

The Photoluminescence of Lanthanide Complexes and Energy Transfer Theories

Wakeel Ahmed Dar¹ and Ruqiya Bhat²

¹Department of Chemical Sciences,
Jamia Millia Islamia, New Delhi-110025, INDIA.

²Department of Physics,
University of Kashmir, Srinagar (J&K)-190006, INDIA.
email: Chemistakeel@gmail.com

(Received on: October 26, 2017)

ABSTRACT

The luminescence of lanthanide complexes is one of the most interesting feature. The intensity of the emission peaks of the luminescent lanthanide ions can be increased by several orders of magnitude by coordinating them with the organic chromophores of high absorption coefficient. The chromophores are excellent light harvesting and sufficiently populate the emitting levels of the lanthanide ions by efficiently transferring absorbed energy to the lanthanides via a well-known 'antenna effect'. The different energy transfer theories are there to explain the mechanism of energy transfer mechanism in such complexes. The commonly accepted mechanism is one proposed by Crosby and Whan.

Keywords: luminescence of lanthanide complexes, organic chromophores.

INTRODUCTION

Perspective

The luminescence of lanthanide complexes is one of the most fascinating features and covers an exceptionally wide spectral range. Lanthanide ions can be divided into the (a) non-emissive: La(III) ($4f^0$) and Lu(III) ($4f^{14}$); (b) UV-emitter: Gd(III) ($4f^7$) ion; (c) Visible light emitters: Pr(III), Sm(III), Eu(III), Tb(III), Dy(III) and Tm(III); (d) NIR emitters: Nd(III), Yb(III), Ho(III) and Er(III); (e) Visible and NIR emitters: Pr(III), Sm(III), Ho(III), Tm(III) and Dy(III). Therefore, the emission can be easily tuned by choosing the appropriate lanthanide ion. The luminescence from lanthanide complexes are typically characterized by narrow line-like emission peaks, Richardson's shift¹ and relatively longer lifetimes (*microseconds to*

milliseconds).² However, the 4f-4f transitions of trivalent lanthanide ions are parity forbidden with low molar absorption coefficient ($\epsilon < 10 \text{ LM}^{-1} \text{ cm}^{-1}$) due to which the direct excitation is not fruitful.^{3, 4} The 4f-4f transitions are magnetic-dipole (MD) and induced electric-dipole (ED) transitions in nature. The MD transitions are insignificant to the chemical environment while ED transitions are highly sensitive to it.⁵ The intensity of the emission peaks of the luminescent lanthanide ions can be increased by several orders of magnitude by coordinating them with the organic chromophores of high absorption coefficient.^{6, 7} The chromophores are excellent light harvesting and sufficiently populate the emitting levels of the lanthanide ions by efficiently transferring absorbed energy to the lanthanides via a well-known 'antenna effect'.⁸ These chromophores also shield the lanthanide ions and protect the emission from disadvantageous effect of non-radiative deactivation. The choice of a good sensitizer which can efficiently transfer the energy to the lanthanide ions is a challenging task. Weismann⁹ first discovered the intense metal-centered luminescence from the lanthanide complexes upon excitation in an absorption band of the organic ligand. For example, luminescence was observed in the europium (III) complexes of salicylaldehyde, benzoylacetone, dibenzoylmethane and *meta*-nitrobenzoylacetone by exciting in the ligand absorption range. His work was recognized after 20 years,¹⁰ although Sevchenko and Trifimov¹¹ showed that his experiments could be reproduced. The mechanism of the energy transfer from the organic chromophore to the lanthanide ion was investigated in the early 1960s. The commonly accepted mechanism is one proposed by Crosby and Whan.^{12, 13} According to them, upon irradiation in the ultraviolet region, the organic chromophores coordinated to the lanthanide complex undergoes an excitation to the ligand localized singlet state (S), followed by an intersystem crossing (ISC) to the lowest lying triplet energy state (T) and as a consequence of a non-radiative intramolecular energy transfer from the triplet state (T) of the ligand to the emitting level of the Ln(III) ion, followed by emission from the later.

CONCLUSIONS

The luminescent lanthanide complexes are excellent candidates as emitting materials for light emitting diodes (LEDs), luminescent sensors, colour indicators and biological probes since they emit line-like emission, which results in high colour purity. The chromophores (organic ligands) are outstanding light harvesting and adequately helps in transferring absorbed energy to the emitting levels of the lanthanide ions *via* a well-known 'antenna effect'. The various energy transfer theories are there to explain the mechanism of energy transfer mechanism in lanthanide complexes.

REFERENCES

1. P. A. Tanner, *Chemical Society Reviews*, 42, 5090-5101 (2013).
2. K. Binnemans, *Coordination Chemistry Reviews*, 295, 1-45 (2015).
3. A. J. Amoroso and S. J. A. Pope, *Chemical Society Reviews*, 44, 4723-4742 (2015).

4. G. F. de Sá, O. L. Malta, C. de Mello Donegá, A. M. Simas, R. L. Longo, P. A. Santa-Cruz and E. F. da Silva Jr, *Coordination Chemistry Reviews*, 196, 165-195 (2000).
5. G. S. Ofelt, *The Journal of Chemical Physics*, 37, 511-520 (1962).
6. J.-C. G. Bünzli, *Coordination Chemistry Reviews*, 293–294, 19-47 (2015).
7. K. Binnemans, in *Handbook on the Physics and Chemistry of Rare Earths*, eds. J.-C. G. B. Karl A. Gschneidner and K. P. Vitalij, Elsevier, vol. Volume 35, pp. 107-272 (2005).
8. N. Sabbatini, M. Guardigli and J. M. Lehn, *Coordination Chemistry Reviews*, 123, 201-228 (1993).
9. S. I. Weissman, *The Journal of Chemical Physics*, 10, 214-217 (1942).
10. N. Filipescu, G. W. Mushrush, C. R. Hurt and N. McAvoy, *Nature*, 211, 960-961 (1966).
11. A. N. Sevchenko and A. K. Trifimov, *J. Exp. Theor. Phys.*, 21, 220 (1951).
12. G. A. Crosby, R. E. Whan and R. M. Alire, *J. Chem. Phys.*, 34, 743 (1961).
13. R. E. Whan and G. A. Crosby, *J. Mol. Spectrosc.*, 8, 315 (1962).