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**Volume Editors** V. Balzani · S. Campagna

# Photochemistry and Photophysics of Coordination Compounds II

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# Photochemistry and Photophysics of Coordination Compounds II

Volume Editors: Vincenzo Balzani · Sebastiano Campagna

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## Preface

Photochemistry (a term that broadly speaking includes photophysics) is a branch of modern science that deals with the interaction of light with matter and lies at the crossroads of chemistry, physics, and biology. However, before being a branch of modern science, photochemistry was (and still is today), an extremely important natural phenomenon. When God said: “Let there be light”, photochemistry began to operate, helping God to create the world as we now know it. It is likely that photochemistry was the spark for the origin of life on Earth and played a fundamental role in the evolution of life. Through the photosynthetic process that takes place in green plants, photochemistry is responsible for the maintenance of all living organisms. In the geological past photochemistry caused the accumulation of the deposits of coal, oil, and natural gas that we now use as fuels. Photochemistry is involved in the control of ozone in the stratosphere and in a great number of environmental processes that occur in the atmosphere, in the sea, and on the soil. Photochemistry is the essence of the process of vision and causes a variety of behavioral responses in living organisms.

Photochemistry as a science is quite young; we only need to go back less than one century to find its early pioneer [1]. The concept of coordination compound is also relatively young; it was established in 1892, when Alfred Werner conceived his theory of metal complexes [2]. Since then, the terms coordination compound and metal complex have been used as synonyms, even if in the last 30 years, coordination chemistry has extended its scope to the binding of all kinds of substrates [3, 4].

The photosensitivity of metal complexes has been recognized for a long time, but the photochemistry and photophysics of coordination compounds as a science only emerged in the second half of the last century. The first attempt to systematize the photochemical reactions of coordination compounds was carried out in an exhaustive monograph published in 1970 [5], followed by an authoritative multi-authored volume in 1975 [6]. These two books gained the attention of the scientific community and certainly helped several inorganic and physical chemists to enter the field and to enrich and diversify their research activities. Interestingly, 1974 marked the beginning of the series of International Symposia on the Photochemistry and Photophysics of Coordi-

nation Compounds. The venue of the 17th symposium of this series is Dublin and will be held in June 2007.

Up until about 1975, most activity was focused on intramolecular photochemical reactions. Subsequently, due partly also to the more diffuse availability of flash techniques, the interest of several groups moved to investigations of luminescence and bimolecular energy and electron transfer processes. In the last decade of the past century, with the development of supramolecular chemistry, it was clear that photochemistry would play a very important role in the achievement of valuable functions, such as charge separation, energy migration and conformational changes [7], related to applications spanning from solar energy conversion to signal processing and molecular machines [8, 9]. In the last few years, an increasing number of scientists have become involved in these fields. Because of their unique ground and excited state properties, metal complexes have become invaluable components of molecular devices and machines exploiting light (often sunlight) to perform useful functions [8, 9, 10]. The photochemistry of coordination compounds can also contribute to solving the energy crisis by converting sunlight into electricity or fuel [11]. In the meantime, the basic knowledge of the excited state properties of coordination compounds of several metal ions has increased considerably. However, this has resulted in an unavoidable loss of general knowledge and an increase in specialization. Currently, all scientists working in the field of the photochemistry and photophysics of coordination compounds have their own preferred metal. There is, therefore, an urgent need to spread the most recent developments in the field among the photochemical community. To write an exhaustive monograph like [5], however, would now be an impossible enterprise. For this reason, we decided to ask experts to write separate chapters, each one dealing with a specific metal whose complexes are currently at the frontier of research. It has been a delight as well as a privilege to work with an outstanding group of contributing authors and we thank them for all their efforts. We would also like to thank all the members of our research groups for their support.

Bologna and Messina, March 2007

Vincenzo Balzani  
Sebastiano Campagna

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# Photochemistry and Photophysics of Coordination Compounds: Lanthanides

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**Abstract** This article is concerned with the recent advantages in the design of lanthanide complexes as luminescent devices such as sensors and switches. Herein the fundamental concepts of how to produce lanthanide complexes that can have their luminescence properties manipulated by external sources is first discussed, followed by a review of selected examples from the recent literature.

