



## Optical properties of binuclear zinc (II) macrocyclic complexes derived from 4-methyl-2,6-diformylphenol and 1,2-diaminobenzene

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### ABSTRACT

In this work, we present the synthesis and optical study of the binuclear zinc(II) macrocyclic complexes, derived from 4-methyl-2,6-diformylphenol and 1,2-diaminobenzene (H<sub>2</sub>L). Two zinc macrocyclic complexes with different anions were prepared and characterized: [Zn<sub>2</sub>Cl<sub>2</sub>] $\cdot$ H<sub>2</sub>O (**1**) and [Zn<sub>2</sub>L](NO<sub>3</sub>)<sub>2</sub> (**2**).

The complexes are emissive, both in the solid state and in solution at room temperature. Spectroscopic properties of the macrocyclic complexes were investigated using stationary and time resolved methods in solutions of dimethylsulfoxide (DMSO), and in solid state. DMSO solutions show two emission bands centered at 480 and 521 nm for complex (**1**), and at 527 nm with a shoulder at 480 nm for (**2**). The emission spectra of these compounds in solid state show a red shifted band, presenting the maxima at 565 nm for (**1**) and 575 nm for (**2**). The emission lifetimes for these compounds are very short, viz. 650 and 480 ps for macrocycles (**1**) and (**2**), respectively.

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### 1. Introduction

The rich chemistry of complexes of dicompartmental ligands binding two metals has been applied to the investigation of magnetic exchange interactions between these centres, the stabilisation of mixed valence species and the activation of small molecules [1–7]. Besides, macrocycles derived from 4-methyl-2,6-diformylphenol and 1,2-diaminobenzene are studied since they show a high electronic delocalisation due to the planar structure that they present.

Luminescent metal complexes are gaining significant attention as sensors and probes in view of their applications in light emitting diodes (LEDs), biomedical analyses, fluorescence imaging and possibly in cancer phototherapy [8]. For example, metal complexes are promising luminescent materials for their applications as LEDs, owing to their ability to enhance, shift and quench luminescent emission of organic ligands by metal coordination. Many polynuclear zinc(II) compounds exhibit promising luminescent properties, especially those with ligands containing heteroaromatic rings, since the metal centres enhance the fluorescence of the aromatic moieties. Therefore, they are currently of interest in the development of fluorescent materials [9–11].

The zinc(II) macrocyclic complexes, derived from 4-methyl-2,6-diformylphenol and 1,2-diaminobenzene were prepared and characterized. We herein report an optical study of the binuclear macrocyclic compounds shown in Scheme 1.

### 2. Experimental

The reagents and solvents employed were used as received without further purification. Elemental analyses (C,H,N) were determined with a Perkin–Elmer elemental analyzer. The percentage of zinc was determined by atomic absorption with a Perkin–Elmer equipment, model 1100B. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm<sup>-1</sup> on a Bruker-IFS 28 spectrophotometer. The low frequency region, from 400–200 cm<sup>-1</sup>, was recorded on a Bruker Vector 22 spectrophotometer. Micro-Raman spectra for (**1**) and (**2**) were recorded on Renishaw systems 2000, using laser excitation at 785 nm. All measurements were made in a back-scattering geometry, using a spatial resolution of 1 μm<sup>2</sup>; the laser beam had circular polarization and laser powers of 10%. Single point spectra were recorded with 10 s accumulation times. In order to reduce the high fluorescence showed by the zinc macrocyclic complexes, the sample was deposited over a glass covered with gold nanoparticles in terms to get an enhanced Raman signal. The diffuse reflectance UV–Vis spectra were recorded using a Perkin–Elmer Lambda 20 UV–Vis spectrophotometer equipped with a Labsphere RSA-PE-20 diffuse reflectance

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accessory. Magnesium oxide was used as reference and the spectra were recorded in the range 1.5–6.0 eV at room temperature. Reflectance measurements were converted to absorption spectra using the Kubelka–Munk function  $F(R_\infty)$ . Solution absorption spectra were recorded on a Unicam-UV3 spectrophotometer.

