



*Dedicated to Dr. Maria Zaharescu  
on the occasion of her 80th anniversary*

## IONIC SALTS OF NICOTINIC ACID AS MULTIFUNCTIONAL MATERIALS

Maria Angela SPIRACHE,<sup>a</sup> Carmen CRETU,<sup>a</sup> Liliana CSEH,<sup>a</sup> Viorel SASCA,<sup>a</sup> Valentin BADEA,<sup>b</sup> Ramona TUDOSE,<sup>a</sup> Livia Nicoleta DEVESELEANU-CORICI,<sup>a</sup> Otilia COSTISOR<sup>a</sup> and Elisabeta I. SZERB<sup>a\*</sup>

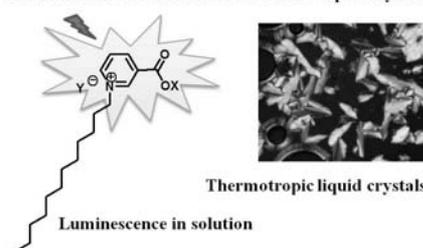
<sup>a</sup>Institute of Chemistry Timișoara of Roumanian Academy, 24 Mihai Viteazu Bvd, 300223 - Timișoara, Roumania

<sup>b</sup>Politehnica University of Timișoara, Faculty of Industrial Chemistry and Environmental Engineering, 6 Vasile Parvan Bvd, 300223 - Timișoara, Roumania

*Received July 31, 2017*

New thermotropic ionic liquid crystalline (ILCs) salts of nicotinic acid with different counterions have been synthesized and characterized by spectral (AAS, IR, UV-Vis and <sup>1</sup>H NMR) methods and molar conductivity. Their thermal behaviour was investigated by thermal analysis. The liquid crystalline properties were evidenced by polarized optical microscopy (POM). The mesomorphic behaviour of ILCs is influenced by the nature of anionic species and/or presence of metal ion. The synthesized compounds exhibit fluorescence at room temperature in solution.

Multifunctional materials based on ionic liquid crystals



### INTRODUCTION

Ionic liquid crystals (ILCs) are continuing to attract significant attention over several decades due to the possibility of combining their special features with properties like luminescence or redox activity making them attractive multifunctional materials for molecular electronics, batteries, fuel cells, capacitors, catalysis.<sup>1</sup> ILCs are materials consisting of cations and anions that combine the characteristics of liquid crystals (anisotropy of physical properties, order and mobility) with some of the properties of ionic liquids (such as ionic conductivity). In particular, many of the “classical” metallomesogens (metal containing liquid crystals) are ILCs because of their structural characteristics, being composed of alkali metal, alkaline earth metal, d-block transition metal, lanthanide cations surrounded by neutral and/or mesogenic/non-

mesogenic ligands in their coordination sphere and small negative counterions in ionic sphere.<sup>2-5</sup> The commonly used anions in ILCs are metal-containing complex  $[MX_n]^{m-}$  singly or doubly negatively charged or perfluorinated anionic species, typically used in ionic liquids as  $Cl^-$ ,  $Br^-$ ,  $[BF_4]^-$ ,  $[PF_6]^-$ ,  $[CF_3SO_3]^-$ ,  $[N-(SO_2CF_3)_2]^-$ .<sup>6-10</sup> The nature of anionic species influence the mesogenic stability of ILCs with changing in the mesophase type.<sup>1</sup> The first ILCs were reported in 1938 by Knight and Shaw,<sup>11</sup> who obtained mesogenic long-chain 1-alkylpyridinium salts soluble in water, forming more stable emulsions with oils. Latest publication of ILCs are based on heterocyclic nitrogen compounds containing one or more nitrogen atoms (e.g. triazolium, pyrazolium, benzimidazolium, quinolinium, 1,10-phenanthroline) with interest in imidazolium, pyrimidinium and quaternary ammonium, as organic cations and halide

\* Corresponding author: szella73@gmail.com

salts, perfluorinated species, metal-containing complex or organic compounds having solubilising groups ( $\text{SO}_3^-$ ,  $\text{COO}^-$ ) as counterions.<sup>1</sup>

Luminescent liquid crystalline materials are highly researched as potential candidates for optoelectronic device applications, especially for the production of linearly polarized light.<sup>12</sup> Thus, in an attempt to obtain multifunctional materials, herein we report on the synthesis and characterization of new ionic derivatives based on nicotinic acid that exhibit both liquid crystalline properties and luminescence in solution at r.t.

