

Advanced Materials Research
Volumes 1-2 (1994)

Physical Chemistry of Solid State Materials

- REMCES VI -

Proceedings of the 6th International Seminar on
the Physical Chemistry of Solid State Materials,
El Jadida, Morocco, 1993



Editors:

J. Aride
A. Bendriss
K. Benkhoulja
A. Boukhari
A. El-Jazouli
I. Mansouri
A. Nadiri
B. Tanouti
M. Zahir
D. Zakaria

SCITEC PUBLICATIONS

Physical Chemistry of Solid State Materials

- REMCES VI -

Proceedings of the 6th International Seminar on the Physical
Chemistry of Solid State Materials, El Jadida, Morocco, 1993

Edited by

J. Aride

A. Bendriss

K. Benkhoulja

A. Boukhari

A. El-Jazouli

I. Mansouri



SCITEC PUBLICATIONS

Copyright © 1994 Scitec Publications Ltd, Switzerland
Member of the Trans Tech Group of Publishers

ISBN 3-908450-05-5

Volumes 1-2 of
Advanced Materials Research
ISSN 1022-6680

Distributed in the Americas by

Trans Tech Publications Ltd
LPS Distribution Center
52 LaBombard Rd. North
Lebanon, NH 03766
USA

Phone: (603) 448 0037

Fax: (603) 448 2576

and worldwide by

Trans Tech Publications Ltd
Hardstrasse 13
CH-4714 Aedermannsdorf
Switzerland

Fax: (++41) 62 74 10 58

E-Mail: scitec@transtech.ch

Advanced Materials Research

ISSN 1022-6680

Advanced Materials Research specializes in the rapid publication of international conference proceedings in every area of Materials Science, Solid State Physics and Solid State Chemistry. This permits such proceedings to be conveniently referenced, abstracted and read. It also guarantees that the proceedings are available in major libraries within two to three months of the close of the conference. *Advanced Materials Research* also publishes, on a regular basis, collections of research and review papers on topics of current interest.

Advanced Materials Research is published by Scitec Publications, Member of the Trans Tech Group of Publishers.

Please ask for more details or place your order:

Editorial Office:

Scitec Publications
Hans Neber-Aeschbacher
Untermueli 11
CH-6300 Zug
Switzerland

Fax: (++41) 42 32 52 12
e-mail: amr@scitec.ch

Subscriptions:

Trans Tech Publications
Subscriptions Department
Trottenstrasse 20
CH-8037 Zürich
Switzerland

Fax: (++41) 1 272 10 92
e-mail: amr@transtech.ch

Scitec Publications Ltd.

Member of the Trans Tech Group of Publishers

Untermueli 11 - CH-6300 Zug - Switzerland
Fax (++41) 42 32 52 12 - e-mail: scitec@scitec.ch

Physical Chemistry of Solid State Materials

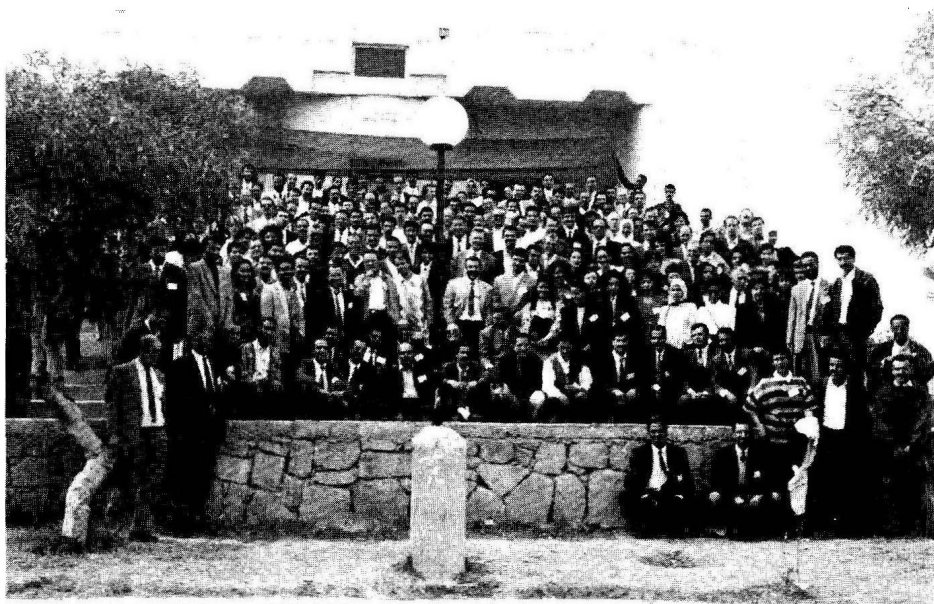
PREFACE :

