proceedings

Improving the luminescent properties of a dysprosium complex in the presence of Zn^{II}: an emissive Zn_2Dy compound

Julio Corredoira-Vázquez*[1], Matilde Fondo[1], Ana M. García-Deibe[1], Jesús Sanmartín-Matalobos[1] and Cristina Nuñez[1,2]

[1] Departamento de Química Inorgánica, Facultade de Química, Universidade de Santiago de Compostela, 15782 Santiago de Compostela. E-mails: julio_corredoira@hotmail.com; matilde.fondo@usc.es; ana.garcia.deibe@usc.es; jesus.sanmartin@usc.es
[2] Oncology Division, Research Unit, Hospital Universitario Lucus Augusti (HULA), Servizo Galego de Saúde (SERGAS), 27002 Lugo, Spain. E-mail: Cristina.Nunez.Gonzalez@sergas.es
* Correspondence: julio_corredoira@hotmail.com

† Presented at the title, place, and date.

Academic Editor: name
Received: date; Accepted: date; Published: date

Abstract: The mononuclear complex $[Dy(H_3L)(H_2O)(NO_3)](NO_3)_2$ (**Dy**) and the heterotrinuclear compound $[Zn_2Dy(L)(NO_3)_3(OH)]\cdot 3H_2O$ (**Zn₂Dy**$\cdot 3H_2O$) can be obtained with the same H_3L compartmental ligand. The single X-ray crystal structure of both complexes shows a DyO_9 core but with different geometries: a muffin-like disposition in **Dy** and a spherical capped square antiprism geometry in **Zn₂Dy**. The luminiscent characterisation of the metal compounds in methanol at 298 K shows a notable increase in the fluorescent emission of the heterotrinuclear complex respect to the mononuclear one, indicating that the presence of zinc improves significantly the fluorescent character of **Zn₂Dy**$\cdot 3H_2O$ respect to **Dy**. Accordingly, **Zn₂Dy**$\cdot 3H_2O$ could be a potential fluorescent probe for imaging applications.

Keywords: Dysprosium, zinc, Schiff base, fluorescence

1. Introduction

One relevant aspect of the lanthanide (Ln) metals is their unusual spectroscopic properties. Ln^{3+} cations display absorption and emission bands that correspond to Laporte-forbidden f-f transitions. Because the 4f orbitals are relatively insensitive to the ligand field, these bands are line-like and characteristic of each metal [1]. Besides, lanthanide ions have other unique features, such as high luminescence quantum yield, long-lived emission, and large Stokes shifts [2]. These properties make them potential candidates for fluorescent probes, light-emitting diodes, and conversion or amplification of light [3]. Nevertheless, lanthanides have low molar absorptivities, making the direct excitation of the metals very inefficient. This problem is overcome by using a strongly absorbing chromophore to sensitize Ln(III) emission, in a process known as the antenna effect. Thus, luminescent emission in lanthanide complexes is usually enhanced by the use of appropriate light-harvesting units, such as organic ligands or metal complexes typically based on d-metal ions (e.g., Zn(II) and Ir(III)) [4-5]. The use of Zn(II) is particularly interesting because Zn^{2+} can be encapsulated in small ligands and has a preference for low coordination numbers (4-6) while Ln ions are more bulky and tend to achieve higher coordination numbers (usually higher than 8). These differences in size and coordination preferences allow predesigning ligands that can allocate both kinds of metal ions in predetermined pockets.

With these considerations in mind, the reported ligand H_3L (Scheme 1) [6] was revised under the light of its compartmental character. The reactivity of H_3L towards Dy(III) and towards Dy(III) and Zn(II) was studied. The results achieved, which include the study and comparison of the luminescent properties of the isolated complexes, are described herein.The introduction should briefly place the study in a broad context and define the purpose of the work and its significance.

2. Methods

2.1. Materials and general methods

All chemical reagents and solvents were purchased from commercial sources and used as received without further purification. Elemental analyses of C, H and N were performed on a FISONS EA 1108 analyser. Infrared spectra were recorded in the ATR mode on a Varian 670 FT/IR spectrophotometer in the range 4000-500 cm^{-1}.