## RESULTS AND DISCUSSION

### 1. Synthesis and characterization

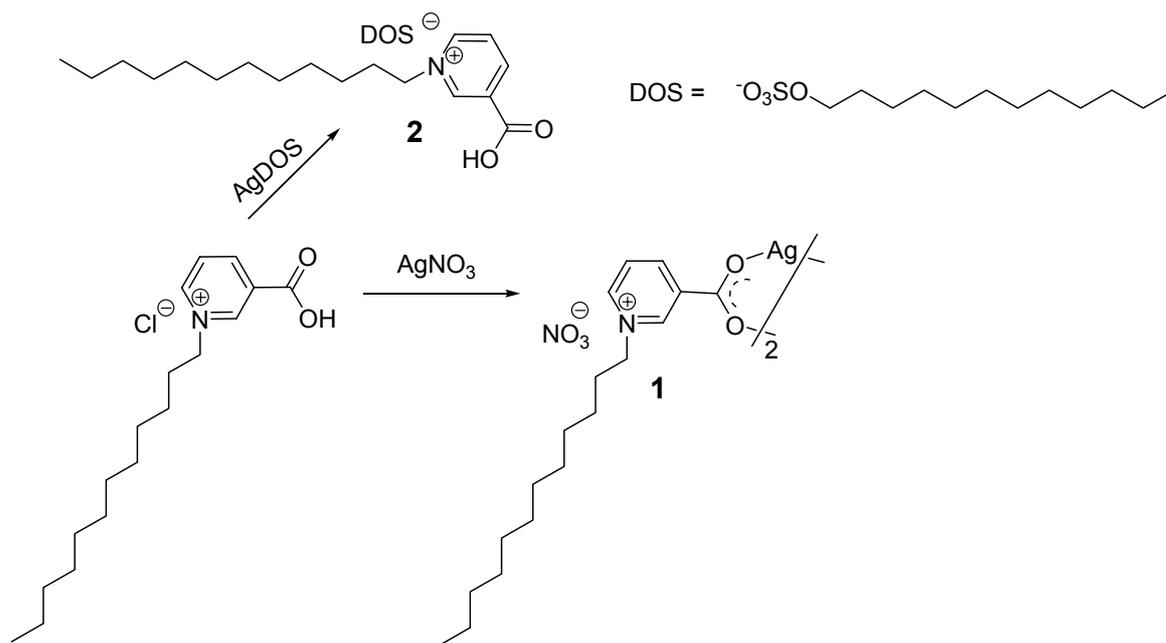
The ionic salts of nicotinic acid were obtained following the reaction pathway described in Scheme 1.

In particular, the chloride salt of 3-carboxy-1-dodecylpyridinium was obtained according to the procedure described in the literature.<sup>13</sup> This compound was subsequently used to obtain the ionic compounds 1 and 2 by reacting it with the silver salts ( $\text{AgNO}_3$  and  $\text{AgDOS}$ ) in ethanol, at room temperature and in vessels protected from light.  $\text{AgDOS}$  was obtained in an equimolecular reaction between  $\text{AgNO}_3$  and  $\text{NaDOS}$  in water. Determination of silver was made by atomic absorption spectroscopy (AAS).

