UNIVERSITY OF BUCHAREST
FACULTY OF CHEMISTRY
DOCTORAL SCHOOL IN CHEMISTRY

LUMINESCENT LIQUID CRYSTALS BASED ON LANTHANIDE COMPLEXES

- Ph.D. THESIS SUMMARY-

PhD Student:
Florentina-Laura BADEA (CHIRIAC)

Thesis supervisor
Conf. dr. habil. Viorel CÎRCU

2019

Luminescent liquid crystals based on lanthanide complexes

TABLE OF CONTENTS[1]

(As in Ph. D. Thesis)

Part I
LITERATURE SURVEY

Part II
ORIGINAL CONTRIBUTIONS

---

[1] *Numbering of figures, tables and bibliographic references is the one from the Ph.D thesis*

Summary

The PhD thesis "Luminescent liquid crystals based on lanthanide complexes" describes the synthesis and characterization of new classes of lanthanide complexes, which have liquid crystals and luminescent properties, known as lanthanidomesogens. The interest given to these materials is due to the special properties obtained by combining the properties of organic liquid crystals (fluidity, anisotropy, polymorphism) with those of lanthanide ions (luminescence), their main applicability is in the field of liquid crystal displays (LCDs).

The main objectives of the doctoral thesis were:

- Synthesis of new classes of ligands and pyridinium salts and tuning their mesogenic properties by using different mesogenic groups in the ligand structure;
- Structural characterization and confirmation of the ligands by various techniques such as ^{1}H-NMR and ^{13}C-NMR spectroscopy, IR spectroscopy, elemental analysis and thermogravimetric analysis;
- Synthesis of new classes of lanthanidomesogens using the new synthesized ligands and Eu^{3+}, Sm^{3+}, Tb^{3+} lanthanide ions as well as hybrid materials starting from pyridinium salts with the polyoxometalated macroanion $EuW_{10}O_{36}\cdot 32H_2O$ (EuW_{10});
- Structural confirmation of these compounds by IR spectroscopy, elemental and thermogravimetric analysis;
- Characterization of the mesogenic properties of ligands, pyridinium salts, lanthanide ion complexes and hybrid materials by differential scanning calorimetry (DSC), polarized optical microscopy (POM) and X-ray powder diffraction at different temperature.
- Characterization of the photophysical properties.

The Ph.D. thesis is structured in two parts: the first part dedicated to the literature survey, in which different classes of ligands used until now to obtain lanthanidomesogens are presented, and a second part in which the original contributions are presented.

Liquid crystals are materials that have similar properties with both liquids and solid crystalline materials. In a liquid crystal, the molecules can have as much fluidity as the liquids, but also a certain orientation of the molecules, just not as strict as in the case of molecular crystals. Lantanidomesogens can be defined as lanthanide complexes with liquid crystals properties or liquid crystals containing lanthanide ions (5). The way they are obtained follows the same pathway as for the organic liquid crystals, namely a rigid, anisotropic core with long flexible terminal chains. Incorporating a metal into an organic compound can lead to new design possibilities, which are not possible in the case of organic compounds (8). These compounds combine the unique properties of lanthanide ions (luminescence, paramagnetism) with those of liquid crystals (fluidity, anisotropy) leading to liquid crystals with coordination number higher than six, by introducing lanthanide ions into the liquid crystal matrix, the number of their coordination becoming 8 (associated with square or dodecahedron antiprism geometry) or 9 (associated with tripiramidated trigonal prism geometry or monopyramidated square antiprism).

The first part of this work is dedicated to a literature survey, focusing on the types of ligands used so far in obtaining lanthanidomesogens and the mesogenic and luminescent properties that the respective complexes exibit. The most employed ligands have been by far the Schiff bases. While ligands of this type had a nematic mesophase, the corresponding complexes had viscous mesophases, such as the SmA phase. (25, 29).

Another class of ligands ranked in the second place in the preference of the researchers looking for the synthesis of lanthanidomesogens, is that of the β-diketonate ligands (70). The first complex of this type was $[Eu(tta)_4]^-$ (tta- -tenoxifluoracetonat) with the imidazole cation with two cholesteryl groups linked by a long alkyl chain (73), which presented a monotropic chiral SmA phase (SmA *).

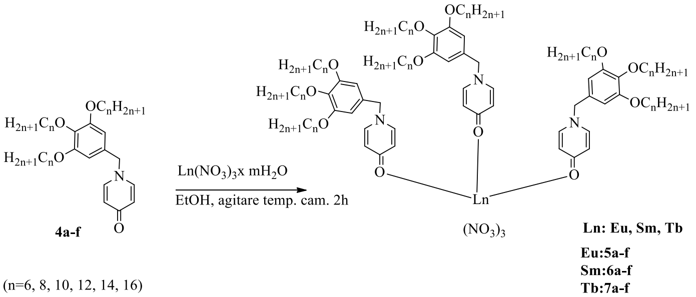
Other types of ligands used in the lanthanidomesogens synthesis are:

- β-enaminoketone ligands, which, although very similar in structure to Schiff bases, their corresponding lanthanide complexes were less studied (66, 67);
- bis(benzimidazolyl)pyridine ligands (90-92);
- phthalocyanine, lutetium complexes with substituted bis (phthalocyaninato) ligands were the first lanthanidomesogens with ligands of this type described in the literature (104);
- polyoxometalate compounds (128-136).

The second part of the thesis presents the original contributions in the field of lanthanidomesogens obtained with N-alkyl-4-pyridone ligands and it is structured in five chapters. The synthesis of lanthanidomesogens with N-alkyl-4-pyridone ligands is an unexplored frield so far; in the literature there are no reported complexes of lanthanides with liquid crystal properties obtained with this type of ligands. Two methods are known for the synthesis of lanthanidomesogens. The first one involves the separation of the coordination unit and the mesogenic group by long flexible alkyl chains, and the second method involves the preparation of the mesogenic ligands by increasing the number of aliphatic chains attached to the coordinating unit. 4-pyridone derivatives are known in the lanthanide's coordination chemistry as O-coordinate ligands, but the use of 4-hydroxypyridine is of particular interest because of the ability to form ligands with various mesogenic groups, alkylated to either the oxygen or nitrogen atom, thus obtaining N-substituted or O-substituted 4-pyridones. This particular feature allows the tuning of the liquid crystal properties of the ligands and, implicitly, of the corresponding lanthanidomesogens by introducing different mesogenic groups either to the oxygen atom ot to the nitrogen atom, or even allows them to be linked to both ends of the coordinating unit. These ligands have an important role both from the point of view of the mesogenic and luminescent properties of the lanthanide complexes, as these ligands play the antenna role, absorbing the light and transferring the excited energy to the emissive levels of the metal ions. The type of mesogenic group attached to the coordination group in question and the place where it is attached to the pyridine ring, leads either to thermotropic liquid crystals or ionic liquid crystals. In this thesis, the lanthanide ions used to obtain compounds with mesogenic properties were, on one hand, Eu^{3+}, Sm^{3+} and Tb^{3+} and, on the other hand, the polyoxometallate macroanion

$EuW_{10}O_{36}^{9-}$ due to their interesting luminescent properties, while the 4-pyridone ligands were obtained through both methods mentioned before.