2.2. Syntheses of the complexes

$[Dy(H_3L)(H_2O)(NO_3)](NO_3)_2$ (**Dy**): to a solution of triethylenetetramine (0.038 g, 0.26 mmol) in methanol (20 mL), 2-hydroxy-5-methyl-1,3-benzenedicarboxaldehyde (0.13 g, 0.79 mmol) and acetonitrile (10 mL) were added. The mixture was stirred for 30 min and $Dy(NO_3)_3{\cdot}6H_2O$ (0.091 g, 0.26 mmol) was added to the obtained yellow solution. The new mixture was stirred for 16 h at room temperature and the resultant yellow solution was concentrated in a rotaevaporator, reducing its volume up to 15 mL. The solution was left to refrigerate in the fridge and after 24 h, single crystals of **Dy**·$0.5CH_3CN$, suitable for X-ray diffraction studies, precipitated. Crystal data: (at 100(2) K): monoclinic, $P2_1$, $C_{34}H_{38.5}N_{7.5}O_{16}$, *MW* = 970.72, with a = 9.9976(12) Å, b = 17.7134(19) Å, c = 11.8299(14) Å and β = 110.076(8), V = 1967.7(4) Å^3, Z = 2; R_1 = 0.0416 and wR_2 = 0.0940 ($I > 2\sigma I$). The crystals were filtered and dried in air, losing the acetonitrile solvate to give rise to **Dy**. Yield: 0.11 (44%). *MW*: 951.10. Anal. calcd. for $C_{33}H_{38}DyN_7O_{16}$: C 41.67, H 4.03, N 10.31 %. Found: C 41.57, H 4.32, N 10.49 %. IR (ATR, $\tilde{\nu}$/cm^{-1}): 3266 (H_2O), 1646 (C=O), 1635 (C=N), 1283, 1303 (NO_3^-).

$[Zn_2Dy(L)(NO_3)_3(OH)]{\cdot}3H_2O$ (**Zn₂Dy**·$3H_2O$): to a solution of triethylenetetramine (0.038 g, 0.26 mmol) in methanol (20 mL), 2-hydroxy-5-methyl-1,3-benzenedicarboxaldehyde (0.13 g, 0.79 mmol) and acetonitrile (10 mL) were added. The mixture was stirred for 30 min and $Zn(OAc)_2{\cdot}2H_2O$ (0.128 g, 0.52 mmol) was added to the obtained solution. This mixture was stirred for 10 min and then $Dy(NO_3)_3{\cdot}xH_2O$ (0.091 g, 0.26 mmol) was added. The new mixture was stirred at room temperature for 4 h and the resultant solution was concentrated, reducing its volume up to 15 mL. The solution was left to refrigerate in the fridge and after 4 days a powder solid precipitated. Yield: 0.11 g (35%). *MW*: 1131.91. Anal. calcd. for $C_{33}H_{40}DyN_7O_{16}Zn_2$: C 34.99, H 3.53, N, 8.66 . Found: C 35.15, H 3.81, N 8.70 %. IR (ATR, $\tilde{\nu}$/cm^{-1}): 3391 (H_2O), 1647 (C=O), 1631 (C=N), 1306 (NO_3^-).

Recrystallization of the powder, by diffusion of diethyl ether into a methanol/acetonitrile solution of **Zn_2Dy**·$3H_2O$ with a few drops of cyclohexane, yields single crystals of **Zn_2Dy**·$3H_2O$, suitable for X-ray diffraction studies. Crystal data: (at 100(2) K): orthorhombic, *Pmna*, $C_{33}H_{34}DyN_7O_{19}Zn_2$, *MW* = 1125.91, with a = 22.6964(11) Å, b = 17.2207(8) Å, c = 10.1937(4) Å, V = 3984.2(3)Å^3, Z = 4; R_1 = 0.0442and wR_2 = 0.0889 ($I > 2\sigma I$).