The compounds were characterized by IR and  $^1\text{H-NMR}$  spectroscopies, and elemental analyses. The ionic nature of these compounds was evidenced by molar conductivity measurements.<sup>14</sup> The infrared spectra of the ionic salts (1 and 2) have shown the representative bands attributed to  $\nu_{\text{C=O}}$ ,  $\nu_{\text{C=C}}$  and  $\nu_{\text{C=N}}$  of nicotinic acid in the region  $1700 - 1490 \text{ cm}^{-1}$  and the bands attributed to dodecyl chain present in the range  $3100 - 2850 \text{ cm}^{-1}$ . In particular, a major difference consists in the band attributed to  $\nu_{\text{C=O}}$  of the carboxyl group that is shifted to lower frequencies in the case of complex 1, whereas in the case of complex 2 remains in the same range of frequencies attributed to the carboxylic acid.<sup>15</sup> The presence of the counterion is proven by the corresponding strong vibrational bands as follows: 1 -  $\nu_{\text{NO}_3} = 1382 \text{ cm}^{-1}$  and 2 -  $\nu_{\text{SO}_4} = 1245, 1019 \text{ cm}^{-1}$ .<sup>16</sup>

In the  $^1\text{H-NMR}$  spectra of the ionic compounds were observed the proton signals of pyridine moiety from the chloride precursor shifted to lower values depending of the type of counterion, the shift being more evidenced in the case of complex 1.

Based on these results, we propose the chemical structures presented in Scheme 1 for the two ionic compounds, confirmed by both elemental analysis and AAS (complex 1). Thus, the pyridinic counterion seems to influence the carboxylate group, explainable on the bases of its chemical hard or soft bases character. With  $\text{NO}_3$  carboxylate silver salt is formed, whereas with the bulky  $\text{DOS}$ , the carboxylic acid is conserved.



Scheme 1 – Synthetic route for the synthesis of ILCs 1 and 2.

## 2. Mesomorphic behaviour

Although the precursor (the chloride salt of 3-carboxy-1-dodecylpyridinium) is not mesomorphic melting directly at 180°C into isotropic liquid,<sup>13</sup> both ionic salts 1 and 2 are liquid crystalline as determined using both POM and thermal analysis. A detailed thermogravimetric analysis TGA/DTA revealed that the compounds have relative low decomposition temperatures

starting from around 150°C and marked by several endothermic peaks on heating (Figure 1). In particular, compound 1 has one peak on the DTA curve centred at 114°C before decomposition that starts over 150°C (Figure 1a). Differential scanning calorimetry (DSC) confirmed this behaviour, as showed in Figure 2a, where on heating, at 113°C, a considerable enthalpy change indicated the melting into liquid crystalline state, corresponding to an evident optical change on POM (Figure 3a).

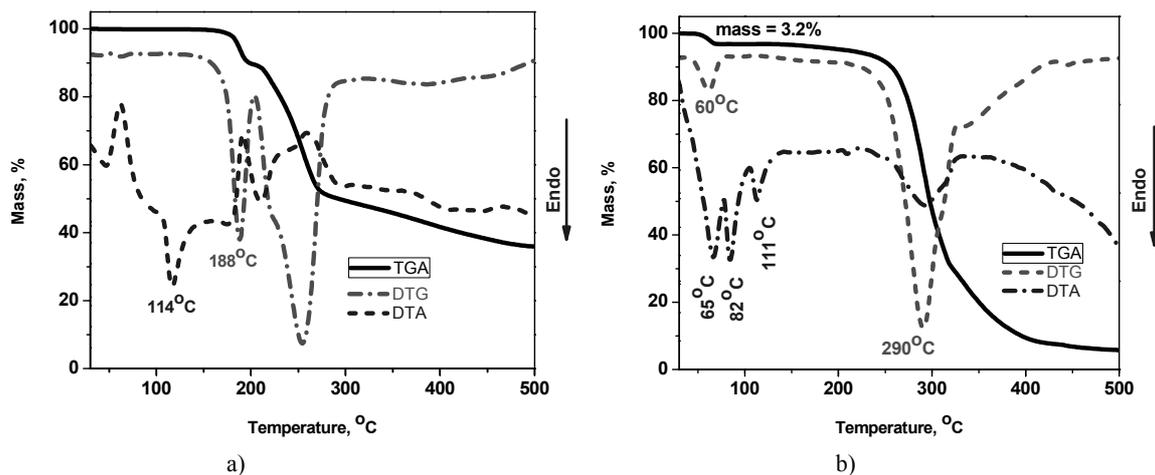


Fig. 1 – TGA, DTG and DTA traces for compound 1 (a) and compound 2 (b).