Solution fluorescence spectra in DMSO were performed on a Spex Fluorolog 2τ2 spectrophotometer. Fluorescence lifetime measurements were performed using Time-Correlated Single Photon Counting (TCSPC) technique [12]. Approximately 100 femtosecond excitation pulses with tunable wavelength (360–470 nm) were generated by doubling the fundamental frequency of a mode-locked Ti:sapphire laser (Spectraphysics Tsunami) pulses in β-barium borate crystal. The laser repetition rate was reduced to 2 MHz by a home-made acousto-optical pulse picker in order to avoid saturation of the chromophore. TCSPC system is equipped with an ultrafast microchannel plate photomultiplier tube detector (Hamamatsu R3809U-51) and an electronics board (Becker and Hickl SPC-630), and has instrument response time less than 50 ps. Triggering signal for the TCSPC board was generated by sending a small fraction of the laser beam onto a fast (400 MHz bandwidth) Si photodiode (Thorlabs Inc.). Fluorescence signal was dispersed in Acton Research SPC-300 monochromator after passing through a pump blocking, long wavelength-pass, autofluorescence-free, interference filter (Omega Filters, ALP series). The monochromator is equipped with a CCD camera (Roper Scientific PIXIS-400B) allowing for monitoring of the fluorescence spectrum. Fluorescence transients were not deconvolved with the instrument response function since their characteristic time-constants were much longer than the width of the system response to the excitation pulse.

Emission spectra in solid state at room temperature were recorded using a Perkin–Elmer LS55 UV/Visible spectrometer. The solid sample were prepared by mixing the complexes with an inert silicone, and deposited on a quartz sample slice.

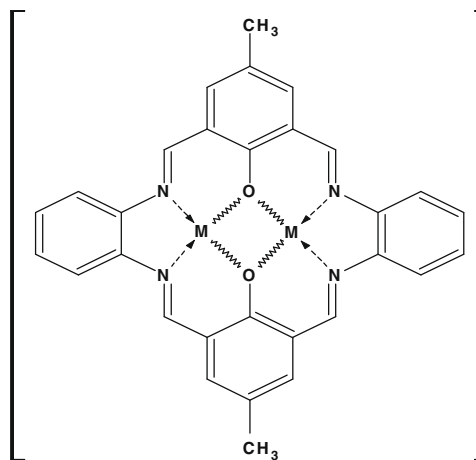
Thermogravimetric analyses (TGA) were performed from room temperature to 800 °C, under argon with a heating rate of 10 °C min<sup>-1</sup>, using a Netzsch thermogravimetric analyzer, model 209-F1.

### 2.1. Synthesis of the partially reduced macrocyclic ligand derived from 4-methyl-2,6-diformylphenol and 1,2-diaminobenzene. ( $H_2L'$ : 7,16-dihydroxy-6',13'-dimethyl-1,4,10,13-tetraaza-tetrabenzo[2,3-a;6,7,8-f,a;11,12-a;15,16,17-f,a]cyclooctadeca-2,6,9,11,15,18-hexaene)

The template reaction, using  $Mg^{2+}$  or  $H^+$  ions as template agents, was done by reacting under reflux 2-hydroxy-5-methyl-1,3-benzenedicarbaldehyde with 1,2-diaminobenzene in boiling methanol. The isolated macrocyclic ligand ( $H_2L'$ ) was the partially reduced amino-imine compound, which was characterized by elemental analyses, <sup>1</sup>H NMR and FT-IR spectroscopy. The tetraimine ligand was not obtained with these synthetic conditions. *Anal. Calc* for  $H_2L'$  ( $C_{30}H_{28}N_4O_2$ ): C, 75.61; N, 11.76; H, 5.92. *Found*: C, 74.55; N, 11.61; H, 5.97%. <sup>1</sup>H NMR: s: 2.31 (6H, methyl); d: 4.42 (4H, methylene); s: 6.32 (2H, amine); m: 6.75–7.27 (12H, aromatic); s: 8.60 (2H, azomethine); s: 13.5 ppm (2H, OH). FT-IR:  $\nu_{N-H}$  = 3406 cm<sup>-1</sup>;  $\nu_{C=N}$  = 1617 cm<sup>-1</sup>.