2.3. Spectrophotometric and spectrofluorimetric measurements

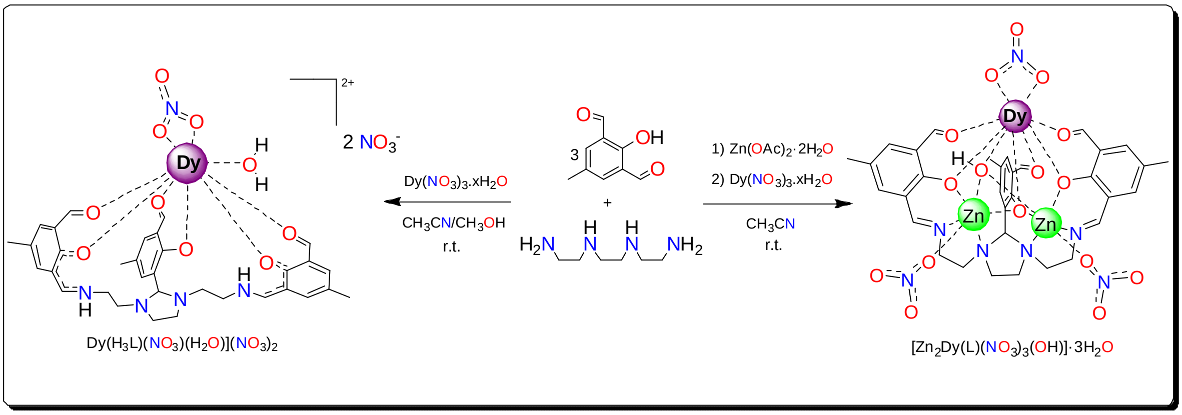
Absorption spectra were recorded on a JASCO V-630 spectrophotometer and fluorescence emission spectra on a JASCO FP-8300 spectrofluorimeter. The linearity of the fluorescence emission *vs* concentration was checked in the concentration range used M).

The spectrophotometric characterisation was made by preparing stock solutions of **Dy**, and **Zn$_2$Dy**·3H$_2$O in methanol (*ca.* 10^{-3} M). The studied solutions were prepared by appropriate dilution of the stock solutions up to 10^{-5} M. Fluorescence quantum yields were determined using a 0.1 M solution of quinine sulphate in 0.5 M H_2SO_4 as standard ($\phi = 0.546$) and all values were corrected taking into account the solvent refraction index [7]. All the measurements were taken at 298 K.

3. Results and discussion

3.1. Synthesis and spectroscopic characterisation

The mononuclear complex [Dy(H$_3$L)(NO$_3$)(H$_2$O)](NO$_3$)$_2$·0.5CH$_3$CN (**Dy**·0.5CH$_3$CN) was obtained in the form of single crystals by template synthesis, as summarised in Scheme 1. Drying of the crystals leads to loss of the acetonitrile solvate, generating **Dy**.



Scheme I: Reaction scheme for the isolation of **Dy** and **Zn$_2$Dy**·3H$_2$O

[Zn$_2$DyL(NO$_3$)$_3$(OH)]·3H$_2$O (**Zn$_2$Dy**·3H$_2$O) could be also obtained by template synthesis, by mixing the dialdehyde, the tetramine, Zn(OAc)$_2$·2H$_2$O and Dy(NO$_3$)$_3$·xH$_2$O in 3:1:2:1 molar ratios. Single crystals of **Zn$_2$Dy**·3H$_2$O were isolated by diffusion of diethyl ether into a methanol/acetonitrile solution of the powder sample, with a few drops of cyclohexane.

The formulations of both compounds were confirmed by microanalysis, IR spectroscopy and by single X-ray diffraction studies. Their luminescence properties were also analysed.

The IR spectra of **Dy** and **Zn$_2$Dy**·3H$_2$O show a sharp band at *ca.* 1645 cm^{-1}, assigned to ν(C=O)$_{\text{aldehyde}}$. When the aldehyde group of this ligand remains uncoordinated, it gives rise to an IR band at 1673 cm^{-1} [6], and, accordingly, the low wavenumbers observed for this vibration in these complexes suggests the involvement of the O$_{\text{aldehyde}}$ atom in the coordination to the metal ions. In addition, sharp bands at *ca.* 1635 and 1300 cm^{-1} are also present, indicating the existence in both compounds of imine [6,8] moieties and nitrate groups [8], respectively.