REMCES (the acronym is formed from the French title of the Moroccan Forum for Solid State Chemistry) meets every two years to discuss the latest advances in the physical chemistry of solid state materials. Numbers of participants have grown from **50 participants** at the first meeting, held in **Rabat** in **1983**, to **300** at the sixth meeting which took place in **El Jadida** from October 28 to 30, **1993**.

This sixth meeting, entitled International Seminar of Physical Chemistry of Solid State Materials, brought together researchers from Algeria, France, Germany, Japan, Spain, Switzerland and Tunisia, as well as from Morocco itself.

The aims of the seminar were to discuss the progress of scientific research, strengthen ties between industry and universities, and promote cooperation in the field of solid state chemistry at national and international level. The topics presented covered methods of preparing solid state materials, their physical properties and industrial applications.

The coordinating committee



Group photo

ACKNOWLEDGEMENTS

* * * * *

The organizing committee wishes to thank the following :

- **The Minister for National Education** for his interest in this meeting, for his encouragement and support, and for the honour he conferred on us by chairing the opening session of the meeting;
- **The Governor** of the Province of El Jadida for the facilities he generously accorded us ;
- **The Rector of Chouaïb Doukkali University, El Jadida**, for his help and encouragement during the preparation of the meeting ;
- **The Dean of the Faculty of Science of Chouaïb Doukkali University, El Jadida**, for his interest in the meeting and his encouragement throughout the period of preparation.
- **The Municipal Council of the Town of El Jadida**, for contributing materially to the organisation of this meeting.

We thank the following warmly for their support and financial assistance :

- The Ministry of National Education
- The Rectorate of Hassan II University, Ain Chock, Casablanca
- The Rectorate of Cadi Ayad University, Marrakesh
- The Rectorate of Moulay Ismaïl University, Meknes
- The Faculties of Science at the following Universities :
 - Hassan II University, Ain Chock, Casablanca
 - Hassan II University, Ben M'sik, Casablanca
 - Cadi Ayad University, Semailia, Marrakesh
 - Moulay Ismaïl University, Meknes
- Ecole Supérieure de Technologie, Casablanca
- Centre National de Coordination et de Planification de la Recherche Scientifique et Technique.
- ORMVA Doukkala

We wish to express particular thanks to the company SEDEL for their generous support.

Our thanks are also due to the following companies :

- SOMADIR
- Digital Equipement, Casablanca
- Africaine de Bureautique, Casablanca
- Etablissement G. MOYAT
- ERAMEDIC

Finally, we gratefully acknowledge the continuing and efficient help and support given by the staff of the faculty of Science, El Jadida, and by Miss BELLEKHAL and Mrs Alatheia EL HAJBI.

