

FINAL JOINT REPORT

Bilateral Project Romania - France

TITLE OF THE PROJECT: Luminescent Material Based on Liquid Crystal Metal Complexes and Metallic Cluster Core

Program Hubert Curien (PHC) Brancusi 2009 - 2010

Romanian Partner: University of Bucharest, Inorganic Chemistry Department, Coordinator: Dr. Viorel Circu

French Partner: Equipe Chimie du Solide et Matériaux, UMR 6226 Sciences Chimiques de Rennes, Université Rennes 1, Coordinator: Dr. Yann Molard

Scientific Results:

The Romanian team prepared a new series of organometallic platinum(II) complexes based on mixed ligands: imine derivatives carrying three alkoxy groups on one side and different benzoylthiourea on the other side, that showed very good luminescence properties both in solution and in the solid state at room temperature. Besides the photophysical properties, these organometallic complexes showed liquid crystalline properties with very low transition temperatures, showing both nematic and smectic A phases stable at room temperature. This type of complexes represent the first example of such compounds (metallomesogens based on platinum(II)) that have been studied for their luminescence properties in the liquid crystalline state.

The French partner developed the synthesis of several carboxylic acids, bearing specific promesogenic units (such as 4-biphenyl-carbonitrile or just biphenyl groups), varying their number and position, optimising the reaction conditions as well as their yields. The organic promesogenic ligands were grafted onto metal clusters giving rise to the first generation of clustomesogens – a concept introduced for the very first time by the two teams and patented in USA by the French team. The obtained results have been declared newsworthy by the editor of *Angewandte Chemie*, one of the most prestigious journal in the chemistry multidisciplinary category, who did his best to disseminate the work as widely as possible and to popularize it in an attempt to put it in a better light with the general public; (<http://www3.interscience.wiley.com/journal/26737/home/press/201015press.html>) and also, a special attention was given in the *News* section of *Materials Today* magazine (www.materialstoday.com).

The luminescent properties of the new materials were studied by fluorescence spectroscopy both in solution and solid state while the liquid crystalline properties of the new products were analysed by two complementary techniques: polarised optical microscopy and differential scanning calorimetry (DSC). Further confirmation of mesophase type was done by the means of small angle X-ray diffraction on solid state (SAXS). On the other hand several experiments regarding the coupling of organometallic Pt(II) complexes with metal clusters were done in the

Romanian lab and the results obtained so far being very encouraging. These new materials have potential applications in the field of bio, electronic and imaging technologies.

Publications :

1. "Clustomesogens: liquid crystal based transition metal clusters", Y. Molard, F. Dorson, V. Circu, T. Roisnel, F. Artzner, S. Cordier, *Angew. Chem. Int. Ed.*, 2010, 49, 3351-3355
2. "Synthesis, mesomorphism and luminescence properties of palladium(II) and platinum(II) complexes with dimeric Schiff base liquid crystals", A.S. Mocanu M. Ilie, F. Dumitrascu, M. Ilie, V. Circu, *Inorg. Chim. Acta*, 2010, 363(4), 729-736.
3. "Liquid crystal properties resulting from synergetic effects between non mesogenic organic molecules and a one nanometer sized octahedral transition metal cluster" A. S. Mocanu, Y. Molard, M. Amela-Cortes, V. Cîrcu, S. Cordier, *Chem. Commun.*, 2010, submitted.

Oral communications:

