ions [20]: 4f–5d transitions, charge-transfer transitions (metal-to-ligand or ligand-to-metal), and 4f–4f transitions. Because there are seven 4f

* Corresponding author. Tel.: +1 313 577 2070; fax: +1 313 577 8822.

E-mail addresses: zlin@chem.wayne.edu (Z. Lin), mallen@chem.wayne.edu (M. J. Allen).

orbitals, the trivalent lanthanides have multiple, well-defined transitions; however, these transitions are usually weak, with molar absorptivities in aqueous solution of $<1 \text{ M}^{-1} \text{ cm}^{-1}$. The 4f–5d and charge-transfer transitions are parity allowed and are usually high energy (UV), and the 4f–4f transitions tend to be lower in energy (often in the visible region). These 4f–4f transitions are occasionally perturbed by the environment and the occasional perturbations are useful in studying bond-forming reactions as described later in this article.

The 4f–4f transitions can be divided into electric dipole transitions, magnetic dipole transitions, and electric quadrupolar transitions. Electric dipole transitions between states with the same parity are forbidden according to Laporte's parity selection rule [21]. As a consequence, electric dipole transitions in lanthanide ions have low probabilities of occurrence. However, this selection rule can be circumvented with non-centrosymmetric lanthanide complexes that lead to transitions called induced electric dipole transitions. While electric dipole transitions need special circumstances to increase their chances of occurring, magnetic dipole transitions are allowed by Laporte's parity selection rule [21]. Nevertheless, these transitions are weak and not influenced by the environment of a lanthanide ion, resulting in intensities from magnetic dipole transitions being in the same magnitude of intensity as induced electric dipole transitions. Finally, like electric dipole transitions, electric quadrupolar transitions are sensitive to the environment. However, electric quadrupolar transitions are weaker than magnetic dipole transitions and are rarely observed due to their low intensity [20].

Because direct excitation of lanthanide ions does not always lead to sufficient emissions for a given application, ligand sensitization is often used with lanthanide complexes to increase luminescent emissions. In ligand-sensitized luminescence of lanthanides, a nearby molecule called an antenna is conjugated to the lanthanide complex as represented in Fig. 1A. Antenna molecules are often aromatic or unsaturated organic molecules that absorb light more efficiently than lanthanide ions. These molecules can be conjugated to the lanthanide complex via a linker or by direct coordination to the ion. Excitation of the antenna and subsequent energy transfer to a lanthanide ion is depicted schematically in Fig. 1. In this illustration, the antenna is excited from its ground state to a singlet excited state and then released to its triplet state through intersystem crossing (ISC). Energy transfer (ET) occurs from the triplet state of antenna to the excited state of the lanthanide ion. The use of an antenna can increase the quantum yield of lanthanide ions up to 61% in aqueous solution [22].

Two types of luminescence occur when excited lanthanide ions return to their ground states: fluorescence and phosphorescence. Lanthanide ions can undergo either of these types of luminescence or both simultaneously. Fluorescence does not involve a spin change [for example, $^4\text{F}_{9/2}(\text{excited state}) \rightarrow ^4\text{I}_{15/2}(\text{ground state})$ for Er^{III} , where the superscript 4 does not change]. The superscript portion of the term symbol, the spin multiplicity, is equal to $2S + 1$. If this number does not change, then the spin does not change. The other type of luminescence, phosphorescence, involves a spin change [for example, $^5\text{D}_0(\text{excited state}) \rightarrow ^7\text{F}_0(\text{ground state})$ for Eu^{III} , where the superscript 5 changes to 7]. Compared to organic lumophores and quantum dots, luminescent lanthanides have many advantages. Lanthanide luminescence occurs over a broad range of energy that is covered by the ions in aqueous solution from UV to near-IR [20], a feature caused by the multiple electronic states of lanthanide ions. The broad range of possible emissions enable lanthanide ions to be used in a diverse range of applications. Furthermore, trivalent lanthanide luminescence is in the form of sharp emission lines that reduce the loss of spectral information