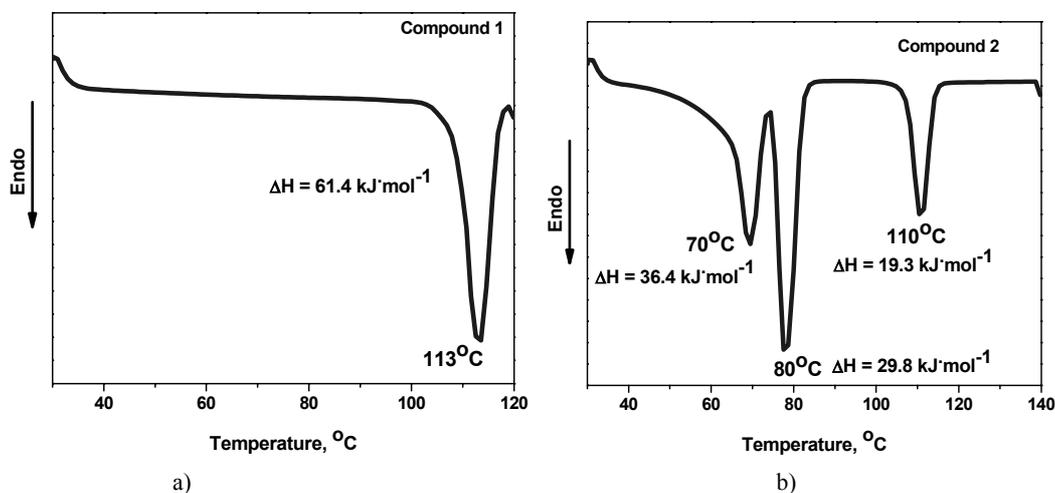


Fig. 2 – DSC traces for compound 1 (a) and compound 2 (b), on first heating.

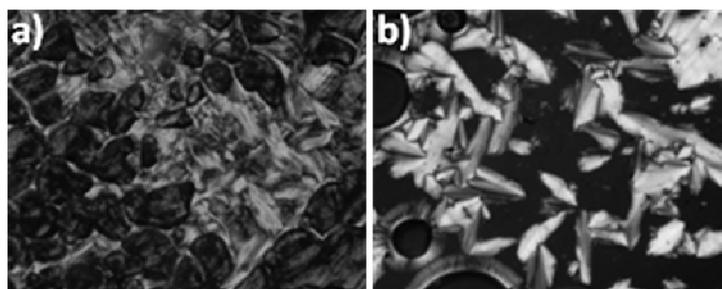


Fig. 3 – Optical textures (magnification 50x) of the mesophases of compounds: a) 1 as observed on heating at 120°C and b) 2 as observed on cooling at 127°C.

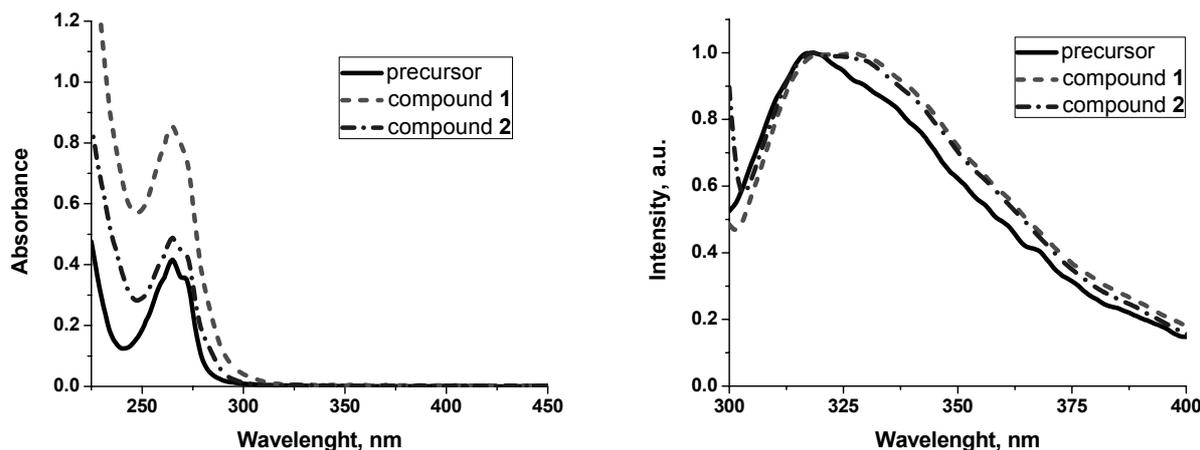


Fig. 4 – Absorption spectra (a) and emission spectra (b) of 1 – 4 in methanol solution ( $10^{-4}$ M).