3.2. X-ray difraction studies

3.2.1. [Dy(H$_3$L)(NO$_3$)(H$_2$O)](NO$_3$)$_2$·0.5CH$_3$CN (**Dy**·0.5CH$_3$CN)

Figure 1 shows an ellipsoid diagram for **Dy** and selected bond distances and angles are recorded in Table 1.

The unit cell of **Dy**·0.5CH_3CN contains $[Dy(H_3L)(H_2O)(NO_3)]^{2+}$ cations, two nitrate anions per cation and acetonitrile as solvate. In the cation, H_3L is fully protonated and the hydrogen atoms linked to heteroatoms were found in the Fourier map nearer to the N_{imine} atoms than to O_{phenol} ones, which seems to indicate that the keto-amine form of the ligand is more stable than the phenol-imine one.

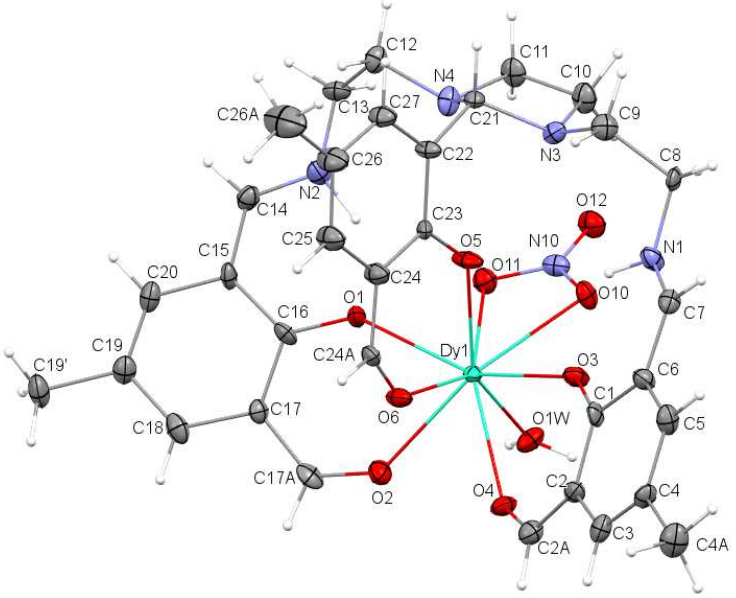


Figure 1. Ellipsoid (50% probability) diagram for the cation $[Dy(H_3L)(H_2O)(NO_3)]^{2+}$ in **Dy**.

Table 1. Main bond distances (Å) and angles (°) for **Dy**·0.5CH_3CN.

Dy1—O1	2.350(6)	Dy1—O3	2.346(6)	Dy1—O10	2.520(8)
Dy1—O2	2.452(7)	Dy1—O4	2.485(7)	Dy1—O11	2.503(8)
Dy1—O5	2.299(4)	Dy1—O6	2.363(3)	Dy1—O1W	2.378(3)
O1-Dy-O3	147.5(2)	O10-Dy-O11	50.77(13)		

In this complex, H_3L acts as hexadentate, using all its oxygen atoms (three O_{phenol} and three $O_{aldehyde}$) to bind the Dy^{3+} ion, with all the nitrogen atoms remaining uncoordinated. The coordination spheres of the lanthanide ions are completed by a nitrate ligand, acting as bidentate chelate, and a water molecule. Accordingly, the Dy^{3+} ion reaches a coordination number of 9. The distortion from the ideal DyO_9 core was computed using SHAPE software [9] and the less deviation has been found for a muffin-like structure, as shown in Figure 2

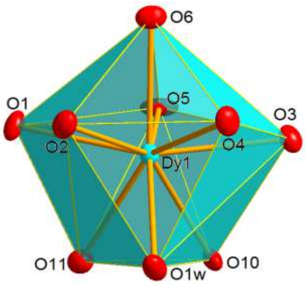


Figure 2. Coordination environments for the Dy ion in **Dy**, showing the muffin structure.