1. "Clustomesogens: liquid crystalline hybrid organic/inorganic nanomaterials containing transition metal clusters ", Y. Molard, F. Dorson, V. Cîrcu, T. Roisnel, F. Artzner, S. Cordier , International Workshop on Transition Metal Clusters, 29/09 – 2/10/2010, Rostock, Germany
2. "Transition metal cluster for the design of functional nanomaterials", Y.Molard, F. Dorson, F. Grasset, V. Cîrcu, S. Cordier, GECOM-CONCOORD 2010, 30/05-4/06/2010, Lyon, France
3. "Functional hybrid materials containing octahedral metallic cluster building blocks", Y.Molard, S. Cordier, F. Dorson, F. Grasset, V. Cîrcu, C. Perrin, French-Australian Workshop on NLO-Active Molecules: Trends and Perspectives in Molecular Design (NLO-Mol 2010), 8-9/04/2010, Rennes, France
4. Luminescent liquid crystals based on organometallic platinum(II) and palladium(II) complexes, V. Cîrcu, C. A. Artimon, Y. Molard, The XXXIst National Conference of Chemistry, 06 – 08 October, Ramnicu-Valcea, Romania
5. Mesomorphic and electro-optical properties of liquid crystals based on organometallic Pd(II) and Pt(II) complexes - V. Cîrcu, Y. Molard, C. Roşu, D. Mănăilă-Maximean, The 2nd International Colloquium "Physics of Materials" (PM-2), University "Politehnica" of Bucharest, 8th October 2010, Bucharest, Romania

Posters:

1. "Low melting luminescent liquid crystalline materials", V. Circu, Y. Molard, International Conference on Physical Chemistry - ROMPHYSICHEM - 14, 2/06- 4/06/2010, Bucharest, Romania

2. "Clustomesogens : transition metal based liquid crystal compounds", Y. Molard, F. Dorson, V. Cîrcu, S. Cordier, GECOM-CONCOORD 2010, 30/05-4/06/2010, Lyon, France

Seminars:

1. "Luminescent liquid crystals based on cyclometallated Pt(II) and Pd(II) complexes"- V. Circu, 22.09.2009, Université de Rennes – 1 – France

2. Transition metal clusters: From the solid state to hybrid materials – 09.06.2009, Y. Molard, University of Bucharest, Romania

3. Functional nanomaterials containing luminescent transition metal clusters – 29.11.2010, Y. Molard, University of Bucharest, Romania.

Patents:

1. "Luminescent hybrid liquid crystal", Y. Molard, S. Cordier, M. A. Amela-Cortes, F. Dorson, patent USA n°61/264 888, 30/11/ 2009

Table of mobility

Mobility	To France	To Romania
1. Name, position and age	Dr. V. Circu, Lecturer, 40 years	F. Dorson, PhD student, 25 years
Travel period	21.09 – 27.09.2009	25.05 – 13.06.2009
2. Name, position and age	Dr. M. Ilis, Assistant, 40 years	Dr. Y. Molard, Lecturer, 36 years
Travel period	21.09 – 27.09.2009	08.06 – 11.06.2009
3. Name, position and age	Dr. V. Circu, Lecturer, 40 years	Dr. Y. Molard, Lecturer, 36 years
Travel period	07.11 – 15.11.2009	29.11 – 02.12.2010
4. Name, position and age	V. Circu, Lecturer, 40 years	Dr. M. Amela-Cortes, Postdoc Fellow, 35 years
Travel period	11.11 – 24.11.2010	29.11 – 02.12.2010

Research training for young researcher

One French PhD student (F. Dorson) spent 3 weeks in the Romanian lab and received extensive training in liquid crystals characterisation techniques. These results were included in his PhD thesis and he successfully obtained the PhD degree, "Nanomatériaux hybrides luminescents à base de clusters d'éléments de transition", of the University of Rennes in 2010 under the supervision of Dr. Stephane Cordier and Dr. Yann Molard. A.S. Mocanu from the Romanian team spent 40 days in the French lab where she was trained in different synthetic protocols (synthesis and grafting of organic ligands onto metallic cluster). This stage was funded by an ongoing project of the Romanian team.

In this way she obtained preliminary results that were further developed in the French lab by the newly appointed Dr. Maria Amela Cortes in 2010. These results were submitted for publication in November 2010 (position 3 in the list of publications).

French Team:

Dr. Yann Molard – Coordinator

Dr. Stéphane Cordier

Frédéric Dorson

Dr. Christiane Perrin

Dr. Maria Amela Cortes

Romania Team:

Dr. Viorel Circu - Coordinator

Dr. Monica Ilis

Dr. Claudia Maria Simonescu

Ana Sorina Mocanu

Signed in Bucharest, 4 (four) copies, one for each partner and one for their respective funding body.

02.12.2010

Romanian Partner

French Partner

Dr. Viorel Circu

Dr. Yann Molard