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Lanthanide luminescence

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Abstract

Luminescent properties of trivalent lanthanides are extensively studied because of their use not only in analytical chemistry and biomedicine (Caravan et al., 1999; Selvin, 2002). In this contribution, luminescence properties of selected lanthanide complexes will be discussed.

Keywords: luminescence, lanthanides, lanthanide complexes

Introduction

Several trivalent lanthanide ions may provide noteworthy luminescent properties especially when located in coordination complexes. These include extraordinarily long luminescence life–times reaching hundreds of microseconds, Stokes shift much greater than in case of common organic fluorophores, and tight emission peaks matching the selected ion energy transitions (Choppin and Peterman 1998). An antenna effect, which allows the ligand to act as a light energy collector, is said to be responsible for such spectroscopic behavior (Selvin 2002).

Generally, the energy absorbed by the ligand may be consumed by various de–excitation ways involving irradiative processes, ligand fluorescence or phosphorescence; or it may be used for excitation and luminescence of the central ion. Thus the luminescence intensity and life–time are enormously influenced by a central ion surrounding (Bunzli and Piguet 2005).

The lanthanide complexes have been intensively studied in past few years, particularly for their use as relaxation (Gd^{3+}) reagents in magnetic resonance imaging in a medicine field of knowledge, or as labeling (Tb^{3+}, Eu^{3+}) reagents for time–resolved luminescence spectroscopy and related techniques (Caravan et al. 1999; Selvin 2002).

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Materials and methods

All luminescence measurements were performed on Luminescence spectrometer AMINCO–Bowman Series 2 in quartz cuvette with optical length 10 mm at a temperature of 25°C. Data were evaluated in AB2, Microsoft Office Excel and OriginPro.

Results and Discussion

Lanthanide complexes containing various ligands provided different luminescence intensities and life–times, which was related to the first coordination sphere of the lanthanide ion. This enabled to determine a number of water molecules enclosing the central ion, which has shown to be an important issue in biomedicine, since non–complexed lanthanides are toxic (Barthelemy and Choppin 1989).

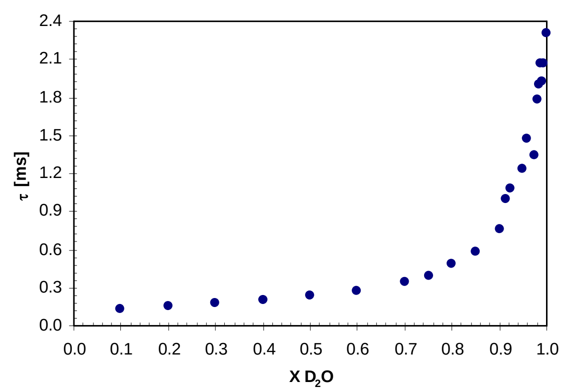

Figure 1: The luminescence life–time of Eu3+ ions as a function of D2O/H2O molar ratio

Luminescence quenching experiments in various permittivity media have been performed resulting in a strong dependence of luminescence on the presence of –XH oscillators (–OH, –NH, –CH, H_2O) in the closest Ln^{3+} ambience (Choppin and Peterman, 1998). Moreover, the quenching ability of the oscillators has been studied under different D_2O/H_2O ratios. The luminescence life–time of Eu^{3+} ions in the presence of D_2O molecules has been significantly longer than in the presence of H_2O molecules (Fig 1), which makes it suitable for D_2O purity verification or examination of water traces in other organic solvents.

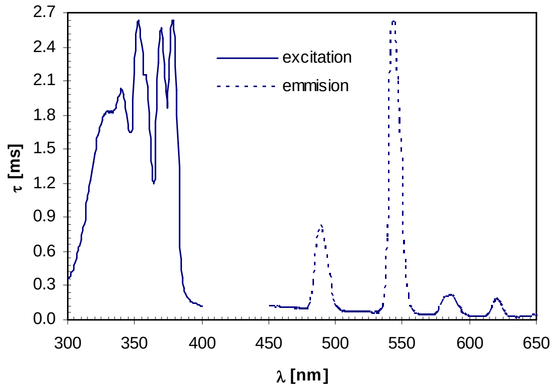

Figure 2: Excitation and emision spectrum of Tb(NO3)3 with DPPHO2 as a ligand

Finally, luminescence characterization of newly synthesized coordination compounds with bis(diphenylphosphino)alkane dioxide ligands, alkane being ethane, butane or hexane and lanthanide salt being $Tb(NO_3)_3$, $Dy(NO_3)_3$, $Sm(NO_3)_3$ and $Eu(NO_3)_3$, has been performed. Preliminary results have shown differences in luminescence lifetimes (luminescence lifetime correlated to the alkyl chain length) and emission spectra (Fig 2) of different complexes. This variation is assumed to be dependent on the length of alkane chain (Table 1).

Table 1: Luminescence properties of the studied Ln^{3+} coordination polymers

Salt	Ligand	Excitation/ emission (nm)	Life-time (ms)	Reference
$Tb(NO_3)_3$	$DPPEO_2$	343/544	1.356	This work
$Tb(NO_3)_3$	$DPPBO_2$	378/544	1.439	This work
$Tb(NO_3)_3$	$DPPHO_2$	378/543	1.539	This work
$Dy(NO_3)_3$	$DPPEO_2$	389/573	0.083	This work
$Dy(NO_3)_3$	$DPPBO_2$	453/573	0.077	This work
$Dy(NO_3)_3$	$DPPHO_2$	454/573	0.089	This work
$Sm(NO_3)_3$	$DPPEO_2$	404/597	0.075	This work
$Sm(NO_3)_3$	$DPPBO_2$	404/597	0.089	This work
$Sm(NO_3)_3$	$DPPHO_2$	404/597	0.103	This work
$Eu(NO_3)_3$	$DPPEO_2$	395/618	1.426	Pekarkova, 2011
$Eu(NO_3)_3$	$DPPBO_2$	395/618	1.566	Pekarkova, 2011
$Eu(NO_3)_3$	$DPPHO_2$	395/618	1.598	Pekarkova, 2011

Conclusion

Luminescence properties of selected lanthanide complexes have been characterized for future deployment in several fields of knowledge, such as biomedicine, quality assessment or material synthesis and development. The lanthanide complexes sphere of action is far–reaching and should be enriched by further applications in addition to fundamental research.

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