In this structure, all the distances and angles about the metal ion are within their usual range and do not merit further consideration [10-11].

3.2.2. $Zn_2DyL(NO_3)_3(OH)]\cdot 3H_2O$ ($Zn_2Dy\cdot 3H_2O$)

Zn_2Dy $\cdot 3H_2O$ consists of trinuclear $[Zn_2DyL(NO_3)_3(OH)]$ (**Zn_2Dy**) units (Figure 3) with water as solvate. **Zn_2Dy** has a symmetry plane that contains the Dy^{3+} ion and the central phenol ring, and that bisects the nitrate ligand, thus making both halves of the molecule crystallographically equivalent.

Zn_2Dy can be understood as a $[Zn_2L(NO_3)_2(OH)]^{2-}$ fragment that acts as a metalloligand towards a Dy^{3+} ion. Thus, in this fragment, the Schiff base, which is fully deprotonated, allocates a zinc(II) ion in each one of its internal *N*2O compartments (O1N1N2). In addition, both zinc centres are bridged by an endogenous phenolate oxygen atom (O3) of the central ligand arm, the carbonyl oxygen atoms remaining uncoordinated. The coordination spheres of the zinc centres are completed by two nitrate anions, coordinated each one to a Zn^{II} ion as a monodentate terminal donor, and by a hydroxide ligand, acting as a bridge between the zinc atoms. This gives rise to a coordination number of 6 for the zinc atoms, with distorted octahedral geometry.

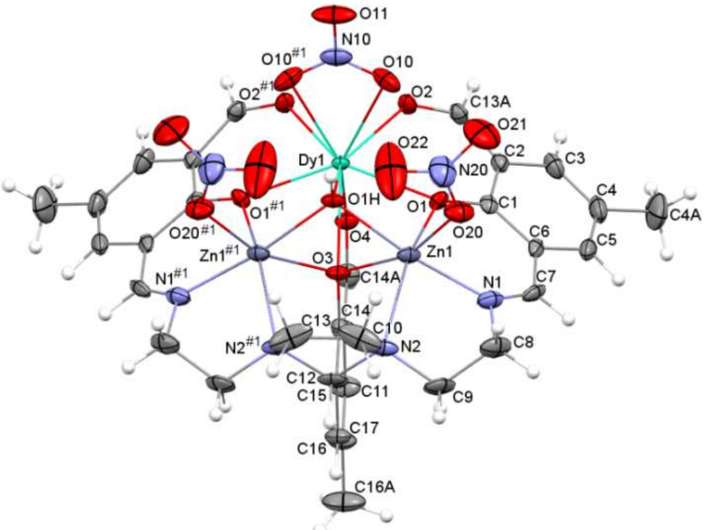


Figure 3. Ellipsoid (50% probability) diagram for **Zn_2Dy**.

Table 2. Main bond distances (Å) and angles (º) for **Zn_2Dy**$\cdot 3H_2O$

Dy1-O1	2.314(4)	Dy1-O4	2.411(5)	Zn1-N1	2.034(5)	Zn1-O1	2.154(3)
Dy1-O2	2.363(4)	Dy1-O3	2.439(5)	Zn1-O1H	2.047(3)	Zn1-O3	2.222(3)
Dy1-O1H	2.366(5)	Dy1-O10	2.489(4)	Zn1-O20	2.102(4)	Zn1-N2	2.232(4)
Dy1···Zn1	3.2009(7)			Zn1···Zn1#1	3.289(1)		
O10#1-Dy1-O10	51.1(2)	O4-Dy1-N10	159.21(18)	Zn1-O1H-Dy1	92.71(17)	Zn1-O1-Dy1	91.45(13)
N1-Zn1-O1H	173.06(18)	O20-Zn1-O3	161.19(17)	Zn1-O3-Dy1	86.61(14)	Zn1-O3-Zn1#1	95.46(19)
						Zn1-O1H-Zn1#1	106.9(2)