### 2.2. Synthesis of $M_2LX_2 \cdot nH_2O$ ( $H_2L'$ : 7,16-dihydroxy-6',13'-dimethyl-1,4,10,13-tetraaza-tetrabenzo[2,3-a;6,7,8-f,a;11,12-a;15,16,17-f,a]cyclooctadeca-2,4,6,9,11,13,15,18-octaene); $M = Zn(II)$ , $X = Cl$ (**1**); $X = NO_3^-$ (**2**))

The synthesis of the zinc(II) tetraimine macrocyclic compounds was achieved in a step by step synthesis. Initially 2-hydroxy-5-methyl-1,3-benzenedicarbaldehyde (1.84 mmol, 0.300 g) was refluxed for 3 h with  $MX_2 \cdot nH_2O$  (1.84 mmol, 0.250 g for  $X = Cl^-$  or 0.480 g for  $X = NO_3^-$ ) in 2-propanol (40 mL), under an inert atmo-



**1 = Zn(II), Cl<sup>-</sup> 2 = Zn(II), NO<sub>3</sub><sup>-</sup>**

**Scheme 1.**

sphere ( $N_2$ ). The dinuclear metal aldehyde complex was formed, and was used as the precursor for the formation of the macrocyclic compound. 1,2-Diaminobenzene (1.84 mmol, 0.199 g) dissolved in 2-propanol (10 mL) was added drop by drop to the 2-propanol solution of the precursor, and was left at ambient temperature with stirring for 90 min.; the macrocyclic complex  $M_2LX_2 \cdot nH_2O$  precipitated as a brick-red solid. The solid was first washed with acetone and then with methanol, and the purity was verified by column chromatography. *Anal. Calc.* for (**1**) ( $C_{30}H_{24}N_4O_3Cl_2Zn_2$ ): C, 52.20; N, 8.12; H, 3.50; Zn, 18.95. *Found*: C, 52.6; N, 8.0; H, 3.7, Zn, 18.6%. *Anal. Calc.* for (**2**) ( $C_{30}H_{22}N_6O_8Zn_2$ ): C, 49.68; N, 11.59; H, 3.06; Zn, 18.04. *Found*: C, 49.8; N, 11.2; H, 3.2; Zn, 18.1%.

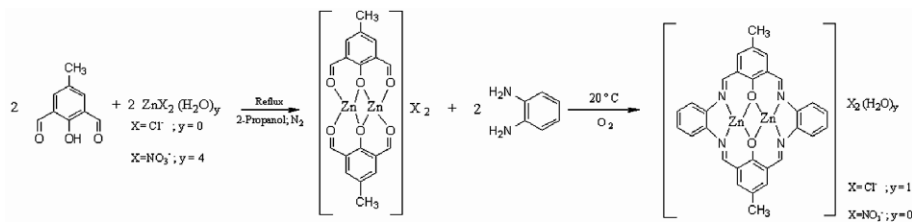
The zinc(II) macrocyclic complexes (**1**) and (**2**) were also synthesized by an alternative synthetic route, which involves a solvent free mechanochemical synthesis. Complexes (**1**) and (**2**) were obtained without any applied heating. The metal salts (2 mmol) and 2-hydroxy-5-methyl-1,3-benzenedicarbaldehyde (2 mmol) were mixed by grinding in a porcelain mortar for 10 min, till a strong yellow color of the solid was observed. Later, 1,2-diaminobenzene (2 mmol) was added to the reacting mixture, and this was also ground; a brick-red solid was obtained within a few minutes. The analyses gave the same percentage values, and the infrared spectra presented the same absorption bands as those obtained for the complexes synthesized by the traditional procedure.

## 3. Results and discussion

### 3.1. Syntheses

The reaction of dicarbonyl compounds with diamines is much more complicated than the simple Schiff condensation of mono carbonyl compounds with amines [13]. Moreover, the Schiff condensation with macrocyclic closure is usually obtained by a template reaction, in which metal ions [14] or anions of protic acids [15] are used as template agents. The introduction of a template agent is the most reliable method to prevent the formation of oligomers, and assures the presence of the macrocyclic compound.

