

“SMART” MOLECULAR ENGINEERING OF METALLOMESOGENS BASED ON Pt(II) TERPYRIDINE COORDINATION COMPLEXES

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Abstract

A series of ionic tetracoordinated Pt(II) complexes based on terpyridine ligand were synthesized and characterized. Their chemical structures were engineered by using counterions of different coordination strengths and dimensions, namely non-coordinating BF₄, weakly coordinating bulky gallate units, and small and strongly coordinating chlorine (Cl). The complexes containing lipophilic gallate units exhibit low temperature liquid crystalline properties. The mesomorphic properties were investigated by polarized optical microscopy (POM), differential scanning calorimetry (DSC) and X-ray diffraction studies (SWAXS). Photophysical properties were determined in solution and condensed states.

Introduction

In recent years, a particular interest has been granted to Pt(II) terpyridine (*tpy*) complexes, which, due to the rapid progress in the area of structure/reactivity/interaction with biomolecules such as DNA and proteins, present a great potential to expand the applications of this family of coordination compounds in biomedical fields[1]. Moreover, some ionic Pt(II) complexes with *tpy* or functionalised *tpy* ligands were showed to be good candidates for obtaining luminescent supramolecular assemblies both in liquid crystalline phases and gels,[2-6] owing to the extended aromatic region that favours π - π stacking and short Pt··Pt distances[7]. Herein we report the synthesis of new Pt(II) coordination complexes whose molecular structures are engineered by using ligands and counterions of different coordination strength. The gallate unit was decorated with three long alkyl chains, hence liquid crystalline properties were obtained for the resulting species.

Experimental

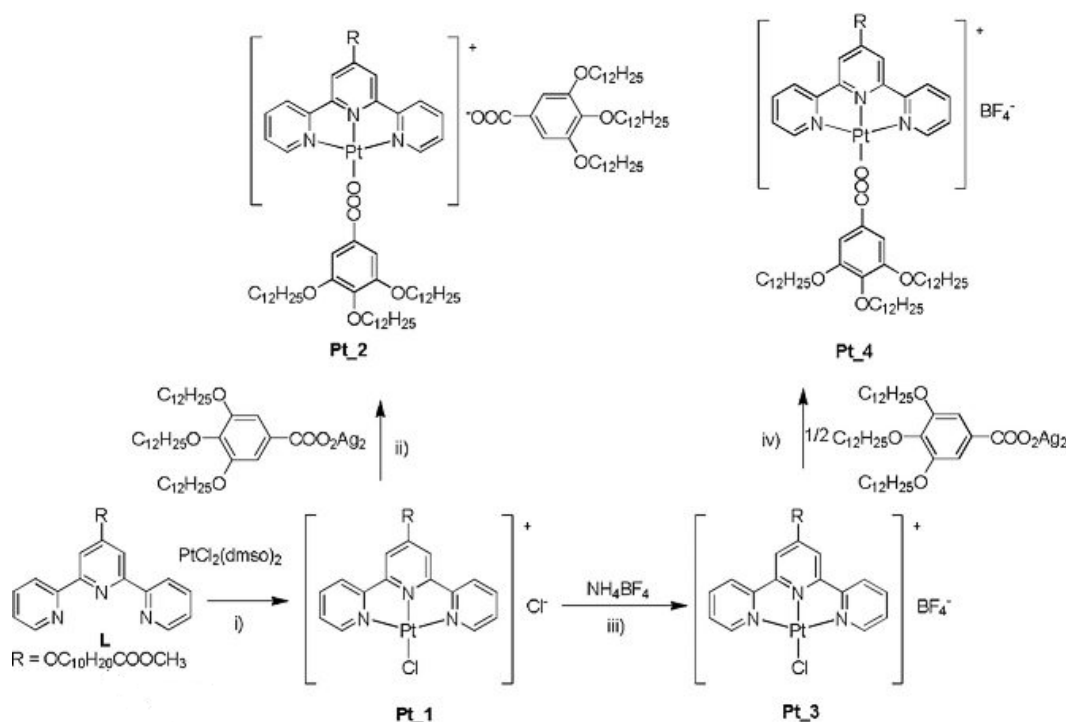
Synthesis and characterization of Pt(II) terpyridine complexes

The ligand **L** and complexes **Pt_1-4** were structurally analysed by means of spectroscopic (Nuclear Magnetic Resonance - 1D and 2D NMR, Fourier-Transform Infrared - FT-IR) and analytic (elemental analysis) investigations that confirmed their structure and purity. The ionic character of the complexes was evidenced by conductivity measurements in solution.

Results and discussion

Due to the Pt(II) ion straightforward coordination chemistry, both neutral and ionic species with different coordination environment depending on the coordination strength of ligands were obtained.

Complex **Pt_1** was synthesized adapting a procedure reported by Annibale *et al.* [8] Complex **Pt_3**, with BF_4^- as counterion, was obtained by reacting complex **Pt_1** with an excess of NH_4BF_4 .



Scheme 1. Synthesis of Pt(II) complexes: i) MeOH, ΔT , 1.5 h; ii) $\text{CHCl}_3/\text{MeOH}$ 1:1, r.t., 2 h; iii) $\text{CHCl}_3/\text{MeOH}$ 1:1, r.t., 1 h; iv) $\text{CHCl}_3/\text{acetone}$ 1:5, r.t., 2 h;

Complexes **Pt_1** and **Pt_3** were used as precursors in reaction with $\text{Ag}(\text{Gal})$, which is known as a mildly coordinating anion. The proposed chemical structures of Pt(II) complexes are supported by IR and accurate 1D and 2D NMR spectroscopy. Also, the ionic character of the Pt(II) complexes was evidenced in solution by conductivity measurements.[9]

The mesomorphic properties of the complexes **Pt_1-4** were first assessed by POM observations. As expected, complexes **Pt_1** and **Pt_3** did not possess liquid crystalline behaviour, melting at temperatures greater than 250°C , accompanied by decomposition. Complexes **Pt_2** and **Pt_4** containing the lipophilic gallate unit exhibit low temperature liquid crystalline properties, investigated by accurate POM, DSC and SWAXS measurements. Moreover, the photophysical properties of the Pt(II) complexes will be presented in both solution and condensed states.

Conclusion

Coordination complexes based on square-planar Pt(II) metal ions with luminescent properties are promising functional materials for various display and biomedical applications and there are still relatively few examples reported, which leaves space for the design of new metal–ligand systems to control the phase type, transition temperatures and thermal stability as well as to improve their luminescence in the mesophases.[10] The use of lipophilic gallate unit was shown to be a winning strategy to induce mesomorphic properties, complex **Pt_4** organizing into an original LamCol_r mesophase of $p2mg$ symmetry. In case of **Pt_2**, an erratic behaviour was observed, owing to the thermal dissociation of the gallate counterion, resulting in the co-existence of two or more species by varying temperature. However, the presence of bulky gallate groups resulted detrimental for the luminescence of the Pt(II) complexes. The sensitivity

of the metal ion to the molecular environment however is a potentially good property to be exploited in sensing applications.

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