



Selecting pyrazole-based silver complexes for efficient liquid crystal and luminescent materials



Lorena Soria^{a,1}, Paloma Ovejero^{a,1}, Mercedes Cano^{a,*}, José A. Campo^{a,1},
M. Rosario Torres^{b,2}, Cristina Núñez^{c,d,e}, Carlos Lodeiro^{c,f}

^a Departamento de Química Inorgánica I, Facultad de Ciencias Químicas, Universidad Complutense, 28040 Madrid, Spain

^b CAI de Difracción de Rayos-X, Facultad de Ciencias Químicas, Universidad Complutense, 28040 Madrid, Spain

^c REQUIMTE-CQFB, Chemistry Department, Faculty of Science and Technology, University NOVA of Lisbon, 2829-516 Monte da Caparica, Portugal

^d Department of Inorganic Chemistry, Faculty of Chemistry, University of Santiago de Compostela, Spain

^e Department of Geographical and Life Sciences, Canterbury Christ Church University, CT1 1QU Canterbury, United Kingdom

^f ProteoMass Scientific Society, Madan Parque, Rua dos Inventores, 2825-182 Caparica, Portugal

ARTICLE INFO

Article history:

Received 21 February 2014

Received in revised form

2 April 2014

Accepted 5 April 2014

Available online 18 April 2014

Dedicated to the memory of Prof. Dr. José Vicente Heras Castelló.

Keywords:

Luminescent silver complexes

Liquid crystals

Luminescent metallomesogens

Pyrazole based complexes

Bifunctional materials

Molecular design

ABSTRACT

The liquid crystal and luminescent properties of two families of silver complexes (**A** = [Ag(L)₂][NO₃] and **B** = [Ag(L)(NO₃)] based on 3,5-alkyloxyphenyl, 3-pyridyl-5-alkyloxyphenyl and 3-alkyloxyphenyl substituted pyrazole ligands (L) were analysed on the light of the influence of factors as the stoichiometric metal to ligand ratio or the nature of the substituents on the pyrazole ring. This latter is related to the presence of the pyridine groups or the symmetrical or asymmetrical alkyloxyphenyl substitution. The interest of the research was focused on determining the molecular characteristics that optimise the mesomorphic properties/structure relationship. The thermal behaviour of **A** revealed that an “H” molecular shape was an imperative factor to achieve the best mesomorphic properties, while the mesomorphism of **B** was clearly dependent on the number and/or on the symmetric or asymmetric alkyloxyphenyl substitution on the pyrazole ring. The fluorescent properties of both types of compounds were also examined and compared.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Molecular materials with properties like light emission or electronic transport have received significant attention due to their potential applications in the growing research field of displays, OLED's, sensors, information storage, solar cells and active components for image and data treatment storage [1]. In particular, the combination of the supramolecular ordering of the mesophases with luminescent properties in the same material (giving rise to intrinsic fluoroforic liquid crystal materials) is of significant interest to generate new molecular electronics.

In this context it is important to mention that the presence of certain metals like silver has been strategically used to achieve luminescent metallomesogens [2].

Previous works from our lab were focused on designing silver complexes supported by mesogenic or promesogenic pyrazole-based ligands. So, mono- or di-alkyloxyphenyl substituted pyrazole compounds and the related pyridine functionalised ones were used towards different silver salts AgA (A = NO₃, BF₄, PF₆, CH₃-p-C₆H₄SO₃ (PTS), CF₃SO₃ (OTf)), giving rise to mesomorphic ionic complexes that exhibited SmA and SmC mesophases [3].

However due to the results were quite dispersed, because of the many variables included, we consider that a systematic study could be used as an important tool in order to determine the structure/properties relationship. In addition, the analysis of the photoluminescent properties of the compounds involved in this study could also be included to determine their potential ability as bifunctional materials.

With that idea in mind we are interested in determining the characteristics of pyrazole-based silver metallomesogens, which lead to the optimisation of the mesomorphism.