The first chapter presents the synthesis and characterization of a new series of lanthanidomesogens with N-alkyl 4-pyridone ligands with 3,4,5-tri (alkyloxy) benzyl (n = 6, 8, 10, 12, 14 and 16 carbon atoms in the hydrocarbon chains, **4a-f**) and 3,5-di (alkoxy) benzyl (with 12 and 14 carbon atoms in the aliphatic chains, the compounds **11a** and **11b**) mesogenic groups.



Both the ligands **4a-f** and their coresponding complexes **5a-f**, **6a-f** and **7a-f** exibit liquid crystal properties. In the case of uncoordinated ligands, the study of their thermal behavior by DSC and POM led to the observation of an enantiotropic hexagonal columnar mesophase. This mesophase was first identified by the optical texture observed by POM and then confirmed by X-ray powder diffraction.

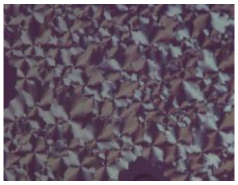


Figure 1.8. Image obtained by POM for ligand **4b** at 45^{o}C

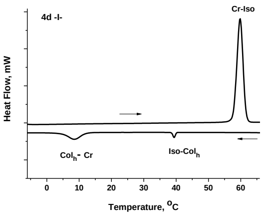


Figure 1.6. DSC curves recorded for ligand **4d**

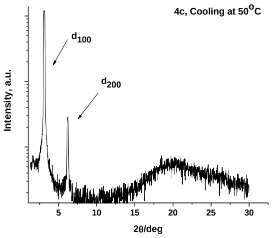


Figure 1.10. The XRD pattern for ligand **4c** recorded at cooling from the isotropic phase

The lanthanide complexes have been shown to form two types of mesophases, a lamellar and a columnar phase, over a large temperature range. It was observed that the evolution of the mesogenic properties is not influenced by the nature of the lanthanide ion but rather by the length of the alkyl chains. Depending on the mesogenic behavior, the complexes can be divided into three categories. Complexes with short aliphatic chains exhibited an enantiotropic, stable and reproducible mesophase. The identification of the mesophase by POM was not sufficient due to its weak birefringence. The diffractograms recorded for these complexes showed four equidistant Bragg diffraction peaks, in the small angles' region, in a ratio of 1:2:3:4, specific to a lamellar arrangement. Thus, the liquid crystal phase was attributed to the SmA mesophase.

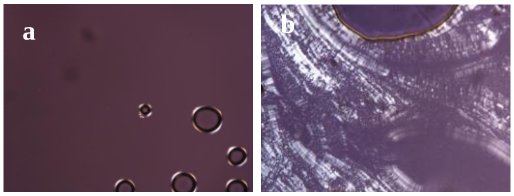


Figure 1.18. POM pictures for complex **5a** at 205ºC (a), and after “shearing” (b)

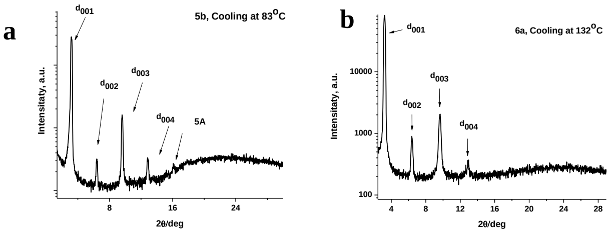


Figure 1.25. The XRD patterns recorded for complexes with short alkyl chains n=8 (a) and 6 (b) carbon atoms respectively

For compounds with intermediate carbon atoms in the aliphatic chain (n = 10), the formation of two liquid crystal phases with different textures was observed. These were initially identified by POM analysis, the correct attribution being supported by the data obtained from the X-ray powder diffraction, recorded at different temperatures.

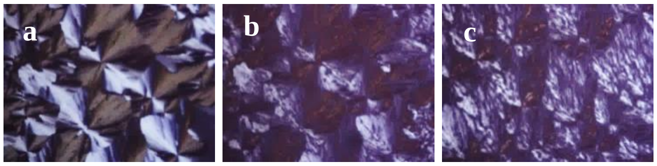


Figure 1.20. Modification of the optical texture of the complex **6c** at 180ºC (a), 120ºC (b) and 60ºC (c) on cooling from the isotropic state

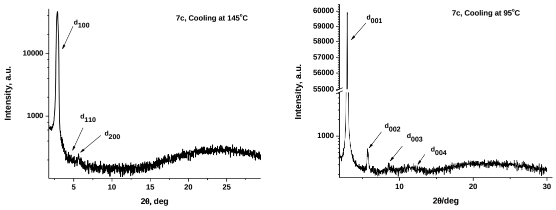


Figure 1.26. The XRD patterns recorded for complex **7c** at 145ºC (a) and 95ºC (b)

High temperature diffractograms showed three sharp Bragg diffraction peaks, in the ratio of 1:√3:2 specific for hexagonal columnar mesophase, while low temperature diffractograms showed 4 equidistant Bragg diffraction peaks, 1:2:3:4, characteristic of a lamellar arrangement. It can be said that these complexes exibit a SmA mesophase at low temperatures and a Col$_h$ mesophase at high temperatures. Complexes with long aliphatic chains (with 14 and 16 carbon atoms) have a single mesophase, the formation of which was observed both on heating and cooling the materials. This was identified on the characteristic texture observed by POM as the Col$_h$ mesophase, the correct attribution being confirmed by X-ray powder diffraction.

Figure 1.23. POM pictures for complex **5d** at 223ºC

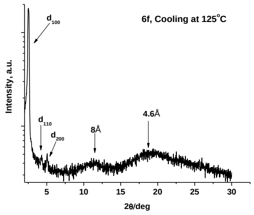


Figure 1.27. The XRD pattern recorded for the complexe **6f** at 83ºC

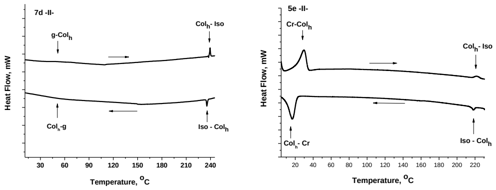


Figure 1.15. DSC curves recorded for complexes with higher numbers of carbon atoms (n = 12, 14) in the alkyl chain

Another feature of these classes of complexes was that the isotropic temperature does not depend on the size of the lanthanide ion, so that the lowest isotropic temperature was recorded for **5c** and

6c complexes, 189°C, while the highest temperature was measured for complex **6d**, at 238°C. All 18 complexes showed, in solid state, the characteristic emission of the corresponding lanthanide ions, when these complexes were excited with light in the UV region.