**Keywords** Lanthanide luminescence · Luminescent devices · Sensors · Switches · Tb(III) and Eu(III) complexes

## 1

### Introduction

The development of luminescent signalling systems is an active area of research in supramolecular chemistry because of their many possible applications [1–19]. The use of metal-based complexes for *in vivo* applications is well documented and the majority of applications have focused on using such complexes as therapeutic drugs, biological probes and assays [20–32], as they can overcome the problematic issue of autofluorescence [33–35]. This chapter will focus on some examples of the use of lanthanide complexes as luminescent signalling systems. This is a fast growing area, as the lanthanides have become popular for use in biological applications because of their unique photophysical properties such as their relatively long-lived luminescence [36–38]. The majority of research in this area has concentrated on lanthanide ions that emit in the visible and near infrared spectrum, which is advantageous for *in vivo* applications, and the main part of the discussion herein focuses on these ions [39]. We will then focus our attention towards the development of higher order lanthanide complexes, made by the use of  $f-f$  and mixed  $f-d$  ions. However, this review starts with a short summary of the physical properties of the lanthanide ions and in particular their photophysical properties.

## 2

### Luminescent Lanthanide Complexes

#### 2.1

##### Physical Properties of Lanthanides

The unique magnetic and photophysical properties of the metals in the lanthanide series have attracted great interest over the past few years, due to their potential in medical diagnostics [40, 41], optical imaging [42, 43] and high technological applications [44, 45]. The importance of lanthanides for magnetic and optical materials has long drawn attention to their physical properties and solid-state chemistry, which have both been extensively studied [46]. More recently the development of contrast agents for medical magnetic resonance imaging (MRI) and luminescent chemosensors for optical imaging of cells has shifted the focus towards their coordination chemistry in solution [47, 48]. Moreover, anions can also bind directly to lanthanide ions, or more importantly, as part of their coordination environment, such as when coordinative unsaturated ligands are used. Hence, the sensing of anion by such coordination is possible (exchange of coordination ligands).

Despite their name, “rare earth elements”, lanthanides are in fact not especially rare: each is more common in the earth’s crust than silver, gold or platinum. They possess characteristic  $4f$  open-shell configurations and exhibit

a close chemical resemblance across the periodic series due to the small and regular decrease in their ionic radii. This decrease in radii is known as the lanthanide contraction [47, 48]. Their most stable oxidation state is + 3, particularly in water, with a  $[\text{Xe}]4f^n$  configuration. The lanthanide ions possess relatively high charge densities and have a strong electrostatic nature in their bonding, as the ions are polarising and hard Lewis acids. They can coordinate to a variety of ligands with different coordination numbers, most typically eight to ten. The hard Lewis acidity of the lanthanide ions results into a specific preference towards ligands incorporating atoms that can act as hard Lewis bases or can be easily polarised. Therefore, combinations of amines and carboxylic groups are commonly used in lanthanide complexation [42, 43]. Indeed, one of the most popular ligands in the complexation of lanthanides is 1,4,7,10-tetrakis(carboxymethyl)-1,4,7,10-tetraazacyclododecane (commonly known as DOTA). Its popularity is largely due to its use as a magnetic resonance contrast agent with gadolinium [39, 49–51], where the ion coordinates to the four nitrogens of the cyclen ring and the four carboxylates of the pendant arms, giving rise to an octa-coordination environment.

The role played by the lanthanide ions in many supramolecular systems is mostly based on their optical features and coordination requirements. Lanthanides present special spectroscopic properties due to the shielding of the  $4f$  orbitals, with forbidden intra-configuration  $f-f$  electronic transitions resulting in very low extinction coefficients ( $\epsilon$  typically  $0.1 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ ) [52] and characteristic narrow line-like emission bands, mostly in the visible and near infrared ranges. Most of the lanthanide ions are luminescent, some more than others. Their emission depends on how efficiently their excited state(s) can be populated and their non-radiative deactivation pathways minimised. The main advantage is that the  $f-f$  electronic transitions are easily recognisable for they are almost independent of the chemical environment of the ion. They can be either fluorescent (e.g. Pr(III), Nd(III), Ho(III), Er(III) and Yb(III)) or phosphorescent (e.g. orange Sm(III), red Eu(III), Gd(III) which emits in the UV, green Tb(III), yellow Dy(III) and blue Tm(III)), following the IUPAC rules regarding molecular luminescence spectroscopy [53]. According to these rules, the term “fluorescence” refers to processes that occur without change in spin, typically  $S_1 \rightarrow S_0$  or  $\text{Yb}(^2F_{5/2} \rightarrow ^2F_{7/2})$  transitions. The term “phosphorescence” refers to transitions involving a change in spin, typically  $T_1 \rightarrow S_0$  or  $\text{Eu}(^5D_4 \rightarrow ^7F_J)$  transitions [47, 48]. Two ions, La(III) and Lu(III), have no  $f-f$  transitions and are therefore not luminescent.