GUEST EDITORS :

J. Aride
A. Bendriss
K. Benkhoulja
A. Boukhari
A. El-Jazouli

I. Mansouri
A. Nadiri
B. Tanouti
M. Zahir
D. Zakaria

ORGANIZING COMMITTEES

NATIONAL COMMITTEE :

J. Aride
S. Bendaoud
A. Bendriss
K. Benkhoulja
A. Boukhari
M. El Atmani
L. El Ammari
A. El-Jazouli
B. El Ouadi
A. Erragh
F. Erragh
H. Hannache
M. Lamire
A. Maazaz

I. Mansouri
B. Mernari
R. Moussa
N. Nadi
A. Nadiri
M. Rafiq
A. Rhandour
A. Sadel
A. Tairi
B. Tanouti
M. Zahir
D. Zakaria
M. Zriouil

LOCAL COMMITTEE :

A. Sadel
A. Aamili
L. Badrour
A. Bendriss
K. Benkhoulja
M. Diouri
F. Erragh
M. Fouad

A. Khaoulani
E. Khlar
B. Mernari
F.E. Mouahid
A. Tazi
M. Zahir
D. Zakaria

CONTENTS

Preface	v
Acknowledgements	vii
Guest Editors and Committees	ix
 Light-Converting Molecular Devices: Energy-Transfer Processes in Lanthanide Dinuclear Complexes	
J.-C.G. Bünzli, P. Froidevaux and C. Piguet	1
 Electrochemical Oxygen Intercalation: A New Chimie Douce Route to High Oxidation States of Transition Metal Oxides	
M. Pouchard, A. Demourgues, F. Weill, A. Villesuzanne, A. Wattiaux and J.C. Grenier	11
 Ceramic Fibers from Organosilicon Precursors	
R. Naslain, R. Pailler, G.Chollon, R. Bodet and H. Hannache	19
 Thermal Shock and Fatigue Behaviour of Ceramics	
G. Fantozzi, D. Olagnon and M. Saadaoui	35
 Densification of Yttria Ceramics	
J.-F. Baumard, G. Gasgnier, H. Vesteghem, M. Boncoeur and M. Bougoïn	47
 Dielectric Properties in Nickel-Doped Barium-Strontium Titanate Ceramics	
T. Fukami	55
 Structural Relationships and Magnetic Behaviour in R_2BaMO_5 Oxides (R=Rare Earth; M=Co, Ni and Cu)	
R. Saez-Puche and J. Hernandez-Velasco	65
 Photoluminescent Metaphosphates Activated by Monovalent Silver	
M. Mesnaoui, C. Parent, B. Tanguy, M. Maazaz, G. Le Flem, 7B. Moine and C. Pedrini	83
 Electronic Structure of LaF_9^{6-}, YF_9^{6-} and EuF_9^{6-} Clusters Calculated by the MS-LSD Method	
I. Gérard, H. Chermette and J.C. Krupa	89
 Infrared to Visible Upconversion of Tm^{3+} Doped BIGaZYbTZr Glasses	
B. Jacquier, R. Mahiou, J.L. Adam and J. Lucas	101
 Vitrification of Phosphates of Nasicon-Type Structure	
A. Eljazouli	105

