Research Projects: Polymer Composite Materials

The Romanian National Research Program CERES

Functionalized Polymers for the Optical Signal Treatment

4-180

University of Bucharest – prof. dr. Ana Emandi – the coordinator

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The incorporation of metals into a non-metallic matrix component is a key step in the functional behavior of many industrially important applications like heterogeneous catalysts or ion exchange resins. In all of these cases on one hand the properties of metal containing surfaces are influenced by the binding of the metal atoms to the surrounding matrix and the chemical state of the metal centers like the type of complexation and the possibility for charge transfer. Consequently the possibilities of the obtaining of the polymer metal complexes and their relation to the chemical structure have been intensively investigated in bulk samples. The charge transfer spectra of the thin films of the functionalized poly vinyl alcohol with coordination compounds of transition metals were investigated as the main properties in the generation of the second harmonic.

Selected Publications:

1) Multifunction Coordinative Compounds of Er (III) Based On Azo Derivatives And Schiff Bases Ligands As Chromophores In Nonlinear Optics., *Ana Emandi*[1], *Cristina Vasiliu*[2], *Marilena Vasilescu*[3], *Mariana Voicescu*[3], *Rodica Bandula*[3], Journal of Optoelectronics and Advanced Materials*, (data spre publicare august, 2006).*

2) Magnetic And Spectral Studies On Copper(II) Complexes With 2-Benzothiazolyl Hydrazones. Part. I., *Mirela Calinescu, Ana Emandi, Emilia Ion, Rodica Georgescu.,* Rev. Chem. (data spre publicare septembrie, 2006).

3) The Effect Of Er(III) On The Thermal Behavior Of Azo (-N=N-) and Azomethinic (-CH=N-) Chromophpres*., Mihaela Badea, Rodica Olar, Ana Emandi***,** J. Therm. Anal. Cal., **2006**, 84, 601 – 605.

4) Spectral Studies of Some Ni(II), Pd(II), Cu(II) Azo-Dye Complexes in a Polymeric Matrix of Poly Vinyl Alcohol., *Authors: Ana Emandi,*[*] *Cristina Vasiliu,*[**] *Rodica Georgescu,*[***] *Iulian Ioniță and Mircea Bulinski* [****]*.,* Rev. Chem. (data spre publicare 2005, apare in decembrie 2006).

Proiectul de cercetare: PNCDI-CERES / 4-180/2004

"Polimeri functionalizati pentru tratarea semnalului optic"

Parteneri:

- **Universitatea Bucuresti** – Facultatea de Chimie – Centru de Cercetarea Chimie Anorganica Teoretica si Aplicata, **COORDONATOR**,

director de Proiect prof. dr. Ana Emandi;

- Institututul National de Optoelectronica INOE 2000 – **PARTENER**

responsabil Proiect dr. Ing. Cristina Ileana Vasiliu

Durata: 12.12.2004 – 15.09.2006

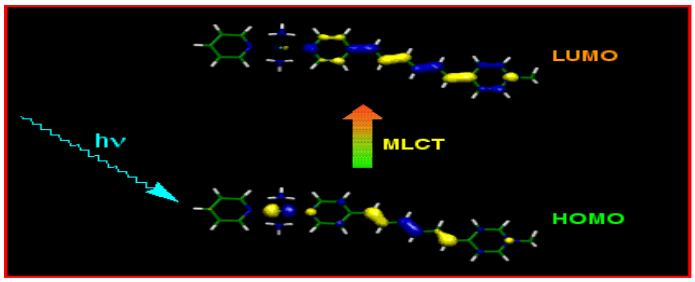
Nivel de finantare: 130 000 RON

Obiectivul proiectului: *Functionalizarea unor matrici polimerice cu combinatii complexe ale diversilor ioni metalici, in vederea obtinerii unui material pentru tratarea semnalului optic intelegand prin aceasta un material cu comporatment optic neliniar si sau prorpietati fluorescente imbunatatite.*