For this purpose we have selected a family of ionic silver complexes built with the following requirements: a) the use of pyrazole

* Corresponding author. Tel.: +34 91 394 4340; fax: +34 91 394 4352.

E-mail address: mmcano@quim.ucm.es (M. Cano).

¹ Tel.: +34 91 394 4340; fax: +34 91 394 4352.

² Tel.: +34 91 394 4284.

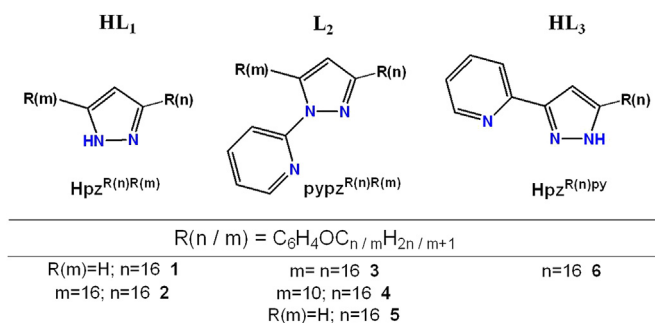


Fig. 1. Schematic representation of the ligands HL₁ 1–2, L₂ 3–5, HL₃ 6.

ligands of the types: HL₁, L₂ and HL₃ (Fig. 1) in which, maintaining a pyrazolic core, variations in the number and position of the pyridine and alkyloxyphenyl substituents are introduced; b) the use of a 2:1 (ligand : metal) stoichiometry to achieve a tetracoordinated environment, and c) the selection of a determined chain length as well as a counterion. Alkyl chains of 16 C-atoms and NO₃⁻ ions are considered as favourable components to improve the liquid crystal properties [4].

Following the above considerations, in the first part of this work, the liquid crystal behaviour of representative examples of metalomesogens of the type [Ag(L)₂][NO₃] (L = HL₁, L₂, HL₃, 1–6; Fig. 1) named **A**, 7–10, (Fig. 2) was analysed.

The study was also extended to new 1:1 (metal:ligand) silver complexes of the type [Ag(L₂)(NO₃)] **B** based on the bidentate L₂ ligands. These L₂ type ligands were selected in order to study and compare the effects that different variations at the pyrazole (mono- vs. di-substitution or symmetrical vs. asymmetrical alkyloxyphenyl disubstitution) produce on the liquid crystal properties of the complexes. Then, pypz^{R(16)R(16)}, pypz^{R(10)R(16)} and pypz^{R(16)} (L₂ ligands 3–5; Fig. 1) were used towards AgNO₃ to reach the new silver compounds [Ag(L₂)(NO₃)] named **B**, 11–13 (Fig. 3).

In summary we describe and analyse several factors that should contribute to achieve the improvement of the liquid crystal behaviour of silver-pyrazole complexes.

Table 1 shows the classification and numbering of all the compounds involved in the present work.

2. Experimental

2.1. Materials and physical measurements

All commercial reagents were used as supplied. Elemental analysis for carbon, hydrogen and nitrogen were carried out by the

Microanalytical Service of Complutense University. IR spectra were recorded on a FTIR Thermo Nicolet 200 spectrophotometer in solid state, with samples as KBr pellets, in the 4000–400 cm⁻¹ region. ¹H NMR spectra were performed at room temperature on a Bruker DPX-300 spectrophotometer (NMR Service of Complutense University) from solutions in CDCl₃. ¹H Chemical shifts (δ) are listed relative to Me₄Si using the signal of the deuterated solvent as reference (7.26 ppm), and coupling constants *J* are in hertz. Multiplicities are indicated as s (singlet), d (doublet), t (triplet), dd (doublet of doublets), td (triplet of doublets), m (multiplet) and br (broad). The ¹H chemical shifts and coupling constants are accurate to ±0.01 ppm and ±0.3 Hz, respectively. Phase studies were carried out by optical microscopy using an Olympus BX50 microscope equipped with a Linkam THMS 600 heating stage. The temperatures were assigned on the basis of optic observations with polarised light. Measurements of the transition temperatures were made using a Perkin Elmer Pyris 1 differential scanning calorimeter with the sample (1–4 mg) sealed hermetically in aluminium pans and with a heating or cooling rate of 5–10 K min⁻¹ Fig. S1 recovers the nomenclature used in the NMR assignments.