Intercalation of Organic and Inorganic Anions into Anionic Clays A. De Roy, C. Forano and J-P. Besse	115
Phase Transitions in V_2O_5 Intercalation Compounds H. Katzke and W. Depmeier	129
Relaxation Study in Y_2O_3 after Polarization Induced by an Electron Beam G. Moya, A. Sami and D. Moya-Siesse	137
Precipitation and Formation Mechanism of Type AB Carbonate Apatites Analogous to Dental Enamel A. Barroug, C. Rey and J.C. Trombe	147
Removing Cadmium from Phosphate Ores by Pyrometallurgical Process A. Nounah, M. Ferhat and J.L. Lacout	155
Optimization of a Hydraulic Calcium Phosphate Cement E. Mejdoubi, J.L. Lacout, J.C. Heughebaert and P. Michaud	163
A New Nasicon-Like Phosphate $Co_{0.5}Ti_2(PO_4)_3$ A. El Bouari, A. El Jazouli, J.M. Dance, G. Le Flem and R. Olazcuaga	173
The Structure of the High Temperature Forms of $Cu_{0.5}^{II}Ti_2(PO_4)_3$ and $D_{0.5}Cu_{0.5}^I Zr_2(PO_4)_3$ R. Olazcuaga, G. Le Flem, A. Boireau and J. L. Soubeyroux	177
Synthesis and Biocompatibility of New Materials M. Draoui, M. Imbenotte, G. Palavit, L. Montagne and L. Benarafa	189
Investigations of the Acid Properties of the Chabasite-Type Silico-aluminophosphate SAPO-34 Synthesized with Morpholine as the Organic Template M. Achache, H. Kessler and A. Azzouz	195
Synthesis and Crystal Chemistry of the Rare Earth Phosphate: $HoPO_4 \cdot xKOH$ ($x \leq 1$) M. Zaki, A. Aamili, M. El Ghazzi, D. Zambon, M. Zahir, A. Sadel and J.C. Cousseins	201
Crystal Structures of the Isotypical Tetrametaphosphates: $Cd_{0.50}Co_{1.50}P_4O_{12}$ and $Cd_{0.37}Ni_{1.63}P_4O_{12}$ A. Alaoui El Belghiti, A. El Marzouki, A. Boukhari and E.M. Holt	209
Preparation and Characterisation of the Compounds $MFePO_5$ ($M=Ni, Cu$) M. Touaiher and A. El Hajbi	215

New Compounds in the $\text{Bi}_2\text{O}_3\text{-MO-P}_2\text{O}_5$ (M=Cu, Ni) Systems at 800°C	
F. Abraham, M. Ketatni and B. Mernari	223
Polymorphism, Structural and Physical Properties of $\text{Pb}_3(\text{VO}_4)_2$ Related Solid Solutions	
A. Mizrahi, M. Drache, P. Conflant, J.P. Wignacourt, A. Lorriaux-Rubbens and F. Wallart	233
Air Jet Micronisation and Reactivity of Micronised Powders	
M. Ouammou, L. Clerc, A. Benhassaine and A. Nadiri	243
Influence of Testing Temperature on the Weibull Modulus of Post-Hipped $\alpha\text{-SiC}$	
F. Osterstock and A. Charif	249
Damage Accumulation in a Unidirectional SiC-MAS.L Composite Material Tested under Uniaxial Tensile Loading	
M. Drissi-Habti and M.Gomina	257
The Wear Characteristics of Ceramic/Ceramic and Ceramic/Metal Pairs	
J. Takadoun, Z. Zsiga and C. Roques-Carnes	267
Synthesis and Characterization of Siliconated Polymers Fluorinated or not, from Hydroxylterminated Liquid Polybutadienes	
B. Ameduri, B. Boutevin, M. Nouri and M. Talbi	283
Vitrification of the Systems Water-Propanediol 1,2	
A. Nakheli, N. Lotfi and J. Huck	287
Vitrification and Crystallization of the Systems Propylene Carbonate-Toluene	
N. Lofti, A. Nakheli and J. Huck	293
Synthesis Characterization and Protonic Conduction in Mixed Caesium-Ammonium Hydrogenosulphate $\text{Cs}_{0.95}(\text{NH}_4)_{0.05}\text{HSO}_4$	
H. Khemakhem, T. Mhiri, Z. Fakhfakh and A. Daoud	299
Low Temperature Modulated Phase in the Two Dimensional Compound $(\text{C}_3\text{H}_7\text{NH}_3)_2\text{PbCl}_4$	
Y. Abid, M.Kamoun, A.Daoud and F.Romain	309
Synthesis and Crystal Structure of Bis (3,5-Dicarboxypyrazole)-Bis (Aqua) Copper(II) Dihydrate	
B. Mernari, F. Abraham and M. Lagrenee	317
Electrolytic Codeposition of Gold and Synthetic Diamond Particles	
M. Bendahmane, J. Ginies, M. Tachez, M.-P. Gigandet and J. Picaut	325