The photophysical properties of Eu(III) and Tb(III) have generated the most interest to date of all the lanthanides because their emissions occur in the visible region. For example, Eu(III) emits in the red (550–750 nm) while Tb(III) emits in the green (450–650 nm). In terms of energy gap, Eu(III) ( $\Delta E = 12\,300 \text{ cm}^{-1}$ ,  $^5D_0 \rightarrow ^7F_6$ ), Gd(III) ( $\Delta E = 32\,200 \text{ cm}^{-1}$ ,  $^6P_{7/2} \rightarrow ^8S_{7/2}$ ) and Tb(III) ( $\Delta E = 14\,800 \text{ cm}^{-1}$ ,  $^5D_4 \rightarrow ^7F_0$ ) are the best ions for an efficient population of their excited states. However, and as stated above, while Eu(III)



and Tb(III) emit in the visible region of the spectrum, Gd(III) emits in the UV. This makes the latter unsuitable as a luminescent probe for bio-analysis due to the absorption and emission interference (light scattering, etc.) from the organic part of the complexing molecule. The sizable energy gap displayed by Eu(III) and Tb(III) explains why luminescent probes containing these ions have been so popular during the last decade. Besides Sm(III) ( $\Delta E = 7400 \text{ cm}^{-1}$ ,  $^4\text{G}_{5/2} \rightarrow ^6\text{F}_{11/2}$ ) and Dy(III) ( $\Delta E = 7850 \text{ cm}^{-1}$ ,  $^4\text{F}_{9/2} \rightarrow ^6\text{F}_{3/2}$ ), which have been employed in dual luminescent time-resolved immunoassays [54–56], the other lanthanide ions have not found similar applications, due to their very low quantum yield in aqueous solution.  $^5\text{Pr(III)}$  emits both in the visible and near-infrared (NIR) ranges [57] and is often a component of solid state optical materials. This is due to its blue up-conversion, that is the blue emission from  $^3\text{P}_0$  upon two- or three-photon pumping into the  $^1\text{G}_4$  or  $^1\text{D}_2$  states [58]. Thulium is a blue emitter from its  $^3\text{P}_0$ ,  $^1\text{D}_2$  and  $^1\text{G}_4$  levels and as such has found use in electroluminescent devices [44,45]; it is known to be one of the first ions having shown up-conversion [58]. The ions Nd(III), Dy(III), Ho(III) and Er(III) also display up-conversion processes [47,48]. Moreover, Nd(III), Ho(III), Er(III) and Yb(III) have stirred particular interest in the design of lasers (especially Nd(III)) and telecommunication devices owing to their ability to emit in the NIR part of the electromagnetic spectrum [59]. In addition, Nd(III), Er(III) and Yb(III) have been recently employed in the development of luminescent probes for time-resolved imaging of biological tissues, as they are able to efficiently transmit light in the NIR spectral range [60–62].

As explained above, the lanthanide  $f-f$  transitions (electric dipole transitions) are “Laporte-forbidden”, therefore, the generation of fluorescence from the lanthanide ion can be difficult. Direct excitation of the lanthanide ion can be achieved, but this only becomes practical with the use of lasers or at high ion concentrations. However, such inherent disadvantages can be overcome by using sensitisation techniques [63–66] (Scheme 1). This involves using indirect excitation of the lanthanide ion with a sensitising chromophore (often termed as an antenna) [67,68] usually through an intramolecular energy transfer process [64–66,69,70]. The antenna needs to be in close prox-