In order to avoid the abnormal condensation of 2,6-diformyl-4-methylphenol with 1,2-diaminobenzene, accompanied with the reduction of two *trans* C=N double bonds of the macrocycle [16], the aldehyde dinuclear complex was formed, before the diamine was added. The final template formation of the dinuclear zinc(II) macrocyclic complexes was done in the presence of oxygen, in order to avoid any further reduction process (see Scheme 2).



Scheme 2.

### 3.2. Thermogravimetric analyses

Thermal behaviour of the  $[\text{Zn}_2\text{LCl}_2]\cdot\text{H}_2\text{O}$  macrocyclic complex (**1**) shows a weight loss in several steps. At 115 °C an experimental weight loss of 2.6% is found and it can be associated with the weight loss of one water molecule (calculated value is 2.6%). The temperature at which the water molecule is lost in (**1**) permits to infer that it is not coordinated to the metal ion. There is a second weight loss at 335 °C which corresponds to 9.8%; this correlates well with the calculated value for the loss of two chlorides, with a weight loss of 10%. Above this temperature a gradual loss of weight is recorded, associated with the thermal decomposition of the sample (Fig. 1Sa).

In the case of the nitrate complex  $[\text{Zn}_2\text{L}](\text{NO}_3)_2$  (**2**) the thermal behaviour is characterized by a weight loss at 430 °C, corresponding to a 15.9%, which correlates with the loss of two nitrate ions (calculated value is 17.1%). The weight loss above 430 °C is associated with the thermal decomposition of the sample (Fig. 1Sb).

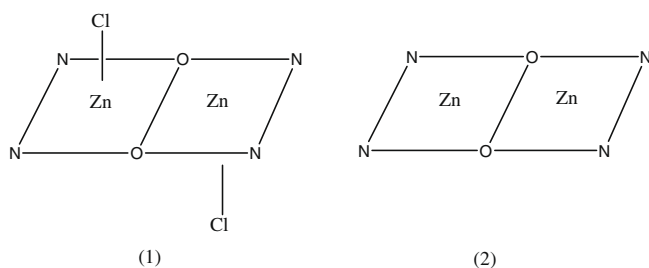
No single crystals of compounds (**1**) and (**2**), suitable for X-ray diffraction were obtained. Due to the low solubility of these macrocyclic compounds in most of the organic solvents, the  $^1\text{H}$  NMR spectra were recorded in  $\text{DMSO}-d_6$ . However, the recorded spectra presented low resolution, which precluded the assignment of the signals. Therefore the proposed structures of the two complexes are written considering the above information. The proposed geometry around the zinc ion can be defined as square base pyramid for (**1**) and square planar for (**2**) (see Scheme 3).

Literature data shows that for zinc, the most common coordination numbers are five and six. Several  $\text{N}_2\text{O}_2\text{X}$  pentacoordinated zinc(II) complexes are found in the literature, where the apical position of the first coordination sphere is occupied by a chlorine atom [17–20]. An example of a pentacoordinated zinc(II) species with a monodentate nitrate ligand is given by Tandon et al. [21] Even though the zinc square planar compounds are scarce, literature data show that square planar zinc(II) complexes can be found for Schiff base species with a  $\text{N}_2\text{O}_2$  first coordination sphere [22–25].

### 3.3. Spectroscopy

#### 3.3.1. Infrared and Raman spectra

Fig. 1 shows the infrared and Raman spectra for (**1**) and (**2**). The IR spectra of both macrocyclic complexes show the fundamental



Scheme 3.

vibration bands of the ligand; the stretching bands corresponding to  $\nu\text{C}=\text{N}$  appear at 1623 and 1618  $\text{cm}^{-1}$ , the stretching vibration of  $\nu\text{C}=\text{C}$  at 1544 and 1535  $\text{cm}^{-1}$ ,  $\nu\text{C}-\text{O}_{\text{ph}}$  at 1330 and 1298  $\text{cm}^{-1}$ , and the bending vibration of aromatic rings  $\nu\text{C}-\text{H}$  at 755 and 758  $\text{cm}^{-1}$  for (**1**) and (**2**), respectively [26]. Furthermore, the macrocyclic complex  $[\text{Zn}_2\text{L}](\text{NO}_3)_2$  presents a sharp and intense band at 1384  $\text{cm}^{-1}$ , which corresponds to a zinc ion, the infrared spectrum presents an absorption band at ca. 1750  $\text{cm}^{-1}$ , band which is absent in the spectrum of the studied macrocyclic complex, suggesting the ionic nature of the nitrate ion.