Effect of Slightly Solubles Solutes on the Recrystallization of Rolled Silver

F. Salhi, J. Aride, J. Bernardini and G. Moya 333

Observation of the Atomic Structures of (111) Σ 3 Boundaries in the Intermetallics Ni₃Al (L₁₂) and TiAl (L₁₀)

C. Derder, R. Bonnet and J.M. Penisson 337

High Temperature XRD and DTA Studies of Sr₃Cu₅O₈, Bi_{1.6}Pb_{0.4}Sr₂CaCu₂O_x, and Sr_{14-y}Ca_yCu₂₄O_z Compositions

H. Faqir, G. Vacquier, P. Conflant and A. Casalot 345

Thermogravimetric Analysis of the Removal of Organic Binders and Plasticizers from an Alumina Matrix

M. El Morabit, J.P. Millet, M. Murat and G. Fantozzi 355

Defects Induced in Silicon by Rapid Thermal Processing

B. Hartiti, H. Amzil, D. Sayah, J.C. Muller and P. Siffert 361

Metakaolinite Behaviour in Aqueous Suspension, the Relationship between Behaviour and Structure

M. Chamoumi, E. Garcia-Diaz, A. Crespy and A. Benhassaine 369

Experimental and Theoretical Approaches to the Internal Stress Field in an Annealed Nickel Base Superalloy

R. Bonnet and A. Ati 375

Vacancy Defects Recovery of Quenched Ni₂Si Intermetallic Compound

A. Jennane, E.H. Sayouti, J. Bernardini, P. Moser and G. Moya 385

Effects of Annealing and Ion Bombardment on Structure and Composition of Ti-Al Alloy Films

M. Fahoume, M. El Khamlichi, C. Baltzinger and C. Burggraf 391

Influence of Thermal Annealing Atmosphere on Electrical Properties of Polycrystalline Silicon Grain Boundaries