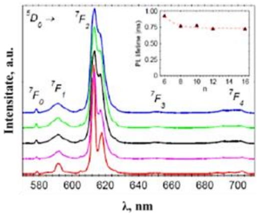


Figure 30. Emission spectra for complexes **5a-f** in solid state

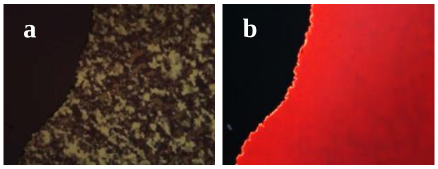


Figure 1.31. POM pictures for complex **5f**: hexagonal columnar mesophase at 55°C (a) and hexagonal columnar mesophase in UV light at 55°C (b)

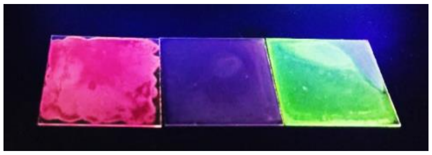
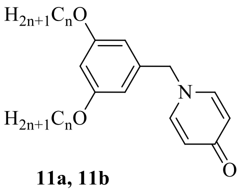


Figure 1.32. Images of complexes **5e**, **6e** and **7e** deposited on glass plate under UV light (254 nm)

The photoluminescence spectra indicate a clear influence of the carbon atoms number in the alkyl chains on the optical properties of the complexes. By analyzing the shape of the emission peaks, it was observed an enlargement of them and a reduction of the lifetimes by about 30% for the complexes with six carbon atoms in the alkyl chain compared to those with 16 carbon atoms in the aliphatic chains. In addition, the emissive properties were also preserved in the liquid crystal phase.

The decrease in the number of aliphatic chains of the ligand, from 3 to 2 alkyl chains, was found to have a major influence on the mesogenic properties in the case of 3,5-alkoxy-benzyl-pyridone ligands, leading to no liquid crystal properties.



11a, 11b

n=12, 14

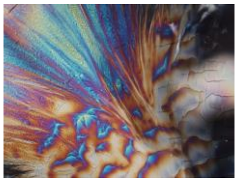


Figure 1.41. POM pictures for ligand **11b** at cooling at 42°C

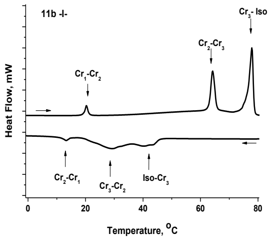
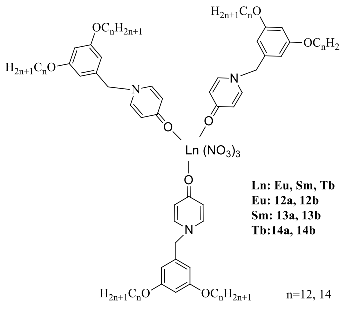


Figure 1.39. DSC curves recorded for ligand **11b**

For the lanthanide complexes having ligands containing two alkoxy chains, it was observed that, although the ligands do not have liquid crystal properties, the complexes **12**, **14** (n = 12, 14) a stable and reproducible enantiotropic mesophase was observed, following the DSC measurements. The phase was attributed to the Col$_h$ phase, based on its specific fan-shape texture, observed by optical microscopy in polarized light and subsequently confirmed by X-ray diffraction. Comparing the transition temperatures to the isotropic phase for the complexes with 3 aliphatic chains in the ligand structure with those containing two aliphatic chains, it was found that the decrease of the number of hydrocarbon chains leads to the decrease of the isotropic temperature of the complexes by over 50°C.



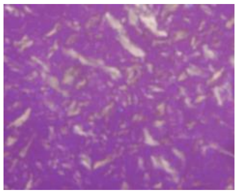


Figure 1.47. POM pictures for complex **12b** at coolig at 148°C

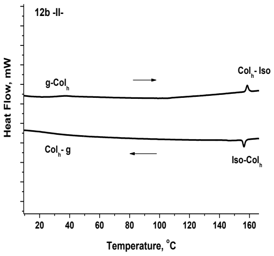
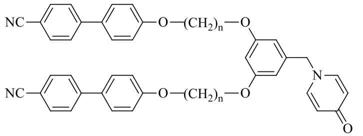


Figure 1.59. DSC curves recorded for ligand **12b**

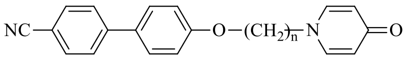
Moreover, it was observed that for complexes **12-14a,b**, the values of the isotropisation temperatures are influenced by both the length of the alkoxy chains and the size of the lanthanide ion. A special feature of these complexes was seen, the isotropic temperatures being higher for the complexes with 12 carbon atoms in the alkoxy chains, than for those complexes with 14 carbon atoms. Regarding the variation of this parameter with the modification of the lanthanide ion, the isotropisation temperature increases with the increasing of the lanthanide ion size (Tb <Eu <Sm), except complex 13b, for which the measured isotropic temperature was lower than that of the other two similar complexes **12b** and respectively **14b**.

The study of the emission spectra of such complexes revealed emission bands characteristic of each trivalent lanthanide ion. Although the emission intensity was lower than in the case of the 3-alkyl chain counterparts, by excitation with light in the UV domain, the red luminescence characteristic of the Eu^{3+} ion, the orange specific of the Sm^{3+} ion and the green characteristic of the Tb^3+ ion could be observed.

Chapter II presents the synthesis and characterization of 3,5-di(alkoxy)-cyanobiphenyl-pyridone and 4-(alkoxy)-cyanobiphenyl-pyridone ligands, in which the 4-pyridone coordinating unit is separated from the cyanobiphenyl mesogenic groups by alkyl chains spacers with different lengths (with 6, 9 and 10 carbon atoms in the aliphatic chain) as well as the synthesis of the corresponding complexes with Eu^{3+}, Sm^{3+} and Tb^{3+}. Both ligands and their related complexes had liquid crystal properties, with the exception of the 4-(hexyloxy)-cyanobiphenyl pyridone ligand and its corresponding complexes.



18a-c



22a-c

For ligands **18a-c** and **22a-c**, a nematic phase was observed, initially identified based on the typical Schlieren texture of the fluid, nematic phase, and subsequently confirmed by X-ray powder diffraction. The presence of a very weak peak at 2θ = 5° and a very wide peak at ~10-22Å are characteristic of the nematic phases. The clearing temperature was found to be higher for ligands with odd number of atoms in the aliphatic chain, for ligands **18a-c**, according to the even-odd effect.