On the other hand, the absence in the spectrum of the band around 1700  $\text{cm}^{-1}$ , characteristic of the carbonyl group indicates the formation of the macrocyclic complex [27], which is in agree-

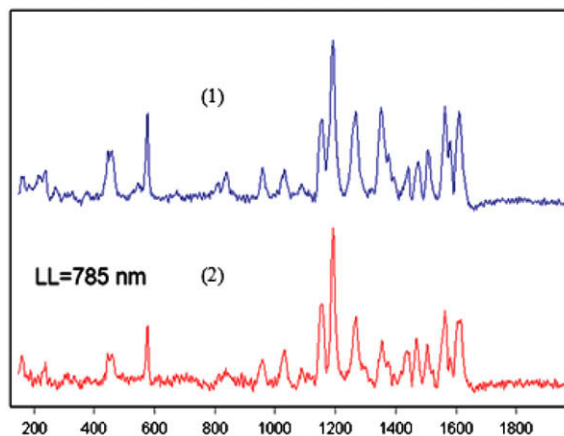
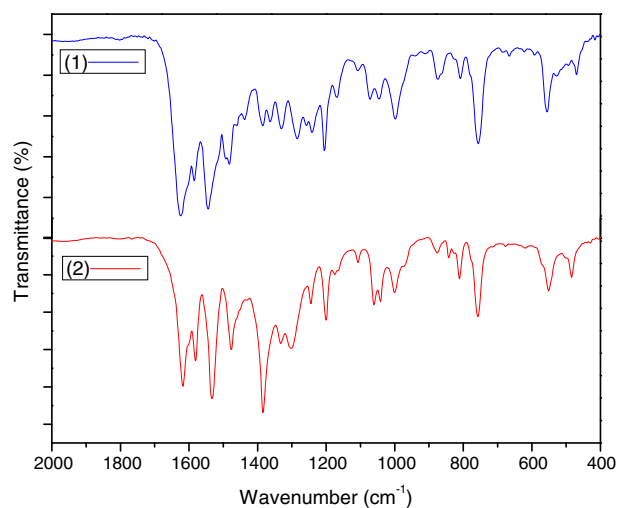


Fig. 1. Above: FT-IR Spectra of macrocyclic complexes,  $[\text{Zn}_2\text{LCl}_2]\cdot\text{H}_2\text{O}$  (**1**),  $[\text{Zn}_2\text{L}](\text{NO}_3)_2$  (**2**); below: Raman spectra,  $[\text{Zn}_2\text{LCl}_2]\cdot\text{H}_2\text{O}$  (**1**) and  $[\text{Zn}_2\text{L}](\text{NO}_3)_2$  (**2**).

ment with similar published data for these types of macrocyclic complexes.

Micro-Raman measurements are shown in Table 1. Characteristic fundamental vibrational modes observed in the Raman spectrum between 1000 and 1600  $\text{cm}^{-1}$  are frequently used to study morphological structure. The measured samples show the typical C–H bending, C=C ring stretching and C=N bands for all complexes in this region, confirming the FT-IR assignments. Between 200 and 600  $\text{cm}^{-1}$ , Zn–O, Zn–N stretching bands and some macrocycle and ring deformations appear, which are not well defined in the FT-IR spectra. Complex (1) presents a band at 285  $\text{cm}^{-1}$  which can be assigned to the M–Cl stretching mode, while in the spectrum of complex (2) this band is absent [28,29].