#1 x, -y+1/2, z

The above described $[Zn_2L(NO_3)_2(OH)]^{2-}$ anion joins a Dy^{3+} ion, using all of its carbonyl and phenolic oxygen atoms (a total of 6) to link to the lanthanide metal, as in the mononuclear complex. In addition, the hydroxide ligand also binds the dysprosium atom, acting now as a μ_3 bridge. The coordination sphere of Dy^{3+} is completed by a bidentate chelate nitrate, thus giving rise to a DyO_9 environment, as in **Dy**. Computations with the SHAPE software [9] indicate that the geometry about the Dy^{3+} ion is now closest to spherical capped square antiprism (Figure 4), but with a significant distortion towards muffin-like. Once again, all the bond distances and bond angles in **Zn_2Dy** (Table 2) are in the usual range [10-11].

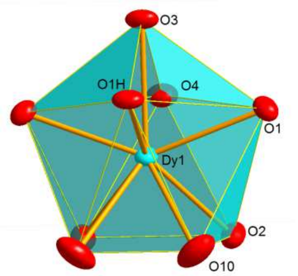


Figure 4. Coordination environment for Dy in **Zn$_2$Dy**, showing the spherical capped square antiprism structure.

3.3. Photophysical properties

All spectrophotometric measurements for **Dy** and **Zn$_2$Dy**·3H$_2$O were taken in methanol solution at 298 K. The photophysical characterisation and the main photophysical data are reported in Table 3 and the absorption and emission spectra both compounds are depicted in Figure 5.

The electronic absorption spectra show three absorption bands at *ca*. 245, 260, 400 nm, which are attributed to π–π* electronic transitions of the phenol rings and the imine bonds present (Table 3) [12,13]. In both cases, the perfect match between the absorption and the excitation spectra rules out the presence of any emissive impurity, in agreement with the high purity of the complexes.

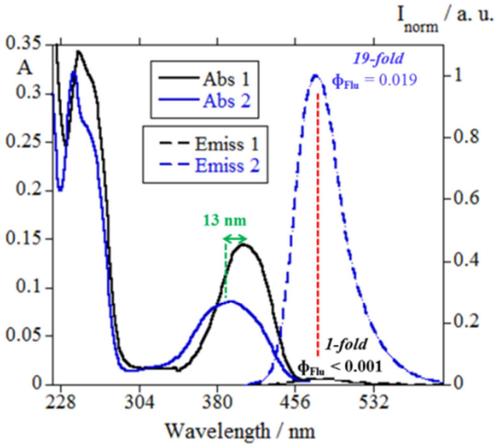


Figure 5. Absorption and emission spectra for **Dy** (Abs1 and Emiss1, color: black), and **Zn$_2$Dy**·3H$_2$O (Abs2 and Emiss2, color: blue, $\lambda_{exc1} = 407$, $\lambda_{exc2} = 394$ nm, and $\lambda_{em1} = 483$, $\lambda_{em2} = 476$ nm).

Table 3. Photophysical data for the metal complexes in methanol at 298 K

Compound	UV/Vis λ_{max} (nm): log ε	Fluorescence		
		λ_{em} (nm)	Stokes' shift (nm)	ϕ_{Flu}
Dy	245: 7.73	483	76	<0.001
	260: 4.68			
	407: 4.29			
Zn$_2$Dy·3H$_2$O	240: 4.60	476	82	0.019
	257: 4.49			
	394: 3.96			

The fluorescence spectra of both compounds display a broad band with a maximum at *ca.* 480 nm, which seems to be a ligand-based emission, given the broad nature of these signals. In addition, the low fluorescence observed for **Dy** can be ascribed to the absence of coordination between the lanthanide ions and the imine groups of the ligand skeleton.

This effect promotes that the Photo-induced Electron Transfer (PET) process takes place from the N_{imine} lone pair to the excited state of the fluorophore (phenol rings) [14]. The coordination of metal ions to these nitrogen atoms prevent PET quenching from the lone pair of electrons of each nitrogen atom to the fluorophore moieties.