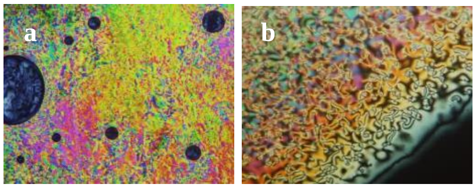


Figure 2.7. POM pictures for **18b** on cooling at 75°C (b) and **18c** la 80°C(c)

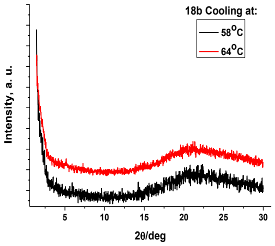
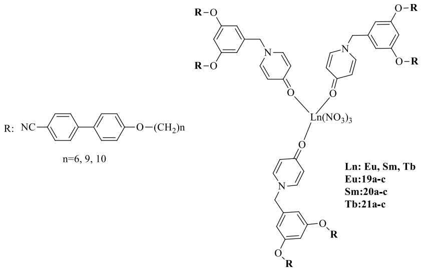


Figure 2.8. The XRD patterns recorded for ligand **18b** on cooling from the isotropic phase

In the case of complexes **19-21a-c**, the connection between the lanthanide ions and the organic liquid crystal led to an increase of the clearing temperature by about 12°Ccompared to the corresponding ligands.



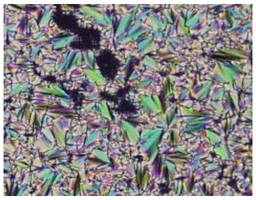


Figure 2.13. POM pictures for complex **19a** at 99°C

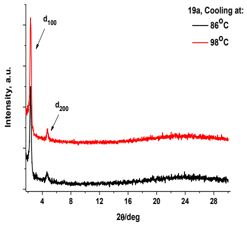
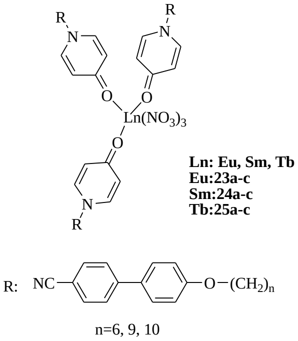


Figure 2.17. X-ray pattern diffraction for complexe **19a** obtained during cooling from the isotropic phase

The textures observed by POM led to the assignment of an enantiotropic SmA mesophase for this series of complexes. The recorded diffractograms presented, in the small angles region, 2 equidistant Bragg diffraction peaks, in the ratio of 1:2, this being an arrangement typical for lamellar phases. Similar to complexes with two cyanobiphenyl mesogenic groups in the ligand structure, complexes with a single cyanobiphenyl group also exhibited an enantiotropic SmA mesophase, except for complexes with six carbon atoms in the aliphatic chain, which did not exhibit liquid crystal properties. SmA mesophase was identified by POM, based on the focal-conical fan-shape texture, this attribution being supported by the data obtained after X-ray powder diffraction. The diffractograms recorded for complex **23b** showed, in the small angle's region, 3 equidistant Bragg diffraction peaks, in the ratio of 1:2:3, thus confirming the correct attribution of the SmA mesophase.



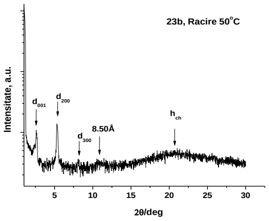


Figure 2.40. XRD pattern recorded upon cooling of complex **23b** from the isotropic phase

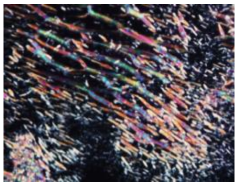


Figure 2.38. POM pictures for the complex **24c** at cooling at 111°C

In the case of **19-21a-c** complexes, the clearing temperature was strongly influenced by the parity of the alkoxy chain. Thus, the transition temperatures of the complexes with nine carbon atoms in the aliphatic chain were higher than for the complexes having alkyl chains with six and 10 carbon atoms.the clearing temperatures for complxes **23-25a-c** do not depend on the size of the lanthanide ion, but on the length of the aliphatic chain. Thus, it was found thet as the number of carbon atoms in the aliphatic chain increases, their isotropisation temperature increases no matterthe nature of the lanthanide ion. All the complexes proved to be emissive in solid state at room temperature.

Assessing the luminescent properties of the complexes, by recording the corresponding emission spectra, sharp emission bands were seen, characteristic of each trivalent lanthanide ion used. A particular feature was observed for the complexes of Sm^{3+} and Tb^{3+} ions with ligands 18a-c; in these cases, the emission spectra are dominated by the emission band of the ligand, their emission colour being light blue and not the typical orange-red for Sm^{3+} and green for Tb^{3+}. The complexes proved to be luminescent not only in solid state at room temperature, but also in the liquid crystal state.

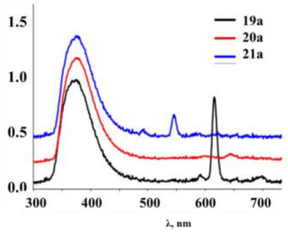


Figure 2.24. Emission spectra of complexes **19a**, **20a** and **21a** recorded in dichloromethane solution at 270 nm

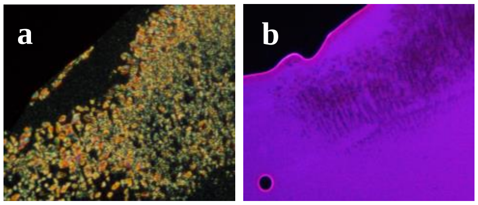
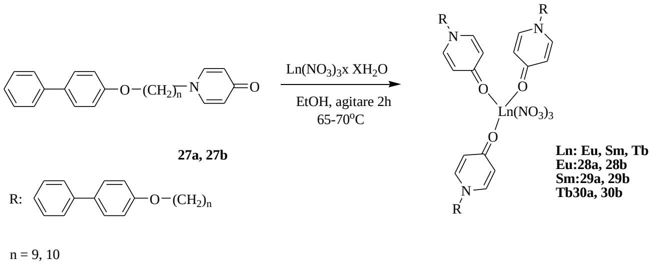


Figure 2.48. POM images of complex **23c** in the mesophase without UV (a) and under UV radiation (b)

As demonstrated in **Chapter II**, the number of cyanobiphenyl mesogenic groups plays a very important role in inducing liquid crystal properties for both ligands and complexes. The decrease of the number of cyanobiphenyl groups attached to the ligand from two, in the case of ligands **18a-c**, to a single cyanobiphenyl group for ligands **22a-c**, gave liquid crystal properties only for ligands with 9 and 10 carbon atoms in the aliphatic chain and their Eu^{3+}, Sm^{3+} and Tb^{3+} related complexes, while the compounds with shorter number of carbon atoms in the aliphatic chain (n = 6), did not exibit liquid crystal properties.