Compound 2 shows three endothermic transitions before the anhydrous form decomposition starts over  $150^{\circ}\text{C}$  (Figure 1b). The first peak is due to the desolvation process of one molecule of water ( $65^{\circ}\text{C}$ ). Based on DSC analysis and POM observations (Figures 2b and 3b), the other two peaks are due to a transition between two crystalline states ( $80^{\circ}\text{C}$ ) and respectively a transition to a liquid crystalline state ( $110^{\circ}\text{C}$ ). The fan-shaped texture (Figure 3b) suggests a smectic mesophase.<sup>17</sup>

### 3. Photophysics

The electronic spectra of the ionic compounds 1 and 2 plotted against their precursor in Figure 4a show the usual pyridine  $\pi$ - $\pi^*$  bands between 250–300 nm with a more pronounced hyperchromic effect observed for 2. The fluorescence spectra of 1 and 2 (Figure 4b) are similar with their precursor, having two emission maxima around 318 nm and 330 nm, the latter being more evident in the case of the ionic salts 1 and 2. Thus, the photophysical properties of the ionic derivatives are not influenced by the type of the counterion.<sup>18</sup>

## EXPERIMENTAL

### 1. Materials and methods

Nicotinic acid, triethylamine and 1-bromododecane were purchased from Merck; sodium dodecylsulphate,  $\text{AgNO}_3$  and KSCN were purchased from Sigma-Aldrich. All reagents were of analytical grade and used without further purification. IR spectra were recorded on a Cary 630 FT-IR spectrophotometer, as KBr pellet, in the  $400$ – $4000\text{ cm}^{-1}$  range.  $^1\text{H-NMR}$  spectra were run on a Jeol-NMR (300 MHz) spectrometer. To determine the silver content the samples were digested using Digesdahl® Digestion Apparatus Models

23130-20, -21 by HACH (USA). The concentration of silver ions was then measured using a Flame Atomic Absorption Spectrometer (SensAA, GBC Scientific Equipment, Australia). For each complex, two determinations were made and the average absorbance value was further used. Elemental analyses of products were carried out using a Perkin Elmer 240C-CHN analyzer. Molar electrical conductivities were measured with a Mettler Toledo FiveEasy plus (FP30) conductivity meter equipped with a Lab conductivity sensor LE740. Fluorescence spectrum was recorded on freshly prepared solution using a Perkin Elmer LS-55 spectrophotometer. Thermal decomposition was carried out using a TGA/SDTA 851-LF 1100 Mettler Toledo thermogravimetric analyzer. The samples with mass of about 10–20 mg were placed in alumina crucible of 150  $\mu\text{L}$ . The experiments were conducted in nitrogen atmosphere in the temperature range of  $25$ – $800^{\circ}\text{C}$  with a heating rate of  $10^{\circ}\text{C min}^{-1}$  and a final isothermal heating in air at  $800^{\circ}\text{C}$  for 30 min. The transition temperatures and associated enthalpy values were determined using a DSC (DSC 882e, Mettler-Toledo Inc., Greifensee, Switzerland) which was operated at a scanning rate  $10^{\circ}\text{C/min}$  in nitrogen against an indium standard. The optical textures of mesophases were carried out using an Olympus BX53M polarizing microscope (POM) equipped with Linkam hot-stage. Images of the various phases were recorded using an Olympus UC90 camera.