This effect is observed in **Zn₂Dy**·$3H_2O$, where the N_{imine} lone pairs are bound to the Zn^{2+}, thus favouring the fluorescence emission [15]. Thus, a remarkable increase of fluorescence intensity was observed for **Zn₂Dy**·$3H_2O$ (19-fold, ϕ_{Flu} = 0.019) compared with **Dy** (1-fold, $\phi_{Flu} < 0.001$), at peak wavelength λ_{max} = 476 nm and λ_{max} = 483 nm, respectively. Accordingly, the presence of Zn in **Zn₂Dy**·$3H_2O$ converts it in a fluorescent compound.

4. Conclusions

New Dy and Zn_2Dy complexes have been obtained from related H_3L. The characterisation by single X-ray diffraction shows that the complexes present DyO_9 cores, with structure between muffin-like and spherical capped square antiprism. The study and comparison of the luminescent properties of both complexes show that the presence of zinc produces an outstanding increase of the fluorescence in **Zn₂Dy**·$3H_2O$ respect to the **Dy**, in such a way that **Zn₂Dy**·$3H_2O$ can be consider as a molecular fluorescent material.

5. Acknowledgements

Authors thank the Spanish Ministerio de Economía y Competitividad (CTQ2014-56312-P) and Xunta de Galicia (GRC2015/009) for financial support. C. Núñez is funded by the Miguel Servet Program (CP16/00139), Instituto de Salud Carlos III, Ministerio de Economía, Industria y Competitividad (Spain).

6. **References**

1. (a) M. C. Heffern, L. M. Matosziuk and T. J. Meade. Lanthanide probes for bioresponsive imaging. *Chem. Rev.*, **2014**, 114, 4496-4539. DOI: 10.1021/cr400477t; (b) S. V. Eliseeva and J. C. G. Bunzli. Lanthanide luminescence for functional materials and bio-sciences. *Chem. Soc. Rev.*, **2010**, 39, 189-227. DOI: 10.1039/B905604C.
2. a) J. Bunzli. Lanthanide luminescence for biomedical analyses and imaging. *Chem. Rev.*, **2010**, 110, 2729-2755. DOI: 10.1021/cr900362e; (b) Y. Cui, Y. Yue, G. Qian and B. Chen. Luminescent functional metal–organic frameworks. *Chem. Rev.*, **2012**, 112, 1126-1162. DOI: 10.1021/cr200101d; (c) J. F. Lemonnier, L. Guenee, C. Beuchat, T. A. Wesolowski, P. Mukherjee, D. H. Waldeck, K. A. Gogick, S. Petoud and C. Piguet. Optimizing sensitization processes in dinuclear luminescent lanthanide oligomers: selection of rigid aromatic spacers. *J. Am. Chem. Soc.*, **2011**, 133, 16219-16234. DOI: 10.1021/ja206806t.
3. L. Armelaoa, S. Quici, F. Barigelletti, G. Accorsi, G. Bottaro, M. Cavazzini and E. Tondello. Design of luminescent lanthanide complexes: From molecules to highly efficient photoemitting materials. *Coord. Chem. Rev.*, **2010**, 254, 487-505. DOI: 10.1016/j.ccr.2009.07.025