Thus, the main scope of the results presented in **Chapter III** was to demonstrate the effect of the nitrile group ge on the liquid crystal properties for both organic ligands, as well as for the corresponding complexes with trivalent lanthanide ions Eu^{3+}, Sm^{3+} and Tb^{3+}.



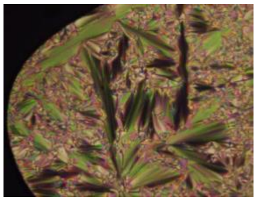


Figure 3.13. POM pictures for complexes **28b** at cooling at 159°C

The study of the thermal behavior of ligands **27a, b** by DSC and POM, revealed that the two ligands do not have liquid crystal properties. Despite the lack of mesogenic behaviour found for the organic ligands, the development of a mesophase was found on cooling the related complexes **28-30b** from the isotropic phase. The characteristic fan-shape texture of the SmA phase seen by MOP observations has led to its identification and attribution. Although reproducible, the crystallization process takes place almost immediately, as the temperature decreases.

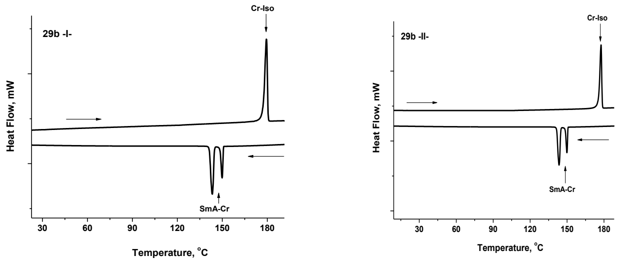


Figure 3.11. DSC curves recorded for complex **29b**

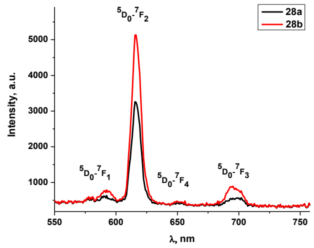
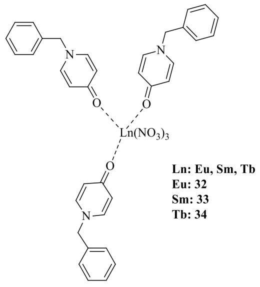


Figure 3.15. Emission spectra for complexes **28(a** and **b)**

In contrast to their counterparts with nitrile groups, for which a chain length with 9 carbon atoms was sufficient to induce liquid crystal properties to the complex, in the case of complexes with **27a, b** ligands a minimum length of 10 carbon atoms in the aliphatic chain is required. Comparing the clearing temperatures of **22a-c** ligands with those of **27a** and **27b** ligands, higher valueswith about 45°C were measured for the latter omplexes. The emission spectra of the six complexes have characteristic bands for the corresponding trivalent lanthanide ions, which are emissive in solid state at room temperature, showing typical emission for each lanthanide ion.

Chapter IV presents the synthesis and characterization of complexes similar to those discussed in the previous chapters, with the purpose to better understanding the coordination of lanthanide ions in the complexes presented in Chapters I-III. For complexes **32** and **34** single crystals were obtained and isolated. Single-crystal X-ray diffraction indicated that the lanthanide ions have coordination number 9, with six oxygen atoms from the three bidentate coordinated nitrogen groups and 3 oxygen atoms from the three ligand molecules.



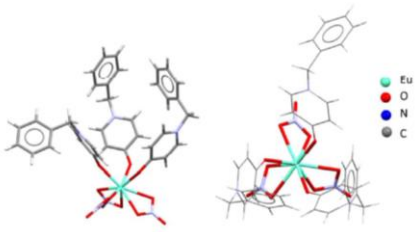


Figure 4.9. Two different perspectives of the molecular structure of the complex **32**

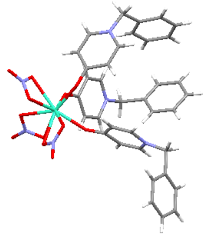
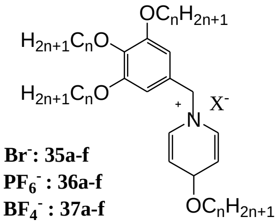


Figure 4.10. Molecular structure of the complex **34**

In **Chapter V**, a series of ionic liquid crystals were sintetized and investigated. These salts are based on pyridinium salts derived from 4-pyridones **4a-f** (**Chapter I.1.**) with various counterions: bromide (Br^-), tetrafluoroborate (BF_4^-), hexafluorophosphate (PF_6^-) and triflate ($CF_3SO_3^-$), including pyridinium salts with cyanobiphenyl groups and pyridinium salts with mixed mesogenic groups, as well as the polyoxometalate compounds of EuW_{10} coupled with these pyridinium salts. The pyridinium salts obtained from compounds **4a-f** were synthesized by alkylation with the corresponding bromoalkane. The obtained salts were involved in the methathesis reaction for the replacement of the Br^- ion with the three other counterions: PF_6^-, BF_4^- and $CF_3SO_3^-$.

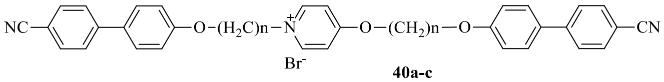


X^-= Br^-: 35a-f
PF_6^- : 36a-f
BF_4^- : 37a-f
$CF_3SO_3^-$: 38a-f

Figure 5.8. POM pictures for compound **35d** at cooling at 107°C (a), 61.7°C (b) and 61.5°C (c) (the transition between the two Col_h mesophases)

It was observed that only the pyridinium salts with the bromide counterion have liquid crystal properties, being, in fact, ionic liquid crystals. The mesophase observed for **35a-f** salts was an enantiotropic hexagonal columnar phase. Moreover, for the compounds with n = 12 and n = 14 carbon atoms, further cooling of the mesophase led to the development of a monotropic mesophases this time. The mesophases were identified as being hexagonal columnar phases, based on the textures seen by POM, the latter one having the same spherulitic texture as the previous one, but more ordered. The correct assignment of the mesophases was also supported by the X-ray studies performed on these compounds.

The pyridinium salts with two cyanobiphenyl mesogenic groups, **40a-c**, display a monotropic mesophase upon cooling from the isotropic phase, thus being considered ionic liquid crystals as indicated by DSC and POM studies. The mesophase observed by POM and identified as being a nematic phase, based on the characteristic textures, was subsequently confirmed by X-ray diffraction studies.