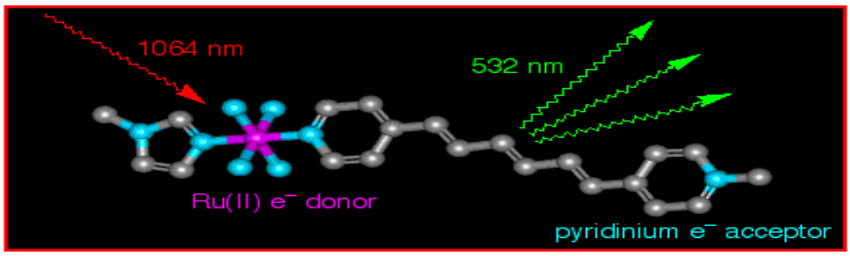
- Incorporarea metalelor intr-o matrice nemetalica este un pas cheie in modularea comprtamentului multor materiale cu incidenta in importante aplicatii industriale cum ar fi cataliza heterogena, rasinile schimbatoare de ioni, modularea semnalului optic. In toate aceste cazuri se pot ajusta proprietatile metalului continut la suprafata prin modul de legare a atomilor metalici de matricea inconjuratoare, prin starea chimica a centrului metalic cum ar fi tipul de complexare si posibilitatea transferului de sarcina. Functionalitatea matricilor polimerice metal-complexe este deasemenea guvernata de structura geometrica a suprafetei.

- In cadrul acestui proiect noi am intentionat sa investigam efectul produs de matricea polimerica asupra benzilor cu transfer de sarcina ale combinatiei complexe introdusa in aceasta matrice.

- Imporatanta benzilor cu transfer de sarcina metal → ligand (MLCT) in special dar si ligand → metal (LMCT) este bine cunoscuta in modularea momentului de dipol electric si dezvolatrea constantei de hiprpolarizabilitatea de orden doi β, prin modificarea polaritatii starii fundamentale HOMO fata de starea excitata LUMO, la interactia cu lumina, ca in figura de mai jos:



- Astfel $\mu = \acute{\alpha}E + \beta E^2$; $\beta \neq 0$, si apare comportamentul optic nelinear pozitiv sau negativ, ilustrat in figura de mai jos:



REALIZARI SI CONCLUZII

(i) Studiul efectului produs de matricea polimerica asupra benzilor cu transfer de sarcina

Motivul exploatarii benzilor MLCT in dublarea frecventei este simplu de inteles. Daca un ligand izolat poseda tranzitii cu transfer de sarcina puternice π (HOMO) $\rightarrow \pi^*$ CT legarea la un ion metalic a retelei π poate introduce o tranzitie optica (LUMO) CT de la un orbital "nonbonding" al metalului care participa la orbitalul (HOMO) catre starea π^* (LUMO) a ligandului. Dupa cum se arata schematic in (figura 1), energia benzii MLCT este de asteptat sa fie spre energii mai joase decat cea banda $\pi \rightarrow \pi^*$ a ligandului izolat. Cercetatorii au recunoscut importanta energiei jopase a benzii cu transfer de sarcina in optimizarea raspunsurilor nerezonante ale neliniaritatii optice.

Figure 1. Reprezentarea schematica a rolului benzilor cu transfer de sarcina.

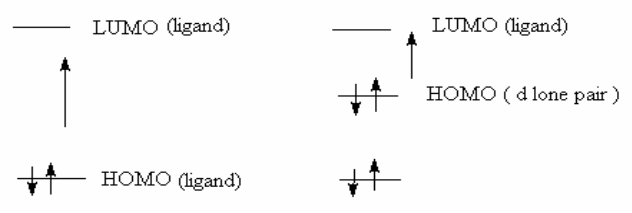
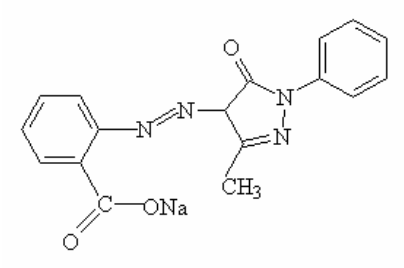
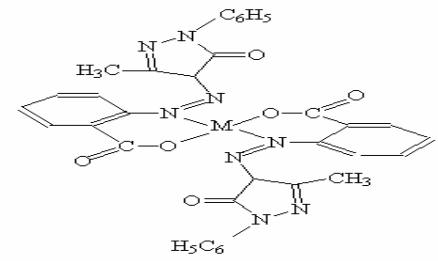