### 3.3.2. Electronic spectra

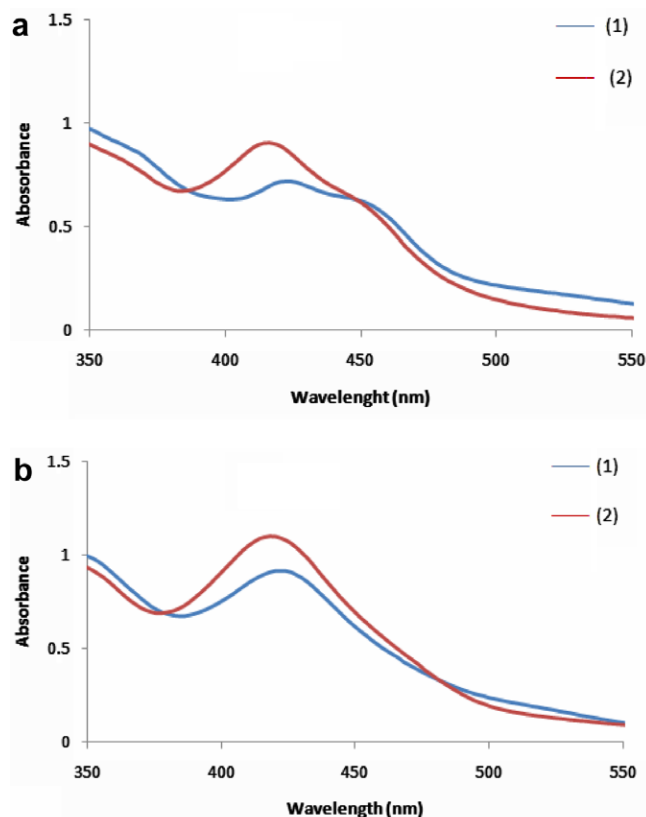
The visible spectra of macrocyclic compounds (1) and (2) are depicted in Fig. 2. The absorption spectra of these dinuclear compounds in pure dimethylsulfoxide solution show two transitions at 422 nm ( $1.7 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ) and 450 nm ( $1.5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ) for (1) and 416 nm ( $2.9 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ) and 450 nm ( $2.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ) for (2) in the visible region (Fig. 2a). The absorption bands, centred approximately at 420 and 450 nm for the zinc complexes may be assigned to the spin allowed MLCT  $d \rightarrow \pi^*$  transition [26d], due to the relatively high extinction coefficient.

If the spectra are recorded in a mixture of DMSO:H<sub>2</sub>O (3:2), changes are observed in the shape of the spectra, reaching a similar pattern for both complexes (Fig. 2b). This effect can be attributed to a change in the first coordination sphere of the complex cations (Scheme 4). In DMSO solution it is possible to propose that the chloride ions are acting as ligands, inside of the first coordination sphere for (1), while the nitrate anions are simple counterions for (2) and do not form part of the first coordination sphere (Scheme 4a). When a mixture of DMSO:H<sub>2</sub>O is used, the water molecules are able to promote the substitution of the coordinated chloride ions, achieving both complexes a similar first coordination sphere (Scheme 4b).

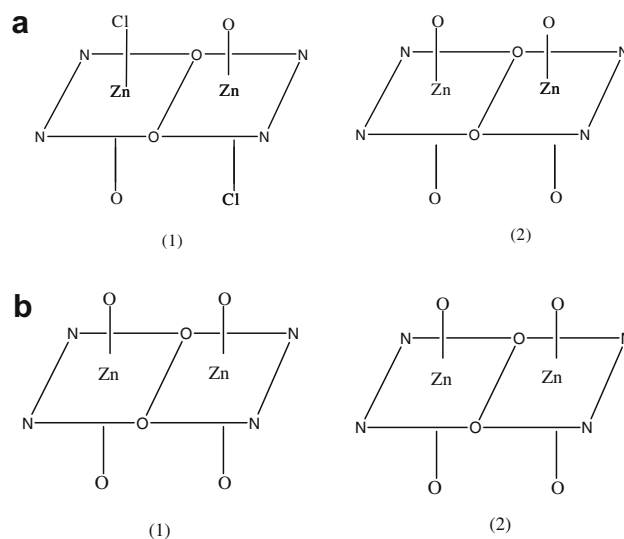
The diffuse reflectance spectrum for (1) is shown in Fig. S2. This  $[\text{Zn}_2\text{LCl}_2]\cdot\text{H}_2\text{O}$  macrocycle possesses an optical band gap of 2.1 eV, which is identical with the one corresponding to (2), and can be associated to the metal to ligand charge transfer process.