40a-c

n=6, 9, 10

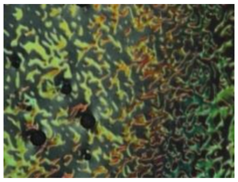
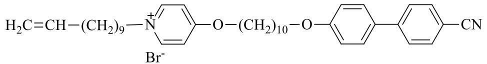
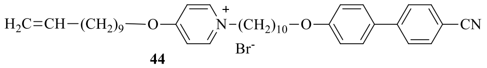


Figure 5.34. Image obtained by POM at cooling, for the pyridinium salt **40b** at 70°C

In the third part of this chapter, the role played by the alkylation of 4-hydroxypyridine by undecene, on one side, and decyloxy-4-cyanobiphenyl on the other side, in order to obtain pyridinium salts with liquid crystal properties and subsequently polyoxometalate compounds was investigated. The two groups were attached, at the same time, either to the nitrogen atom or to the oxygen atom.



43



44

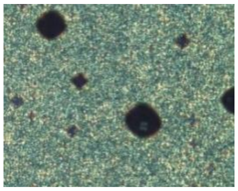


Figure 5.52. POM pictures at cooling for the pyridinium salt **44** at 40°C

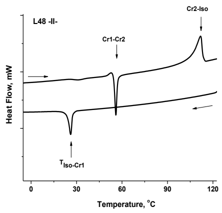
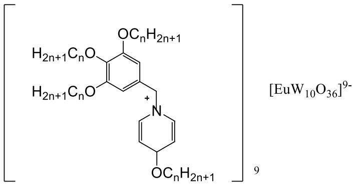


Figure 5.50. DSC curves recorded for pyridinium salt **44**

By DSC and POM studies, it was observed that the position in which the two mesogenic groups are attached to the 4-hydroxypyridine core has a critical effect on the liquid crystal properties of these pyridinium salts. For example, The pyridinium salt **43**, having the decyloxy-4-cyanobiphenyl group is linked to the oxygen atom and the undecene group to the nitrogen atom, has been shown to be an ionic liquid crystal, which presents upon cooling a very viscous SmA mesophase, while the pyridinium salt **44**, where the alkylation of the two groups was reversed, did not exhibit liquid crystal properties.

The **35a-f** pyridinium salts were employed for the preparation of hybrid materials with the polyoxometallate macroanion $EuW_{10}O_{36}\cdot 32H_2O$, giving products **39a-f**.



39a-f

Figure 5.22. POM picturs for the compound **39f** on cooling at 125°C

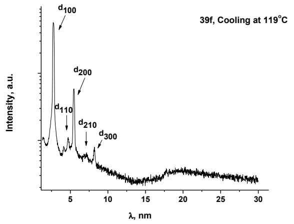
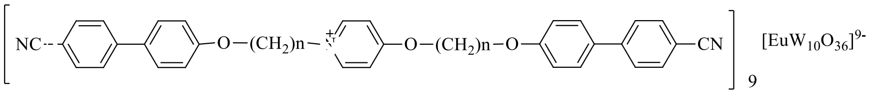


Figure 5.23. X-ray diffraction pattern recorded for compound **39f**

These products exhibit liquid crystal properties, showing a monotropic hexagonal columnar mesophase. POM and X-ray diffraction studies played an important role in highlighting the mesomorphic properties of the compounds, the transitions corresponding to the phase transformations being too wide to be seen on the DSC curves. The mesophase observed by POM was assigned to the Col_h phase, based on its characteristic spherulitic texture. The diffractograms related to these compounds confirmed the correct identification of the mesophase, showing Bragg diffraction peaks in the region of small angles, according to 1:√3:2:√7:3, specific to hexagonal columnar phases.

The hybrid materials **41a-c** showed, upon cooling from the isotropic phase, a reproducible enantiotropic SmA mesophase, the assignment was based on the characteristic textures.



41a-c

n=6, 9, 10

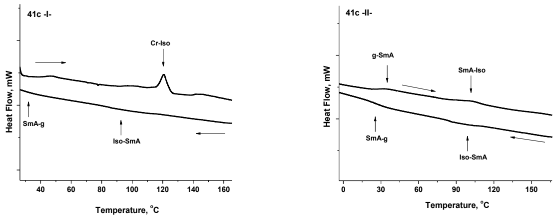


Figure 5.38. DSC curves recorded for compound **41c**

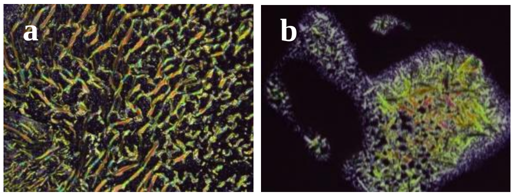
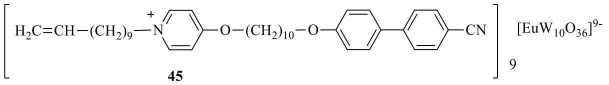
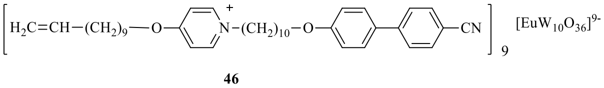


Figure 5.42. POM pictures at cooling for compound **41c** at 92^{o}C (a) and 70^{o}C (b)

For compounds **45** and **46**, the same behavior was observed as for their corresponding salts.



45



46

Compound **45** exibits a SmA mesophase on cooling the material from the isotropic phase, while compound **46** has no liquid crystal properties. For both the pyridinium salt **43** and the corresponding polyoxometalate compound **46**, the liquid crystal phase was identified and attributed based of the specific texture characteristic of the highly viscous SmA mesophase.

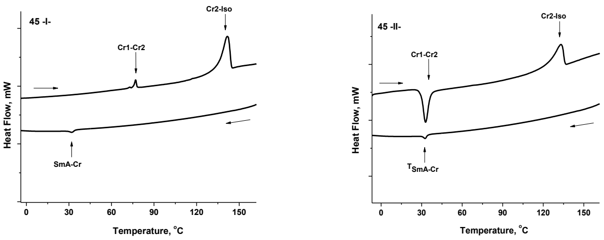


Figure 5.55. DSC curves recorded for compound **45**

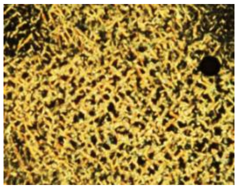


Figure 5.57. Image obtained by POM at cooling for the compound **45** at 45^{o}C

The pyridinium salts **35a-f** show a blue luminescence when they were irradiated with UV light, while the corresponding EuW$_{10}$ compounds have a red-orange light characteristic to the Eu^{3+}ion.