Figure 2. (a) Formula ligandului 1-phenyl-3-methyl-4-azo-(2`-carboxyphenylene)-pyrazol-5-one (LH)





(b) Formula genenerala a complecsilor $[M(L)_2]^0$, unde, M = Ni^{2+}, Cu^{2+} , Pd^{2+}

Table 2. Atribuirea benzilor din spectrul electronic al ligandului liber (LH), al combinatiilor complexe $[M(LH)_2]^0$ si al sistemelor $[M(LH)_2]^0$ / PVA.

Transitions/Assignments	**$\pi \rightarrow \pi^*$ (-N=N-)**	**$n \rightarrow \pi^*$ (-N=N-)**	**Intra ligand (IL)**
Ligand	402 nm (0.47)	334 nm (4.08)	312 nm (3.073)
	λ_{MLCT} ($d_\pi \rightarrow \pi^*$)		
$[Ni(L)_2]$/PVA	410 nm (0.98)	366 nm (2.33)	316 nm (5.13)
$[Ni(L)_2]$	406 nm (0.97)		
$[Cu(L)_2]$/PVA	430 nm (0.97)	358 nm (1.98)	334 nm (4.94)
$[Cu(L)_2]$	412 nm (0.98)		
$[Pd(L)_2]$/PVA	420 nm (0.48)	380 nm (0.46)	320 nm (4.07)
$Pd(L)_2]$	410 nm (0.48)		

Explicarea benzilor cu transfer de sarcina pentru sistemul $[Cu(L)_2]^0$ / PVA

$[Cu(L)_2]^0$ / PVA system Spectrul RPE[12] al complexului $[Cu(L)_2]^0$ (figure 6) prezinta anizotropia $g_\perp > g_{//}$, unde $g_\perp = 2{,}140$ si $g_{//} = 2{,}059$ care corespund unui Cu^{2+} cu stare fundamentala d_z^2.

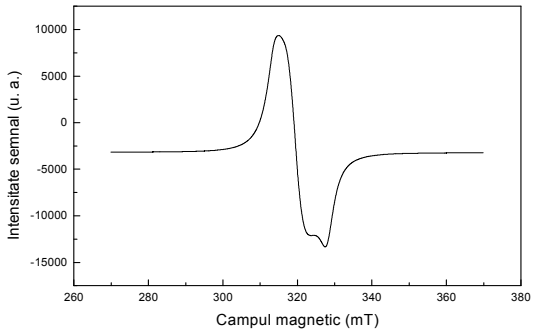


Figura 6. Spectrul RES al complexului $[Cu(L)_2]^0$

Diagrama de orbitali moleculari (figure 7.) a fost construita din orbitalii Cu(II) pentru simetria D_{4h} unde a_{1g} (d_{z2}) si b_{1g} (d_{x2-y2}) nu participa in MLCT deoarece sunt orbitali pseudo "e_g" cu caracter σ. Pseudo orbitalii "t_{2g}" contin e_g (d_{xz}, d_{yz}) si b_{2g} (d_{xy}) care sunt π in caracter. Orbitalul b_{2g} (d_{xy}) este implicat in 3B (HOMO) rezultat din interactia cu orbitalii de simetrie "B" ai ligandului ce apartine grupului punctual D_{2h} ia parte direct la tranzitia MLCT ($3B \rightarrow 4B$). Orbitalul 4B (LUMO) are caracter de orbital π^* al ligandului.