**Table 1**  
Assignment of Raman bands ( $\text{cm}^{-1}$ ) for  $[\text{Zn}_2\text{LCl}_2]\cdot\text{H}_2\text{O}$  (1).

Wavenumber	FWHM	Relative intensity	Assignment
173	17	13	Zn–O stretching
196	17	8	Zn–N stretching
230		Shoulder	Macrocycle deformation
250	10	8	Macrocycle deformation
285	20	8	Zn–Cl stretching
459	18	22	Ring deformation
474	16	19	Ring deformation
590	9	22	Ring deformation
824	23	9	C–H bending
854	20	15	C–H bending
975	15	15	C–H bending
1047	22	17	C–H bending
1106	18	6	C–H bending
1172	19	48	C–H bending
1209	22	100	Ring stretching + C–H bending
1284	27	72	Ring stretching + C–H bending
1371	19	36	Ring stretching
1388		Shoulder	Ring stretching
1459	17	16	Ring stretching
1494	17	22	C=N stretching
1529	17	27	C=N stretching
1585	19	54	C=C ring stretching
1603	9	15	C=C ring stretching



**Fig. 2.** UV-Vis Spectra of  $[\text{Zn}_2\text{LCl}_2]\cdot\text{H}_2\text{O}$  (1) and  $[\text{Zn}_2\text{L}](\text{NO}_3)_2$  (2) in (a) DMSO and (b) DMSO:H<sub>2</sub>O (3:2).



**Scheme 4.**

The complexes are emissive both in the solid state and in solution at room temperature (RT). Spectroscopic properties of the macrocyclic complexes were investigated using stationary and time resolved methods in solutions of dimethylsulfoxide (DMSO) and in solid state. When the DMSO solutions of the macrocyclic complexes (1) and (2) are irradiated with a wavelength of 422 and 420 nm, respectively, a green emission can be observed with bands centred at 480 and 521 nm for complex (1), and at 527 nm with a shoulder at 480 nm for (2) (Fig. 3). It can be observed that

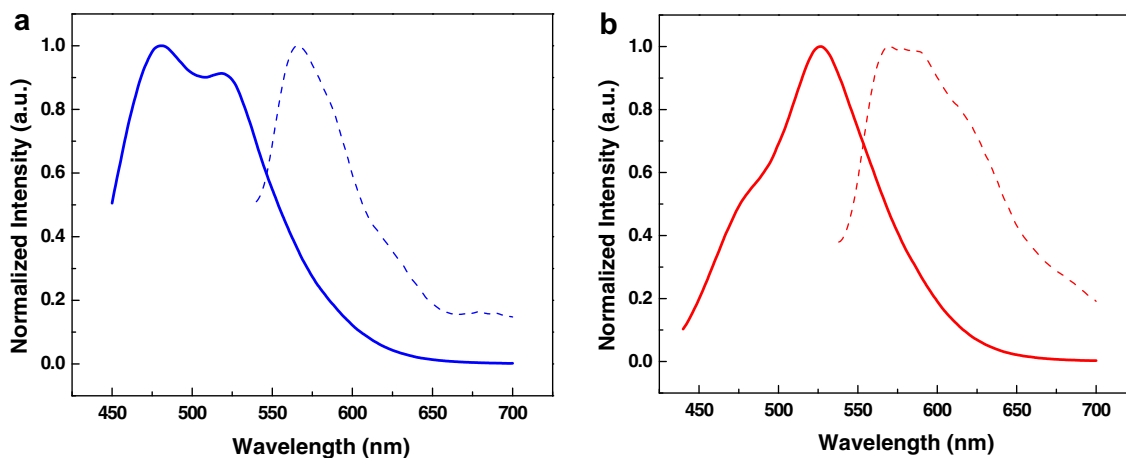


Fig. 3. Emission spectra of the macrocycles in DMSO solution (—) and solid state (----). (a)  $[\text{Zn}_2\text{LCl}_2]\cdot\text{H}_2\text{O}$  (1); (b)  $[\text{Zn}_2\text{L}](\text{NO}_3)_2$  (2).