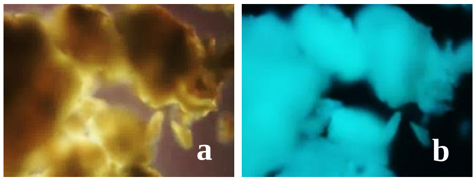


Figure 5.14. Images of compound **35d** in solid state, without (a) and with UV irradiation (b)

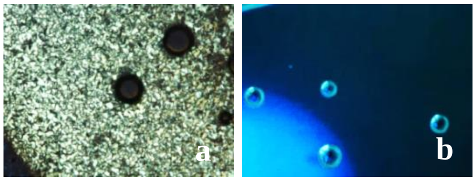


Figure 5.15. Images of compound **35d** in liquid crystal phase, without (a) and with UV irradiation (b)

The emission spectra recorded for all hybrid materials synthesized in this chapter show characteristic bands of Eu^{3+} ion transitions. Involvement of the EuW$_{10}$ anion in the formation of hybrid materials has led to decreased of the symmetry of the Eu^{3+} coordination environment. Comparing the ratio of the intensity of the light emission given by the transition $^5D_0 \rightarrow {}^7F_2$ to the $^5D_0 \rightarrow {}^7F_2$ transition (I($^5D_0 \rightarrow {}^7F_2$)/I($^5D_0 \rightarrow {}^7F_1$)) of all hybrid materials, a decrease of the symmetry in the coordination sphere of the Eu^{3+} ion was observed. In the case of materials with long flexible chains, this symmetry increases with the increase of the number of carbon atoms in the aliphatic chains. In addition, all synthesized hybrid materials have been shown to be luminescent both in solid state, at room temperature, as well as in liquid crystal phase.

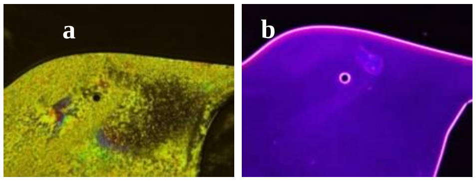


Figure 5.46. POM images of compound **41a** in liquid crystal phase without UV irradiation (a) and with UV light irradiation (b)

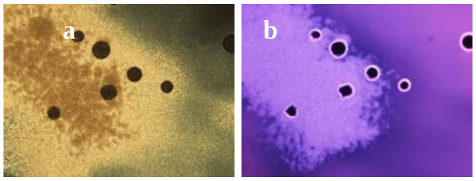


Figure 5.61. Images of compound **45**: SmA mesophase at 41°C (a) and SmA mesophase at UV light at 41°C (b).

In conclusion, this thesis aimed to the synthesis and characterization of new types of luminescent liquid crystals based on lanthanide ions. For this purpose, a total of 144 compounds have been synthesized, of which 17 organic *N*-alkyl-pyridones ligands which led to the preparation of 51 complexes with ilanthanide ions (Eu^{3+}, Sm^{3+} and Tb^{3+}) and a number of 29 pyridinium salts with different mesogenic groups which resulted in 11 hybrid materials with EuW_{10} polyoxometalate anion and 36 precursors.

Selective Bibliography

5. Nozary, H., Torelli, S., Guénée, L., Terazzi, E., Bernardinelli, G., Donnio, B., Guillon, D., Piguet, C., Structural, Thermodynamic, and Mesomorphic Consequences of Replacing Nitrates with Trifluoroacetate Counteranions in Ternary Lanthanide Complexes with Hexacatenar Tridentate Ligands. *Inorg. Chem.*, 45, **2006**, 2989-3003.
8. Giménez, R., Lydon, D.P., Serrano, J.L., Metallomesogens: a promise or a fact? *Curr. Opin. Solid St. M.*, 6, **2002**, 527-535.
25. Galyametdinov, Y.G., Ivanova, G.I., Ovchinnikov, I.V., Liquid-crystalline complexes of rare-earth elements with a Shiff base. *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 40, **1991**, 1109.
29. Binnemans, K., Lodewyckx, K., Van Deun, R., Galyametdinov, Y.G., Hinz, D., Meyer, G., Rare-earth complexes of mesomorphic Schiff's base ligands. *Liq. Cryst.*, 28, **2001**, 279.
66. Kharitonova, O.A., Prosvirin, A.V., Galyametdinov, Y.G., Ovchinnikov, I.V., Synthesis and magnetooptical properties of mesomorphic complexes of lanthanides with β-aminovinyl ketones. *Russ. Chem. Bull.*, 45, **1996**, 2213-1125.
67. Turanova, O.A., Turanov, A.N., Ovchinnikov, I.V., Galyametdinov, Yu.G., Liquid-Crystalline and Orientation Properties of Lanthanide Complexes with β-Enaminoketone. *Russ. J. Coord. Chem.*, 31, **2005**, 757-760.
70. Binnemans, K., Gschneidner Jr., K.A., Bunzli, J.C.G., Pecharsky, V.K., Handbook on the physics and chemistry of rare earths. *Amsterdam: Elsevier*, 35, **2005**.107-272.
73. Goossens, K., Nockemann, P., Driesen, K., Goderis, B., Gorller-Walrand, C., Van Hecke, K., Van Meervelt, L., Pouzet, E., Binnemans, K., Cardinaels, T., Imidazolium Ionic Liquid Crystals with Pendant Mesogenic Groups. *Chem. Mater.*, 20, **2008**, 157-168.
90. Escande, A., Guenee, L., Terrazzi, E., Jensen, T.B., Nozary, H., Piguet, C., Enthalpy/Entropy Compensation in the Melting of Thermotropic Nitrogen-Containing Chelating Ligands and Their Lanthanide Complexes: Successes and Failures. *Eur. J. Inorg. Chem.*, **2010**, 2746.
91. Piguet, C., Bunzli, J.C.G., Donnio, B., Guillon, D., Thermotropic lanthanidomesogens. *Chem. Commun.*, **2006**, 3755-3768.
92. Terazzi, E., Suarez, S., Torelli, S., Nozary, H., Imbert, D., Mamula, O., Rivera, J.P., Guillet, E., Benech, J.M., Bernardinelli, G., Scopelliti, R., Donnio, B., Guillon, D., Bunzli, J.C.G., Piguet, C., Introducing bulky functional lanthanide cores into thermotropic metallomesogens: a bottom-up approach. *Adv. Funct. Mater.*, 16, **2006**, 167.
104. Piechocki, C., Simon, J., Andre, J.J., Guillon, D., Petit, P., Skoulios, A., Weber, P., Synthesis and physico-chemical studies of neutral and chemically oxidized forms of bis(octaalkyloxyphthalocyaninato) lutetium. *Chem. Phys. Lett.*, 122, **1985**, 124-128.
128. Li, W., Yin, S.Y., Wang, J.F., Wu, L.X., Tuning Mesophase of Ammonium Amphiphile-Encapsulated Polyoxometalate Complexes through Changing Component Structure. *Chem. Mater.*, 20, **2008**, 514-522.
129. Lin, X., Li, W., Zhang, J., Sun, H., Yan, Y., Wu, L., Thermotropic Liquid Crystals of a Non-Mesogenic Group Bearing Surfactant-Encapsulated Polyoxometalate Complexes. *Langmuir*, 26, **2010**, 13201–13209.
130. Kim, H.S., Hoa, D.T.M., Lee, B.J., Park, D.H., Kwon, Y.S., Synthesis and photoluminescent property of Eu-containing organic–inorganic hybrid polyoxometalate. *Curr. Appl. Phys.*, 6, **2006**, 601–604.
131. Zhao, Y., Li, Y., Li, W., Wu, Y., Wu, L., Preparation, Structure, and Imaging of Luminescent SiO2 Nanoparticles by Covalently Grafting Surfactant-Encapsulated Europium-Substituted Polyoxometalates. *Langmuir*, 26, **2010**, 18430–18436.
132. Cuan, J., Yan, B., Photofunctional hybrid materials with polyoxometalates and benzoate modified mesoporous silica through double functional imidazolium ionic liquid linkage. *Micropor. Mesopor. Mater.*, 183, **2014**, 9-16.
133. Yin, S., Li, W., Wang, J., Wu, L., Mesomorphic structures of protonated surfactant-encapsulated polyoxometalate complexes. *J. Phys. Chem. B*, 112, **2008**, 3983-3988.
134. Xu, J., Zhao, S., Han, Z., Wang, X., Song, Y.F., Layer-by-Layer Assembly of Na_9 $[EuW_{10}O_{36}]$•$32H_2O$ and Layered Double Hydroxides Leading to Ordered Ultra-Thin Films: Cooperative Effect and Orientation Effect. *Chem. Eur. J*, 17, **2011**, 10365 – 10371.
135. Yin, S.Y., Sun, H., Yan, Y., Li, W., Wu, L.X., Hydrogen-Bonding-Induced Supramolecular Liquid Crystals and Luminescent Properties of Europium-Substituted Polyoxometalate Hybrids. *J. Phys. Chem. B*,113, **2009**, 2355-2364.
136. Wang, Z., Zhang, R., Ma, Y., Peng, A., Fua, H., Yao, J., Chemically responsive luminescent switching in transparent flexible self-supporting $[EuW_{10}O_{36}]^{9-}$agarose nanocomposite thin films. *J. Mater. Chem.*, 20, **2010**, 271-277.