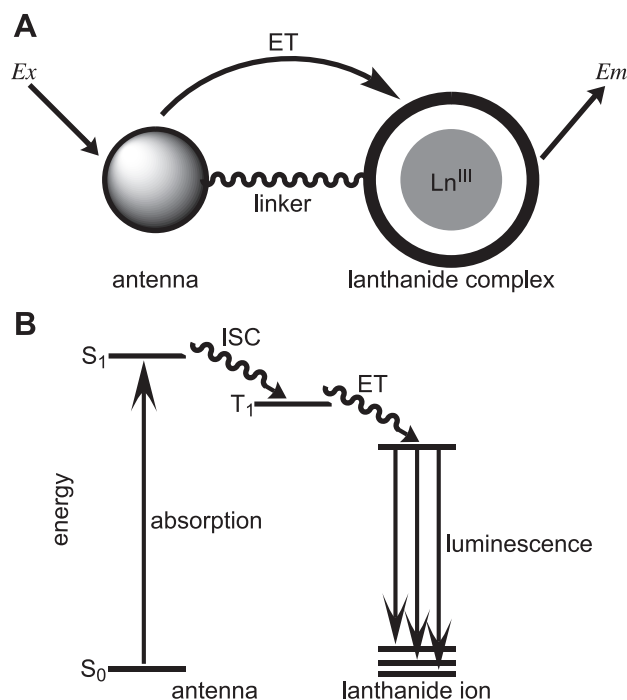


Fig. 1. Ligand-sensitized lanthanide luminescence: (A) Schematic representation of an antenna absorbing light and then transferring the energy (ET) to an attached lanthanide complex to enhance the lanthanide emission. (B) Simplified Jablonski diagram of ligand-sensitized lanthanide luminescence where S_0 is the ground state of the antenna, S_1 is the excited singlet state of the antenna, T_1 is the excited triplet state of the antenna, and ISC is intersystem crossing.

caused by overlapping peaks. Additionally, for many of the lanthanides, luminescence lifetimes are long relative to organic lumophores. For example, the luminescence lifetime of Eu^{III} is often on the order of milliseconds, while luminescence lifetimes of organic lumophores are usually on the order of nanoseconds. Another important feature of lanthanide luminescence is the presence of hypersensitive transitions. Although the luminescence of lanthanides is minimally perturbed by the environment because of the nature of the 4f orbitals, some electric dipole-based emissions of the lanthanide ions are sensitive to the environment, and these transitions are called hypersensitive transitions. For example, in the emission spectra of Eu^{III} -containing complexes, the electric dipole-governed emission ($^5\text{D}_0 \rightarrow ^7\text{F}_2$, $\lambda = 612 \text{ nm}$) is sensitive to quenching by vibrations in the environment, but the magnetic dipole-dominated emission ($^5\text{D}_0 \rightarrow ^7\text{F}_1$, $\lambda = 591 \text{ nm}$) is relatively unperturbed by the surroundings. Consequently, the ratio of the emission intensities at these wavelengths (I_{612}/I_{591}) has been used to study changes in the coordination environment of Eu^{III} . For example, changes in the I_{612}/I_{591} ratio of Eu^{III} were used to study binding of dipicolinic acid [23]. The I_{612}/I_{591} ratio increased from 0.44 to 3.4 when one equivalent of dipicolinic acid was added to Eu^{III} , and the ratio increased to 7.8 when three equivalents were added. The changing ratios are caused by the replacement of the inner-sphere water with dipicolinic acid that changes the symmetry of the Eu^{III} ion resulting in an induced electric dipole transition that increases the intensity of the emission at 612 nm. This ratio is a potential tool to study lanthanide-catalyzed organic reactions that involve coordination changes during the reaction.

The spectroscopic properties of lanthanide ions are important for their applications, one of which is the use of luminescence lifetime measurements to study the coordination environment of lanthanide ions in solution. Details of this application are described in the next section.

Download English Version:

<https://daneshyari.com/en/article/176036>

Download Persian Version:

<https://daneshyari.com/article/176036>

[Daneshyari.com](https://daneshyari.com)