

Metallomesogens based on β -diketone containing pyridinyl group. Luminescent behaviour.

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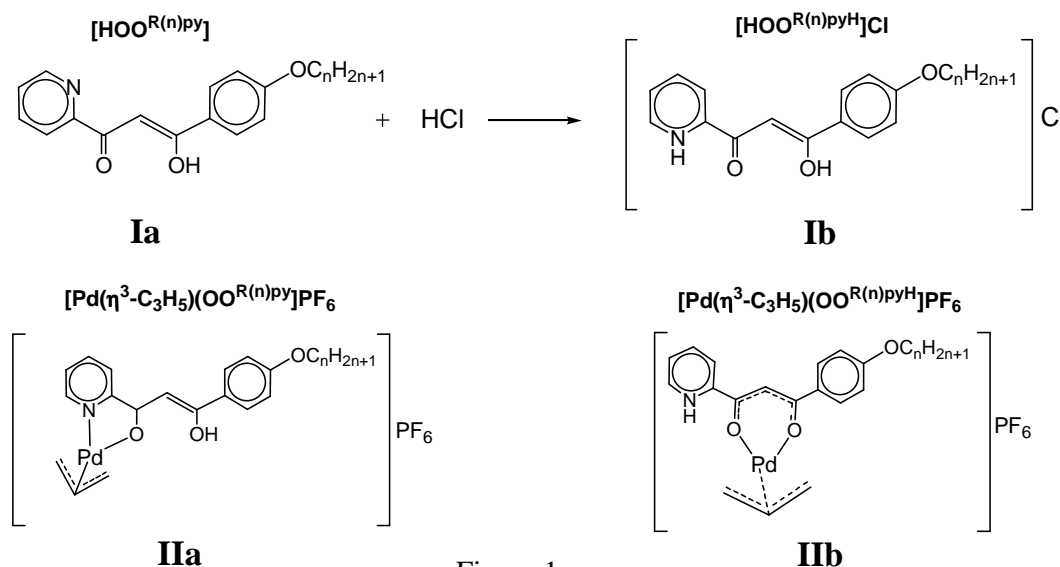
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The research of luminescent liquid crystals is focus of current interest as a support of new materials for technologies based on luminescence.¹ Although many metal complexes are strongly luminescent, metallomesogens displaying photoluminescence are scarce and most of them are related to lanthanides derivatives.² However few examples of those containing transition metals have been reported.³ In this communication we describe the synthetic strategy of molecular species exhibiting liquid crystal and/or luminescent behaviour.

Long-chained 1,3-disubstituted propane-1,3-diones are classical examples of mesogenic organic compounds which are also precursors of mesogenic 3,5-disubstituted pyrazoles, being both types of compounds used as ligands in the synthesis of metallomesogenic complexes.

We are now extended these studies by using pyridine-containing long-chained substituted diketones **Ia** [$\text{HOO}^{\text{R}(\text{n})\text{py}}$] (Fig. 1). Strategically the protonation of these compounds **Ia** has been used to perform the corresponding organic cations which were isolated as chloride salts **Ib** [$\text{HOO}^{\text{R}(\text{n})\text{pyH}}\text{Cl}$] (fig. 1).⁴



The β -diketone derivatives (**Ia** and **Ib**) showed to be non-mesomorphic but all of them displayed intense photoluminescence in the solid state as well as in the solution.

Coordination of both kinds of ligands to $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)]^+$ fragment gives rise to new ionic liquid crystal complexes **IIa** and **IIb** (fig. 1) whose absorption and emission spectra in solution are in agreement with the highly luminescent behaviour. Interestingly the metal complexes are more emissive than those of their respective starting ligands (**Ia** and **Ib**). In addition temperature variable studies evidence that the luminescence is also maintained in the mesophase.

The inclusion of substituents on the ligands with coordination ability as the pyridinyl group provides additional coordinative sites in the molecular periphery which can be used towards other

metal centres. Compounds of this type offer a new approach to explore their applications as chemical sensors for heavy and pollutants metal ions.

The analysis of the luminescence towards Zn(II) and Cu(II) has been explored and is also reported. The starting **Ia** and **Ib** compounds give rise to a fluorescence maxima when one equivalent of Zn²⁺ is added. By contrast the addition of one equivalent of Cu²⁺ quenches the luminescence (fig. 2).

Complexes of type **IIa** and **IIb** have also been proved as chemical sensors. Luminescent variations towards Zn²⁺ and Cu²⁺ additions are studied and reported in this communication.