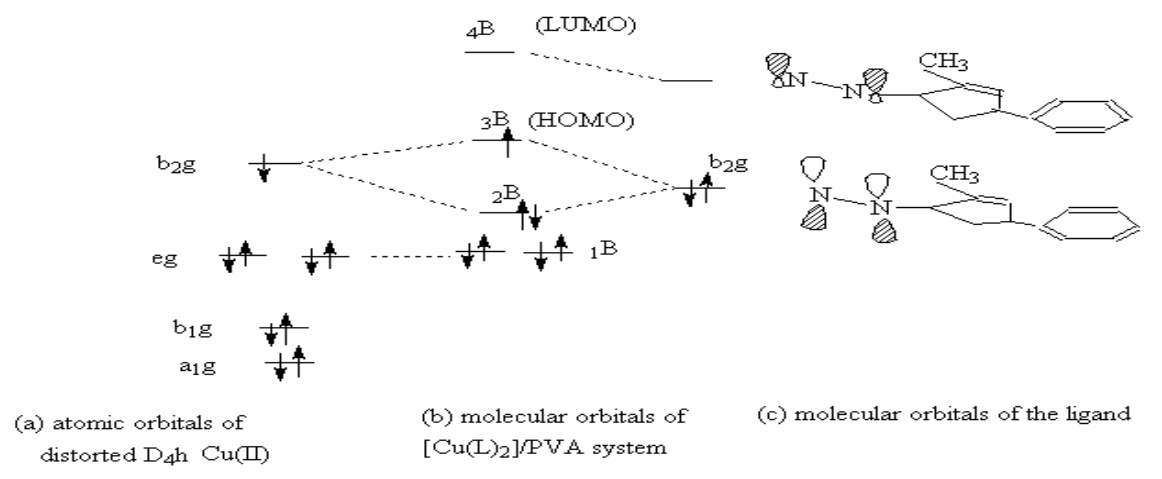


Figure 7. Diagrama de orbitali moleculari ai sistemului $[Cu(L)_2]^0$/PVA: (a) orbitalii atomici ai Cu(II); (b) orbitalii moleculari ai sistemului $[Cu(L)_2]^0$ /PVA; (c) orbitalii moleculari ai ligandului.

Energia transferului de sarcina are o influenta directa asupra marimii coeficientului de hiperpolarizabilitate de ordin doi β_0 conform formulei[13] :

$$\beta_0 = 3\ \Delta\ \mu_{ge}\, M^2_{eg} / (h/2\pi \times \omega_{eg})^2$$

unde:

$\Delta\ \mu_{ge}$ = dipole change between ground state and excited state;

M^2_{eg} = electronic transition moment;

$h/2\pi \times \omega_{eg}$ = energy of optical transition e.g. CT;

In cazul complecsilor de mai sus

$h/2\pi \times \omega_{eg} = \Delta E_{MLCT} = E_{LUMO} - E_{HOMO}$ a tranzitiei MLCT.

Cu cat este mai mare ΔE_{MLCT}, cu ata mai mare este hiperpolarizabilitea β_0. Valoarea energetica a tranzitiei optice a fost calculata cu formula:

$\Delta E_{MLCT} = hc / \lambda_{MLCT} (d_\pi \rightarrow \pi^*)$

si a fost comparata cu ΔE_{MLCT} din complecsii liberi:

$\Delta E_{MLCT}\ d^8\ (Ni^{2+})_{pva} = 484.63.10^{-13}$; $\Delta E_{MLCT}\ d^8\ (Ni^{2+})_{complex} = 489.40.10^{-13}$;

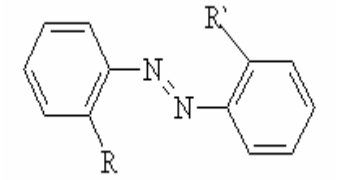
$\Delta E_{MLCT}\ d^8\ (Pd^{2+})_{pva} = 473.09.10^{-13}$; $\Delta E_{MLCT}\ d^8\ (Pd^{2+})_{complex} = 484.63.10^{-13}$;

$\Delta E_{MLCT}\ d^9\ (Cu^{2+})_{pva} = 462.09.10^{-13}$; $\Delta E_{MLCT}\ d^9\ (Cu^{2+})_{complex} = 482.28.10^{-13}$;