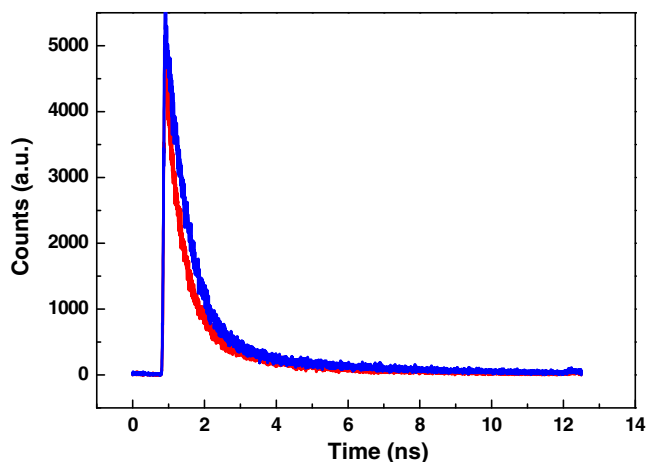


Fig. 4. Time resolved emission decay for  $[\text{Zn}_2\text{LCl}_2]\cdot\text{H}_2\text{O}$ , (1) (blue line) and  $[\text{Zn}_2\text{L}](\text{NO}_3)_2$ , (2) (red line) in DMSO solution at 545 and 550 nm, respectively, following excitation at 425 nm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

macrocyclic complex (1) shows the highest energy of emission. The fluorescent emission may originate from the metal to ligand emission excited state. The emission is broad and structureless, which rules out a ligand centred nature of the emission, which would induce prominent vibrational structure, and makes it consistent with a charge transfer nature of the excited state [30].

The solid-state photoluminescent spectra of the macrocyclic complexes (1) and (2) are depicted in Fig. 3. The emission spectra of these compounds in solid state compared with those in DMSO solutions show a red shifted band at 565 nm (1) and 575 nm (2). Red shifting of emission maxima can be observed for most fluorescent compounds in the solid state, probably due to  $\pi$ - $\pi$  stacking of the aromatic rings in the molecules [31]. Comparing the solution with the solid emission spectra, it is possible to infer that the solvent destroys the  $\pi$ - $\pi$  interactions, and thus the energy of the transition is increased in solution.

Time-resolved luminescent measurements allowed us to follow the intensity of the emission of the macrocycle after a laser excitation pulse at 425 nm. Fig. 4 shows the monoexponential intensity decays for the emission of the zinc macrocycles. The emission wavelengths used were chosen in order to minimize the signal-noise ratio. The emission lifetimes for these compounds are very short, viz. 650 and 480 ps for macrocycles (1) and (2), respectively.

The lifetime difference could be explained in terms of the different coordination sphere for both macrocycles (see Scheme 4). Longer lifetimes have been reported for similar binuclear zinc macrocycles; however the involved transitions were assigned to a ligand centred emission [32] or from an excited state centred on the acceptor in a donor-acceptor system [33].

#### 4. Conclusions

Two zinc macrocyclic complexes with different anions were prepared and characterized:  $[\text{Zn}_2\text{LCl}_2]\cdot\text{H}_2\text{O}$  (1) and  $[\text{Zn}_2\text{L}](\text{NO}_3)_2$  (2).

The infrared, Raman and electronic spectroscopic data were used to define the coordination of the anions; the chloride ions inside the first coordination sphere for (1) and the nitrate ions as simple counteranions for (2). The influence of the first coordination sphere on the fluorescent properties was shown to be important, being the emission lifetime for (1) longer than for (2).

Due to fact that the title compounds present emission at 500 nm, being thermally stable and insoluble in several solvents, they might be promising candidates for further applications as green light emitting materials.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2009.04.027.

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