### 2. Synthesis

**Compound 1:** Silver(I)nitrate (2.13 mmol) in 20 mL ethanol/water (v/v 9:1) was added to a solution of 3-carboxy-1-dodecylpyridinium chloride (1.07 mmol), triethylamine (0.15 mL) in 10 mL ethanol. The reaction mixture was stirred for 2h in the dark at room temperature. The solid was filtrate off and the filtrate was concentrated under vacuum and precipitated with acetone to give a white solid. The product was crystallized from chloroform/acetone. Yield: 0.46 mmol, 86.6%.

IR [KBr,  $\nu$ ,  $\text{cm}^{-1}$ ]: 3061 ( $\text{CH}_3$ ), 2922, 2853 ( $\text{CH}_2$ ), 1643 ( $\text{C}=\text{O}$ ), 1610 ( $\text{C}=\text{N}$ ), 1582 ( $\text{C}=\text{C}$ ), 1382 ( $\text{NO}_3$ );  $^1\text{H-NMR}$  (300 MHz,  $\text{DMSO-d}_6$ ),  $\delta$  (ppm): 9.39 (s, 1H,  $\text{H}^2$ ), 9.07 (d, 1H,  $J = 6.0\text{ Hz}$ ,  $\text{H}^4$ ), 8.85 (d, 1H,  $J = 7.9\text{ Hz}$ ,  $\text{H}^6$ ), 8.11 (dd, 1H,  $J = 7.8, 6.1\text{ Hz}$ ,  $\text{H}^5$ ), 4.65 (t, 2H,  $J = 7.4\text{ Hz}$ ,  $\text{H}^a$ ), 1.91 (d, 2H,  $J = 6.7\text{ Hz}$ ,  $\text{H}^b$ ), 1.25 (d, 18H,  $J = 10.9\text{ Hz}$ ,  $\text{H}^c$ ), 0.85 (t, 3H,  $J = 6.7\text{ Hz}$ ,  $\text{H}^d$ );  $\Lambda_{\text{M}}$  ( $c = 10^{-3}\text{ M}$ , MeOH) =  $155.4\ \Omega^{-1}\text{mol}^{-1}\text{cm}^2$ . Anal. Calcd.  $\text{C}_{36}\text{H}_{56}\text{Ag}_2\text{N}_4\text{O}_{10}$  (922.60 g/mol): C, 46.87;

H, 6.34; N, 6.07; found: C, 46.78; H, 6.15; N, 6.21. AAS: Ag % calcd.: 23.38, found: 23.09.

**Compound 2:** Silver(I)dodecylsulphate (AgDOS) (0.81 mmol) in 20 mL ethanol was added to a solution of 3-carboxy-1-dodecylpyridinium chloride (0.40 mmol) in 20 mL ethanol. The reaction mixture was stirred for 2h in the dark, at room temperature. The solid was filtrate off and the filtrate was concentrated under vacuum and precipitated with diethyl ether to give a white solid. The product was crystallized from chloroform/acetone. Yield: 0.22 mmol, 53.4%. IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ) 2956, 2852 ( $\text{CH}_2$ ), 1726 ( $\text{C}=\text{O}$ ), 1643 ( $\text{C}=\text{N}$ ), 1245, 1019 ( $\text{SO}_4$ );  $^1\text{H-NMR}$  (300 MHz,  $\text{DMSO-d}_6$ ): 9.57 (s, 1H,  $\text{H}^2$ ), 9.24 (d, 1H,  $J=6.0$  Hz,  $\text{H}^4$ ), 8.94 (d, 1H,  $J=8$  Hz,  $\text{H}^6$ ), 8.24 (m, 1H,  $\text{H}^5$ ), 4.67 (t, 2H,  $J=7.4$  Hz,  $\text{H}^a$ ), 3.66 (t, 3H,  $J=6.6$  Hz,  $\text{H}^a$ ), 1.91 (s, 2H,  $\text{H}^b$ ), 1.45 (d, 3H,  $J=6.3$  Hz,  $\text{H}^b$ ), 1.14 (d, 41H,  $J=54.8$  Hz,  $\text{H}^d, \text{H}^e$ ), 0.84 (t, 7H,  $J=6.4$  Hz,  $\text{H}^c, \text{H}^e$ );  $\Lambda_M$  ( $c=10^{-3}$  M, MeOH) =  $93.4 \Omega^{-1}\text{mol}^{-1}\text{cm}^2$ ; Anal. Calcd.  $\text{C}_{30}\text{H}_{55}\text{NO}_6\text{S}\cdot\text{H}_2\text{O}$  (575.84 g/mol): C, 64.59; H, 9.94; N, 2.51; found: C, 63.98; H, 10.08; N, 2.42.