Energia ΔE_{MLCT} transitiei metal-ligand descreste atat in compusii coordinativi liberi cat si in sistemele polimerice functionalizate cu compusi coordinativi fata de banda ligandului in ordinea: Ni > Pd > Cu dar deplasarea MLCT spre energii joase este mult mai pronuntata in sistemele polimerice PVA decat in compusii coordinativi. Prin urmare se asteapta valori mari β_0 in PVA functionalizat. Aceasta comportare o explicam ca datorandu-se unei cresteri a distorsiunii simetriei moleculare din jurul ionului metalic de la grupul punctual D_{4h} spre grupuri punctuale asimetrice pe de o parte si o crestere a polaritatii compusilor coordinativi in starea excitata pe de alta parte. Diferenta ΔE_{MLCT} in seria cationilor este rezultatul structurii lor electronice[1] unde structura open shell structure d^9 Cu(II) contribuie la cresterea polaritatii complexului metalic in starea excitata mai mult decat structura closed shell d^8 a Ni(II) si Pd(II).

(ii) Efectul produs de matricea polimerica asupra proprietatile fluorescente ale unei serii de complecsi de Er(III).

a) Liganzii folositi pentru obtinerea complecsilor



R, R` = OH, COOH; -N=N-, or –CH=N-

b) Formula generala a complecsilor [Er(L)$_3$]

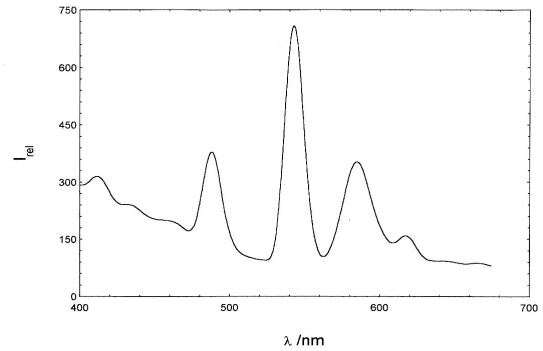
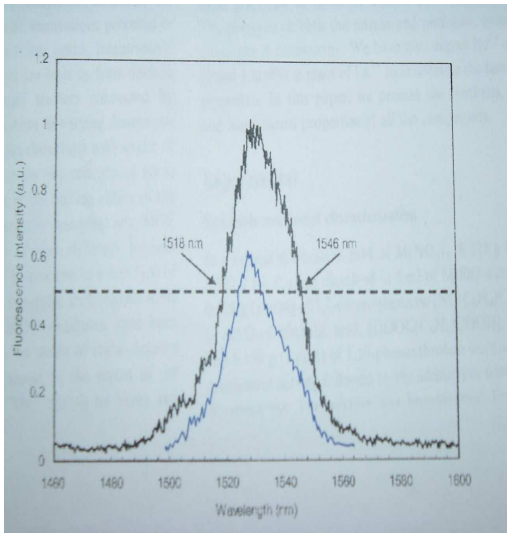


Figure 1. Spectrul de fluorescenta al complexului [Er(DAB)$_3$];
DAB has R, R`=OH; and N=N

Table 3. Atribuirea benzilor din spectrul de emisie al [Er(DAB)$_3$]

Coordination comp.	λ^{max}_{ex} (nm)	Emission λ (nm) and ^nT_j--- ^nT_j transition (j=1,2,3,4,5,6)			
		$^4I_{15/2}\rightarrow {}^4F_{3/2}$	$I_{15/2}\rightarrow {}^4S_{3/2}$	$^4I_{15/2}\rightarrow {}^4F_{9/2}$	$^4I_{15/2}\rightarrow {}^4F_{9/2}$
Er(DAB)$_3$]	300	440	540	590	620

c) efectul produs de matricea polimerica de acid poliacrilic PAA asupra emisiei NIR a Er^{3+}



Tranzitia fluorescenta $^4I_{13/2} - {}^4I_{15/2}$ a Er^{3+} in solution PAA la 355 nm (negru).

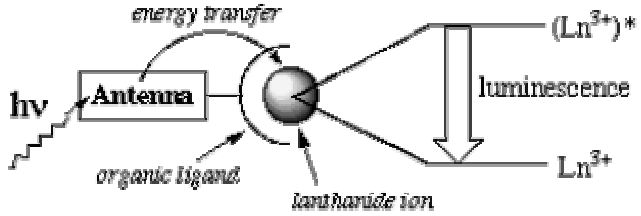
Acidul poliacrilic (PAA) amplifica avntajos tranzitia Er/PAA ~ 1530 nm care prezinta o aliura mai ingusta si mai intense ca la sticlele dopate cu Er(III). .