N. M'Gafad, H. Amzil, B.M. Semega and D. Sayah 399

Thermal Non Destructive Detection of Defect in Multilayer Wall

S. Belattar, A. Elouahlouli and B. Duthoit 405

Structural Approach of Glasses Belonging to the Li₂O-Li₂WO₄-P₂O₅ Ternary System

A. Nadiri, A. Yacoubi, L. Bih, M. Haddad and A. Levasseur 413

ESR Study of Paramagnetic Centers in Irradiated Phosphate Glasses

M.E. Archidi, M. Haddad, A. Nadiri and R. Berger 421

Physico-Chemical Properties of an Hybrid Glass

J.C. Bureau, A. Bakkali, Z. Sassi, C. Mai, J.F. Cornu and F. Babonneau 427

Contribution of Raman and Luminescence Spectroscopies to the Investigation of Phase Demixion in the System $\text{Bi}_x\text{Ln}_{(1-x)}\text{VO}_4$	
A. Lorriaux-Rubbens, J. Corset, J. Ghamri and H. Baussart	433
Correlations between Mn(III) Optical Spectroscopy and Structural and Magnetic Properties in $\text{Ti}_2\text{MnF}_5\cdot\text{H}_2\text{O}$ Single Crystals	
P. Nuñez, F. Rodriguez and M.C. Marco de Lucas	447
Luminescence Properties of Heavily Doped $\text{CaF}_2 : \text{Mn}^{2+}$	
A. Aamili, R. Mahiou, D. Avignant, S. Chou, J.C. Cousseins, M. Zahir and A. Sadel	453
Dielectric Properties of Carbon Black-Epoxy Resin Composites in the Frequency Range of 100Hz-15MHz	
M.E. Achour, L. Salome, K. Benaboud, F. Carmona and J.L. Miane	461
Ferroelastic Domain Study in Crystals with Formula K_3TiOF_5, $\text{K}_3\text{MO}_2\text{F}_4$ and $\text{K}_3\text{M}'\text{O}_3\text{F}_3$ ($\text{M} = \text{Nb, Ta}$; $\text{M}' = \text{Mo, W}$)	
M. Fouad, J.P. Chaminade, J. Ravez and A. Sadel	469
Anionic Conductivity in Fluorapatites: Correlation between Structure and Electrical Properties	
A. Laghzizil, A. Bouhaouss, M. Ferhat, P. Barboux, R. Morineau and J. Livage	479
Conductimetric Determination of the Isotherms 25°C of Ternary Systems $\text{H}_2\text{O}-\text{M}_2\text{HPO}_4-(\text{NH}_4)_2\text{HPO}_4$ ($\text{M} = \text{Na, K}$)	
M. Nadifiyine, R. Lazrak, B. Tanouti, A. Mokhlisse, J. Guion, R. Tenu, J. Berthet and J.J. Counieux	489
Conductivity and Viscosity Studies of Lithium Ion Conductive Electrolytes Gelled with Poly(Methylmethacrylate)	
M. Rezrazi, M. Mullet and O. Bohnke	495
Dependence of the Stored Elastic Energy at Copact Cubic/Cubic Heterointerfaces on the Lattice Misfit	
A. Bouzaher and R. Bonnet	501
$\text{Ag}_2(\text{UO}_2)_2\text{V}_2\text{O}_8$: A New Compound with the Carnotite Structure. Synthesis, Structure and Properties	
F. Abraham, C. Dion, N. Tancet and M. Saadi	511
Theoretical Study of Electro-Optic Effect in the Tetragonal Phase of BaTiO_3 and PbTiO_3	
D. Khatib, B. Jannot and L. Lifsal	521
Effects of Molecular Hydrogen on Electrical Properties of Multicrystalline Silicon Grain Boundaries	
N. M'Gafad, H. Amzil and D. Sayah	531

Thermally Stimulated Current Study of Molecular Motions in Pentachlorotoluene	
A. Bennis, N. Hitmi, A. Lamure and C. Lacabanne	537
Crystallographic and Magnetic Study of Mixed Pyrophosphates $Zn_xM_{2-x}P_2O_7$ ($0 \leq x \leq 2$) (M=Mn, Co, Ni, Cu)	
M. Bettach, K. Benkhrouja, A. Sadel, M. Zahir and M. Drillon	543
Magnetic Properties of some Copper and Nickel Tellurates and Tellurites	
S. Bendaoud, J. Aride, M. Taibi, M. Belaiche, A. Boukhari and M. Drillon	553
Synthesis, Crystal Structure and Magnetic Properties of a Dinickel (II) Complex with 3,6-Diformyl-Pyridazine Dioxime	
B. Mernari, F. Abraham and M. Lagrenee	563
Polynuclear Ferromagnetic Ni(II) Complexes with Pseudohalide as Bridging Ligands	
J. Ribas, M. Monfort, C. Diaz, A. Escuer, R. Vicente, M. Salah El Fallah, X. Solans and M. Font-Bardia	573
Magneto-Structural Correlations in 1-D μ-(1,3-Azido)Nickel(II) Complexes	
A. Escuer, R. Vincente, J. Ribas, M. Salah El Fallah, X. Solans and M. Font-Bardia	581
Stability of a Spanish Sepiolite in Neutral and Basic Media	
S. Martinez-Ramirez, F. Puertas and M.T. Blanco-Varela	587
Study of the Reaction at the Cr/Si Interface	
A. Bouabellou, R. Halimi and N. Benouattas	593
Model of Formation of Thin Insulating Films on Silicon	
J.C. Bureau, K. Chafik, Z. Sassi, B. Balland and A. Glachant	601
The Magnesium Oxide- Mono Aluminium Phosphate Reaction: Mechanism and Concentration Dependence	
I. Borges, J.P. Wignacourt, J.C. Boivin, A. Nonat, A. Lorriaux-Rubbens, F. Wallart and J.M. Canini	609
An Alternative Process for the Valorization of Natural Phosphates: Natural Microphosphates and Reactivity	
M. Ouammou, A. Banhassaine and A. Nadiri	621
Adherence Measurement of Duplex Systems onto Cold Rolled and Zinc Coated Steels	
M. Bouzirri, A. Roche, L. Brochard and L. Pege	627