Publications, posters and presentations

***List of articles published in the field of Ph.D. thesis*:**

1. **Chiriac**, **F.L.,** Manaila-Maximean, D., Ganea, P., Pasuk, I., Circu, V., Thermal, emission and dielectric properties of liquid crystalline Eu(III), Sm(III) and Tb(III) complexes based on mesogenic 4-pyridone ligands functionalized with cyanobiphenyl groups. *J. Mol. Liq.*, 290**, 2019**, 111184.
   FI: 4.561
2. **Chiriac, F.L.,** Pasuk, I., Secu, M., Micutz, M., Cîrcu, V., Wide-Range Columnar and Lamellar Photoluminescent Liquid-Crystalline Lanthanide Complexes with Mesogenic 4-Pyridone Derivatives. *Chem. Eur. J.*, 24, **2018,** 13512–13522.
   FI: 5.160
3. Pană, A., **Badea**, **L.,** Iliș, M., Staicu, T., Micutz, M., Pasuk, I., Cîrcu, V., Effect of counterion on the mesomorphic behavior and optical properties of columnar pyridinium ionic liquid crystals derived from 4-hydroxypyridine. *J. Mol. Struct.*, 1083, **2015,** 245–251.
   FI: 1.780
4. Pană, A., **Chiriac**, **F.L.,** Secu, M., Pasuk, I., Ferbinteanu, M., Micutz, M., Cîrcu, V., A new class of thermotropic lanthanidomesogens: Eu(III) nitrate complexes with mesogenic 4-pyridone ligands. *Dalton Trans.*, 44, **2015**, 14196.
   FI: 4.177

List of scientific communications-Posters / Oral presentations:

1. **Chiriac**, **L.F.,** Ilinca, T.A., Ilis, M., Staicu, T., Micutz, M., Circu, V., Liquid crystal with luminescent properties based on lanthanides(III) and platinum(II) complexes. *9th International Conference of the Chemical Societies of the South-East European Countries*, 8-11 May, **2019**, Targovişte, Romania-Oral presentation.
2. **Chiriac, F.L.,** Manaila-Maximean, D., Ganea, P.C., Circu, V., Design, characterization and dielectric studies of high coordination number of lanthanide(III) complexes with cyanobiphenyl mesogens, *The 6th International Colloquium "Physics of Materials" (PM6)*, November 15-16, **2018**, Bucharest, Romania-Poster.
3. **Chiriac, F.L.,** Staicu, T., Micutz, M., Ilis, M., Circu, V., Liquid crystalline materials with lanthanide ions based on 4-piridona derivatives. *The 6th International Colloquium "Physics of Materials" (PM6)*, November 15-16, **2018**, Bucharest, Romania – Oral presentation.
4. Manaila-Maximean, D., Circu, V., Ganea, P., **Chiriac**, **L.F.,** Luminescent and dielectric properties of a series of lanthanide-containing liquid crystals. *14th European Conference on Liquid Crystals.*, June 25 - 30, **2017**, Moscow, Russia, **-** Poster.
5. **Chiriac**, **F.L.,** Circu, V., Photophysical properties and mesomorphic behavior of a new class of lanthanide (III) complexes with cyanobiphenyl derivatives. *The 5th International Colloquium 'Physics of Materials',* November 10-11, **2016**, Bucharest, Romania – Poster.
6. **Chiriac**, **F.L.,** Cirstea, C., Mitrea, D.G., Circu, V., Bright green light-emitting Tb(III) nitrate complexes based on 4-piridona ligands. *The 5th International Colloquium 'Physics of Materials'*, November 10-11, **2016**, Bucharest, Romania-Poster.
7. **Chiriac**, **F.L.,** Pasuk, I., Rosu, T., Circu, V., Columnar mesophases from discotic Silver(I) cyclometalated metallomesogens. *INCD ECOIND – International Simposium – Simi 2015 "The Environment and Industry"*, **2015**, Bucuresti – Poster.
8. **Chiriac**, **F.L.,** Pana, A., Pasuk, I., Rosu, T., Circu, V., Synthesis and luminescence properties of new lanthanide (III)-doped liquid crystal complexes. *INCD ECOIND – International Simposium – Simi 2015 "The Environment and Industry"*, **2015**, Bucuresti – Oral presentation.
9. **Badea**, **L.,** Pana, A., Micutz, M., Rosu, T., Circu, V., Luminescent liquid-crystalline Eu (III) complexes with 4-piridona derivatives. *The 4th International Colloquium Physics of Materials*, November13-14, **2014**, Bucharest, Romania – Poster.