Absorption spectra were recorded on a JASCO-650 spectrophotometer and fluorescence emission on a Horiba-Jobin-Yvon FluoroMax 4 spectrofluorimeter. The linearity of the fluorescence emission vs. concentration was checked in the concentration range used (10⁻⁵–10⁻⁶ M). A correction for the absorbed light was performed when necessary. All spectrofluorimetric studies were performed as follows: the stock solutions of the ligands (ca. 10⁻³ M) were prepared by dissolving an appropriate amount of the ligand in a 50 mL volumetric flask and diluting to the mark with dichloromethane UVA-sol grade. Fluorescence spectra of solid samples were recorded on the spectrofluorimeter exciting the solid compounds at appropriate λ. Luminescence quantum yields were determined using a 0.1 M solution of quinine sulphate in 0.5 M H₂SO₄ as standard [φ_F = 0.546] [5].

2.2. Synthesis of ligands

The ligands HL₁ 1,2, L₂ 3,5 and HL₃ 6 have been synthesised as it was previously reported by us [4,6].

2.2.1. pypz^{R(10)R(16)}·0.4H₂O (R(10) = C₆H₄OC₁₀H₂₁, R(16) = C₆H₄OC₁₆H₃₃) (4·0.4H₂O)

The new asymmetrically substituted L₂ ligand 4 was synthesised through a Claisen condensation between the corresponding asymmetric β-diketone [7] and NH₂NHpy in EtOH at reflux for 3 days with stirring. The reaction mixture was allowed to cool to r.t.,

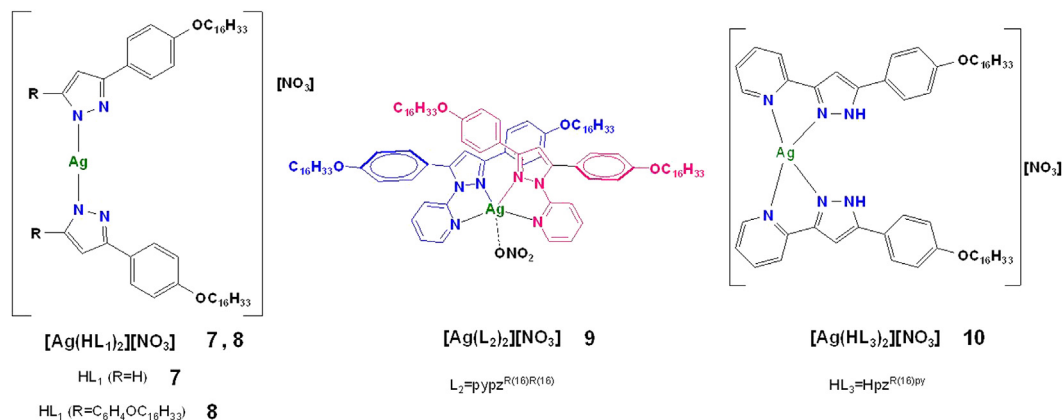


Fig. 2. Complexes **A** ([Ag(L)₂][NO₃] (L = HL₁, L₂, HL₃)) 7–10. The structural representations have been made on the basis of the crystalline structures of analogous complexes.

Download English Version:

<https://daneshyari.com/en/article/176026>

Download Persian Version:

<https://daneshyari.com/article/176026>

[Daneshyari.com](https://daneshyari.com)