## CONCLUSIONS

New thermotropic ionic liquid crystalline salts of nicotinic acid with different counterions have been synthesized and characterized by physical-chemical methods. These ionic derivatives show both liquid-crystalline properties and luminescence in solution. While the mesomorphic behaviour is influenced by the nature of the counterion on the pyridinic fragment and the nature of the carboxylate group, the photophysical properties of the ionic derivatives 1 and 2 are not.

**Acknowledgements:** This work was supported by a grant of Ministry of Research and Innovation, CNCS - UEFISCDI, project number PN-III-P4-ID-PCE-20160720, within PNCDI III. We are thankful to the Roumanian Academy of Science (Project 4.1.).

## REFERENCES

1. K. Goossens, K. Lava, C. W. Bielawski and K. Binnemans, *Chem. Rev.*, **2016**, *116*, 4643–4807.
2. D. Pucci and B. Donnio, “Metal-Containing Liquid Crystals”, in “Handbook of Liquid Crystals”, Vol. 5, “Non-Conventional Liquid Crystals”, 2nd edition, J. W. Goodby, P. J. Collings, T. Kato, C. Tschierske, H. Gleeson and P. Raynes, (Eds.), Wiley-VCH: Weinheim, 2014, p. 175–242.
3. J. L. Serrano, “Metallomesogens: Synthesis, Properties and Applications”, Wiley-VCH: Weinheim, 1996.
4. S. Chen and S. H. Eichhorn, *Isr. J. Chem.*, **2012**, *52*, 830–843.
5. D. Pucci, A. Bellusci, A. Crispini, M. Ghedini, N. Godbert, E. I. Szerb and A. M. Talarico, *J. Mater. Chem.*, **2009**, *19*, 7643–7649.
6. A. Tokarev, J. Larionova, Y. Guari, C. Guérin, J. M. López-de-Luzuriaga, M. Monge, P. Dieudonné and C. Blanc, *Dalton Trans.*, **2010**, *39*, 10574–10576.
7. S. P. Ji, M. Tang, L. He and G. H. Tao, *Chem. Eur. J.*, **2013**, *19*, 4452–4461.
8. A. Getsis, S. F. Tang and A. V. Mudring, *Eur. J. Inorg. Chem.*, **2010**, 2172–2177.
9. H. Tahara, Y. Furue, C. Suenaga and T. A. Sagara, *Cryst. Growth Des.*, **2015**, *15*, 4735–4740.
10. P. Bonhôte, A. P. Dias, N. Papageorgiou, K. Kalyanasundaram and M. Grätzel, *Inorg. Chem.*, **1996**, *35*, 1168–1178.
11. G. A. Knight and B. D. Shaw, *J. Chem. Soc.*, **1938**, 682–683.
12. Y. Wang, J. Shi, J. Chen, W. Zhu and E. Baranoff, *J. Mater. Chem. C*, **2015**, *3*, 7993–8005.
13. H. Pervez, S. O. Onyiriuka, L. Rees, J. R. Rooney and C. J. Suckling, *Tetrahedron*, **1988**, *44*, 4555–4568.
14. W. J. Geary, *Coord. Chem. Rev.*, **1971**, *7*, 81–122.
15. E. I. Szerb, D. Pucci, A. Crispini and M. La Deda, *Mol. Cryst. Liq. Cryst.*, **2013**, *573*, 34–45.
16. K. Nakamoto, “Infrared spectra of inorganic and coordination compounds”, John Wiley & Sons, New York, 1963, p. 112, 173.
17. I. Dierking, “Textures of liquid crystals”, Wiley-VCH Verlag GmbH & Co. KGaA, 2003.
18. A. Pana, M. Ilis, T. Staicu, I. Pasuk and V. Circu, *Liq. Cryst.*, **2016**, *3*, 381–392.