CONCLUZII

1) In studiului transferului de sarcina s-a constatat influenta benefica a matricei polimerice in optimizarea combinatiilor complexe ca si cromofori pentru optica neliniara. Observatiile mentionate au fost explicate in mod calitativ si cantitativ dar explicarea mecanismelor care stau la baza acestor procese necesita studii aprofundate de viitor pe baza unor tehnici performante recunoscute in acest domeniu.

2) studiul proprietatilor fluorescente a concluzionat ca:

- efectul antenna este mai pronuntat la ligandul azoic DAB decat la bazele Schiff;



- Mediile polimerice cu rol de gazda pot intesifica tranzitia fluorescenta $^4I_{13/2} - {}^4I_{15/2}$ a Er^{3+}, comportarea fiind comparabila cu cea a sticlelor dopate cu Er^{3+} .

❖ LISTA SELECTATA A PUBLICATIILOR SI MANIFESTARILOR STIINTIFICE

➢ Articole stiintifice publicate si in curs de publicare:

1) Multifunction Coordinative Compounds of Er (III) Based On Azo Derivatives And Schiff Bases Ligands As Chromophores In Nonlinear Optics., *Ana Emandi[1], Cristina Vasiliu[2], Marilena Vasilescu[3], Mariana Voicescu[3], Rodica Bandula[3],* Journal of Optoelectronics and Advanced Materials*, (data spre publicare august, 2006).*

2) Magnetic And Spectral Studies On Copper(II) Complexes With 2-Benzothiazolyl Hydrazones. Part. I., *Mirela Calinescu, Ana Emandi, Emilia Ion, Rodica Georgescu.,* Rev. Chem. (data spre publicare septembrie, 2006).

3). The Effect Of Er(III) On The Thermal Behavior Of Azo (-N=N-) and Azomethinic (-CH=N-) Chromophpres*., Mihaela Badea, Rodica Olar, Ana Emandi***,** J. Therm. Anal. Cal., **2006**, 84, 601 – 605.

4) Spectral Studies of Some Ni(II), Pd(II), Cu(II) Azo-Dye Complexes in a Polymeric Matrix of Poly Vinyl Alcohol., *Authors: Ana Emandi,[*] Cristina Vasiliu,[**] Rodica Georgescu,[***] Iulian Ioniță and Mircea Bulinski [****].,* Rev. Chem. (data spre publicare 2005, apare in decembrie 2006).

➢ Comunicari stiintifice

1) 7th **Mediterranean Conference on Calorimetry and Thermal Analysis, MEDICTA 2005, Thessaloniki, Greece, 2-6 july, 2005,** poster PI-2, Book of abstracts pg. 53.
Ana Emandi, Mihaela Badea, Rodica Olar, Stefania Stoleriu
`The effect of Er(III) on the thermal behavior of azo (-N=N-) and azomethynic (-CH=N-) chromophores`,

2) 4ème Colloque Franco-Roumain de Chimie Appliquée

N°: Titre : COMPLEXES DU CUIVRE (II) AVEC 2-BENZOTHIAZOLYL HYDRAZONES. SYNTHESE, CARACTERISATION ET ACTIVITE ANTIBACTERIENNE

Auteurs : *Mirela CĂLINESCU[1], Emilia ION[2], Ana EMANDI[1], Rodica GEORGESCU[3], Octavian CĂLINESCU[1], Ticuța NEGREANU-PÎRJOL[4]*

3) ROCAM- Bucharest Romania, 12-14, September, 2006,

Multifunction Coordinative Compounds Of Er (III) Based On Azo Derivatives And Schiff Bases Ligands As Chromophores In Polyacrylic Matrix For Nonlinear Optic., *Ana Emandi[1], Cristiana Grigorescu [2], Cristina Vasiliu[2], M. Elisa[2], Mirela Calinescu [1]*