EMISSIVE Zn(II) METALLOMESOGEN BASED ON TRIDENTATE TERPYRIDINE LIGAND

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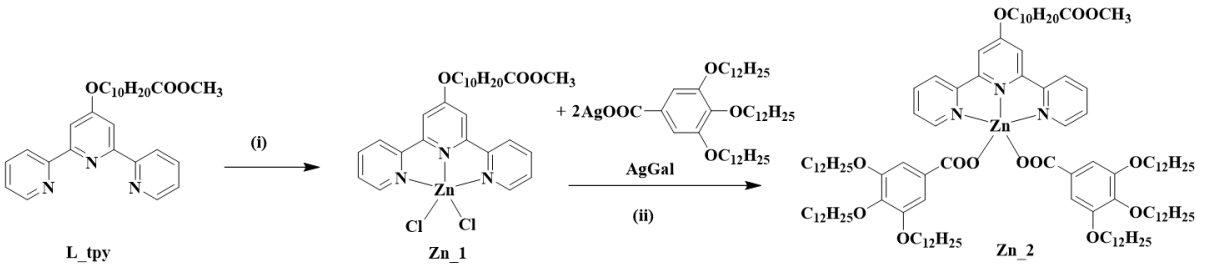
Abstract
A low temperature liquid crystal based on luminescent terpyridine Zn(II) complex is presented. The induction of the mesomorphic properties was achieved using a lipophilic gallate unit as ancillary ligands. The mesomorphic properties were investigated by polarised optical microscopy (POM), differential scanning calorimetry (DSC), thermogravimetric analysis (TA) and X-ray scattering (SWAXS) of bulk materials, while the optical properties of the complex were investigated in solution and in condensed liquid crystalline states.

Introduction
Metallomesogens (metal-containing liquid crystals) combine the supramolecular ordering of liquid crystals with the properties imparted by the metal centre (magnetic, electrical, optical and electro-optical),**[1]** thus leading to advanced materials with potential applications in optoelectronics.**[2,3]** Due to their excellent light emitting efficiencies and high thermal stabilities, Zn(II) complexes are of particularly high interest.**[4]** On this background, we report the synthesis and characterization of a terpyridine (tpy) Zn(II) liquid crystal.

Experimental
The structural characterization of the compounds was realized by employing a variety of analytical and spectroscopic methods: elemental analysis, Nuclear Magnetic Resonance - NMR, Fourier-Transform Infrared - FT-IR, and Ultraviolet–visible - UV-Vis spectroscopies. The thermal behaviour and liquid-crystalline properties were investigated by polarised optical microscopy (POM), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and small- and wide-angle X-ray scattering (SWAXS). Photophysical investigations were carried out in different solvents and condensed states.

Results and discussion
The ligand **L_tpy [5]** and precursor **AgGal [6]** were obtained following reported procedures. The reaction of **L_tpy** with $ZnCl_2$ afforded the neutral complex **Zn_1**, whereas the final complex **Zn_2** was obtained by the displacement of the chlorine ligands with AgGal lipophilic unit,**[7]** as described in Scheme 1.



Scheme 1. Synthesis of Zn(II) complexes: (i) $ZnCl_2$, MeOH/$CHCl_3$, r. t., 1.5 hours; (ii) $CHCl_3$, r. t., 2 hours.

The neutral pentacoordinated complex **Zn_2** self-assembles in a columnar hexagonal phase already at room temperature, as determined by POM, DSC and SWAXS analysis.
The absorption and emission properties were studied in dichloromethane solutions. Both complexes resulted to be fluorescent, with an emission quantum yield of 6.4 % for **Zn_1** and 24.5 % for **Zn_2**. Also, both complexes presented emission in condensed state at room temperature.
The luminescent properties of the liquid crystalline **Zn_2** were also measured in condensed states at various temperatures and found to be kept in the liquid crystalline states, but lost in the isotropic states due to the increase of the vibrational modes by increasing the temperature.

Conclusion

A luminescent liquid crystal based on Zn(II) metal centre was obtained by a straightforward synthetic approach, using a lipophilic gallate derivative as ancillary ligand. The complex was found to be luminescent in solution and in condensed states. In the mesophase, **Zn_2** emits showing a broad band whose maximum depends on the temperature.

Acknowledgements

M. LD and G. DM acknowledge the help granted by Regione Calabria (POR Calabria FESR 2014/2020-Azione 1.2.2) through the MERAVIGLIE project. B.D. and B.H. thank the CNRS and University of Strasbourg for support. A.A.A. P.E, E.I.S. and O.C. acknowledge the Romanian Academy, Program 4. A.A.A. is grateful for an “Ion Heliade Radulescu” mobility scholarship.

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