4. D. Zeng, M. Ren, S-S. Bao, L. Li and L-M Zheng. A luminescent heptanuclear $DyIr_6$ complex showing field-induced slow magnetization relaxation. *Chem Commun.*, **2014**, 50, 8356-8359. DOI: 10.1039/C4CC02951H
5. S. Das, K. S. Bejoymohandas, A. Dey, S. Biswas, M. L. P. Reddy, R. Morales, E. Ruiz, S. Titos-Padilla, E. Colacio and V. Chandrasekhar. Amending the anisotropy barrier and luminescence behavior of heterometallic trinuclear linear [M^{II}-Ln^{III}-M^{II}] (Ln^{III} = Gd, Tb, Dy; M^{II} = Mg/Zn) complexes by change from divalent paramagnetic to diamagnetic metal ions. *Chem. Eur. J.*, **2015**, 21, 6449-6464. DOI: 10.1002/chem.201406666
6. M. Fondo, A. M. García-Deibe, N. Ocampo, J. Sanmartín and M. R. Bermejo. Influence of some reaction conditions on the obtaining of tetra- and dinuclear zinc complexes of some Schiff bases derived from 2,6-diformyl-4-alkyl-phenols. *Polyhedron*, **2008**, 27, 2585-2594. DOI: 10.1016/j.poly.2008.05.016.
7. (a) S. R. Meech and D. *J.* Philips. Photophysics of some common fluorescence standards. *Photochem.*, **1983**, 23, 193-217. DOI: 10.1016/0047-2670(83)80061-6; (b) M. Montalti, A. Credi, L. Prodi and M. T. Gandolfi, *Handbook of Photochemistry*, 3rd ed.; CRC, Taylor & Francis Group: Boca Raton, New York, NY, 2006.
8. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Ed. John Wiley & Sons, New York, 1997.
9. (a) M. Llunell, D. Casanova, J. Cirera, J. M. Bofill, P. Alemany, S. Alvarez, M. Pinsky and D. Avnir, *D. SHAPE v1.1b*, Barcelona, 2005; (b) A. Ruiz-Martínez, D. Casanova and S. Alvarez. Polyhedral Structures with an Odd Number of Vertices: Nine-Coordinate Metal Compounds. *Chem. Eur. J.*, 2008, **14**, 1291-1303. doi: 10.1002/chem.200701137; (c) M. Llunell, D. Casanova, J. Cirera, P. Alemany and S. Alvarez, SHAPE: *Program for the stereochemical analysis of molecular fragments by means of continuous shape measures and associated tools*, University of Barcelona, Barcelona, Spain, 2010.
10. M. Fondo, J. Corredoira-Vázquez, A. M. García-Deibe, J. Sanmartín-Matalobos, J. M. Herrera and E. Colacio. Designing ligands to isolate ZnLn and Zn_2Ln complexes: field-induced single-ion magnet behavior of the ZnDy, Zn_2Dy, and Zn_2Er analogues. *Inorg. Chem.*, **2017**, 56, 5646-5656. DOI: 10.1021/acs.inorgchem.7b00165.
11. A. Zabala-Lekuona, J. Cepeda, I. Oyarzabal, A. Rodriguez-Dieguez, J. A. Garcia, J. M. Seco and E. Colacio. Rational design of triple-bridged dinuclear ZnIILnIII-based complexes: a structural, magnetic and luminescence study. *CrystEngComm*, **2017**, 19**,** 256-264. DOI: 10.1039/C6CE02240E.
12. R. C. Howell, K. V. N. Spence, I. A. Kahwa and D. J. Williams. Structure and luminescence of the neutral dinuclear lanthanide(III) complexes [{Ln(api)}$_2$] {H_3api = (2-hydroxyphenyl)-1,3-bis[4-(2-hydroxyphenyl)-3-azabut-3-enyl]-1,3-imidazolidine}. *J. Chem. Soc., Dalton Trans.*, **1998**, 2727-2734. DOI: 10.1039/A804056G.
13. E. Pretsch, T. Clerc, J. Seibl and W. Simon, *Tables of spectral data for structure determination of organic compounds*, Springer-Verlag, Berlin, 2nd edn., 1989.
14. J. Seixas de Melo, J. Pina, F. Pina, C. Lodeiro, A. J. Parola, J. C. Lima, M. T. Albelda, M. P. Clares, E. García-España and C. J. Soriano. Transport-limited recombination of photocarriers in dye-sensitized nanocrystalline TiO2 solar cells. *Phys. Chem. A*, **2003**, 107, 11307-11315. DOI: 10.1021/jp0304475.
15. C. Núñez, E. Oliveira, L. Giestas, L. Valencia, A. Macías, J. C. Lima, R. Bastida and C. Lodeiro. Synthesis, spectroscopic, structural and complexation studies of a new tetra-naphthylmethylene pendant-armed macrocyclic ligand. *Inorg. Chim. Acta*, **2008**, 361, 2183-2194. DOI: 10.1016/j.ica.2007.11.024.