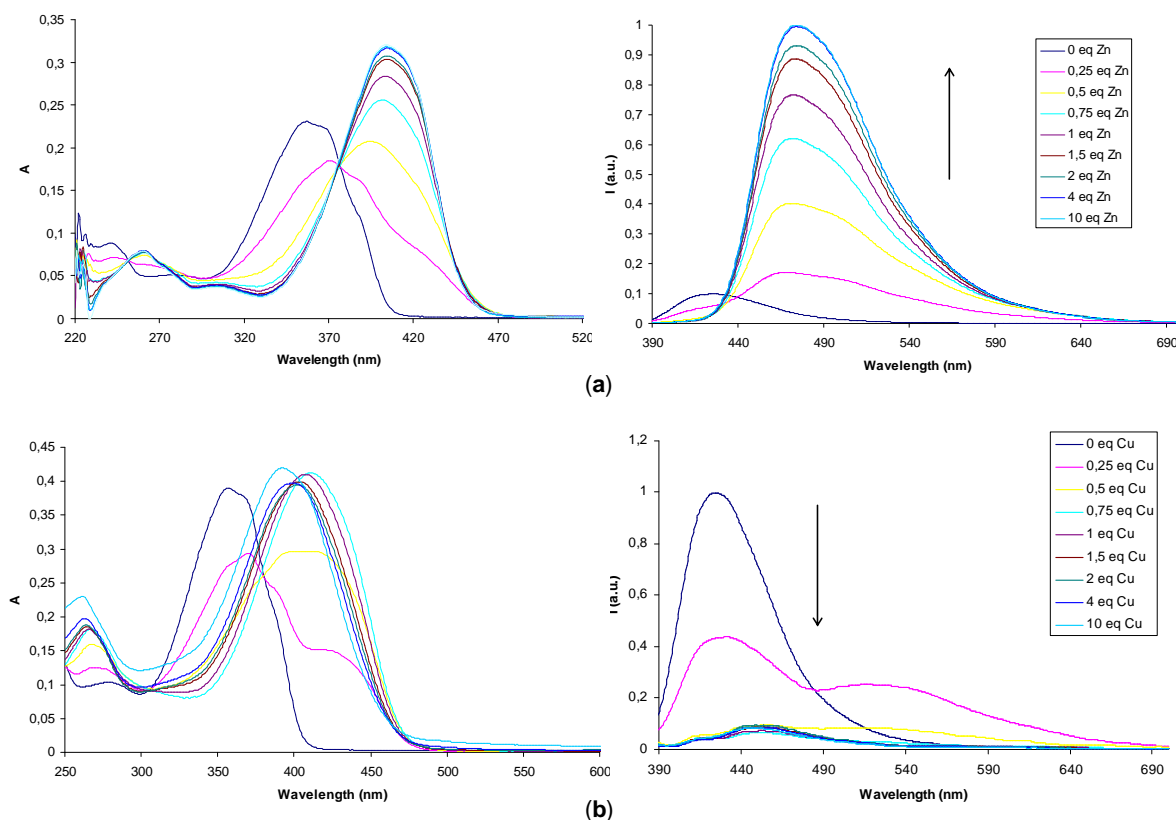


Figure 2. Absorption and emission titrations of [HOO^{R(12)py}] after addition of one equivalent of (a) Zn²⁺ and (b) Cu²⁺ in dichlorometane solution

¹M. O'Neill, S. M. Kelly, *Adv. Mater.* **2003**, *15*, 1131

²(a) T. Cardinaels, J. Ramaekers, P. Nochkemann, K. Driesen, K. Van Hecke, L. Van Meervelt, S. Lein, S. De Feyter, D. Guillon, B. Donnio, K. Binnemans, *Chem. Mater.* **2008**, *20*, 1278; (b) K. Driesen, D. Moors, J. Beeckman, K. Neyts, D. Görrler-Walrand, K. Binnemans, *J. Luminesc.* **2007**, *127*, 611.

³(a) M. J. Mayoral, P. Ovejero, J. A. Campo, J. V. Heras, E. Pinilla, M. R. Torres, C. Lodeiro, M. Cano, *Dalton Trans.* **2008**, 6912; (b) P. Ovejero, M. J. Mayoral, M. Cano, M. C. Lagunas, *J. Organomet. Chem.* **2007**, *692*, 1690; (c) M. Ghedini, D. Pucci, A. Crispini, A. Bellusci, M. La Deda, I. Aiello, T. Pugliese, *Inorg. Chem. Comm.* **2007**, *10*, 243.

⁴M. J. Mayoral, P. Ovejero, J. A. Campo, J. V. Heras, E. Pinilla, M. R. Torres, M. Cano, *Inorg. Chem. Comm.* **2009**, *12*, 214