A Coprecipitation Process Using Heterocyclic Diacids for the Preparation of Conducting Oxides

S. Nadir, J.P. Wignacourt, M. Drache, P. Conflant, M. Lagrenee
and B. Mernari

633

Behaviour of the Alloys F17Ti and AISI 304 in an Atmosphere Containing Hydrogen Sulphide at High Temperature

A. Nyassi, A. Bendriss and J.P. Larpin

639

Gettering of Metallic Impurities by Rapid Thermal Processing

B. Hartiti, H. Amzil, D. Sayah, J.C. Muller and P. Siffert

649

Author Index

657

Keyword Index

661

LIGHT-CONVERTING MOLECULAR DEVICES: ENERGY-TRANSFER PROCESSES IN LANTHANIDE DINUCLEAR COMPLEXES

J.-C.G. Bünzli¹, P. Froidevaux¹ and C. Piguet²

¹ Institute of Inorganic and Analytical Chemistry, University of Lausanne,
CH-1005 Lausanne, Switzerland

² Department of Inorganic, Analytical and Applied Chemistry, University of Geneva,
CH-1211 Geneva-4, Switzerland

Keywords: Lanthanide, Rare Earth, Luminescence, Energy Transfer, Probe, Light Conversion, Calixarene, Dinuclear Complexes, Self-Assembly, Triple Helical Complexes, Aromatic Polyamines

Abstract

The design of efficient light-converting molecular devices containing a lanthanide ion is discussed. In order to unravel the energy transfer processes taking place in such a device, two series of model dinuclear complexes are studied : coordination compounds with calixarenes and self-assembled triple helical complexes based on aromatic polyamines.

Introduction

The 4f-block elements form an extended series of trivalent cations with the same formal charge and with similar chemical properties, mostly due to very weak ligand-field effects. The $4f^n5s^25p^6$ electronic configuration is indeed special in the sense that 4f electrons are shielded by the 5s and 5p subshells, resulting in atom-like absorption and emission spectra. The latter are easy to identify and make luminescent probes based on Eu(III) and Tb(III) especially efficient (Fig. 1). The development of luminescent chemical probes and sensors is the subject of intensive research, both in natural and medical sciences [1][2]. Furthermore, trivalent lanthanide ions may be incorporated into supramolecular complexes acting as molecular photonic devices [3]. In these nanometric machines, the various steps of the overall process involving absorption of light, transfer and re-emission at another wavelength are performed separately by distinct parts of the complex molecule. Such supramolecular constructions are termed light-conversion molecular devices.

To design a good europium (or terbium) luminescent sensor, a unique combination of features must be realized : (i) protection of the included ion from quenching due to the interaction with solvent molecules and/or high-energy vibrations from the ligating groups, (ii) presence of multiple absorbing groups suitable for energy transfer (antenna effect [2]), (iii) high thermodynamic stability and kinetic inertness, and (iv) non-toxicity of the sensor if it is to be used in *in vivo* applications.

The yield of the energy transfer between the donor and the acceptor is related to the donor-acceptor distance. Determination of this distance allows one to realize a fluorescent mapping of large molecules such as proteins, leading to useful structural information, or to calculate the distance between ion sites [1]. In order to unravel the intimate mechanism of energy-transfer processes both between an organic chromophore and a Ln(III) ion and between two lanthanide ions, we have undertaken the study of several classes of heterodinuclear complexes. This paper presents some of the results obtained these last three years on dinuclear complexes with calixarenes and planar multidentate nitrogen-containing ligands analogous to terpyridine.

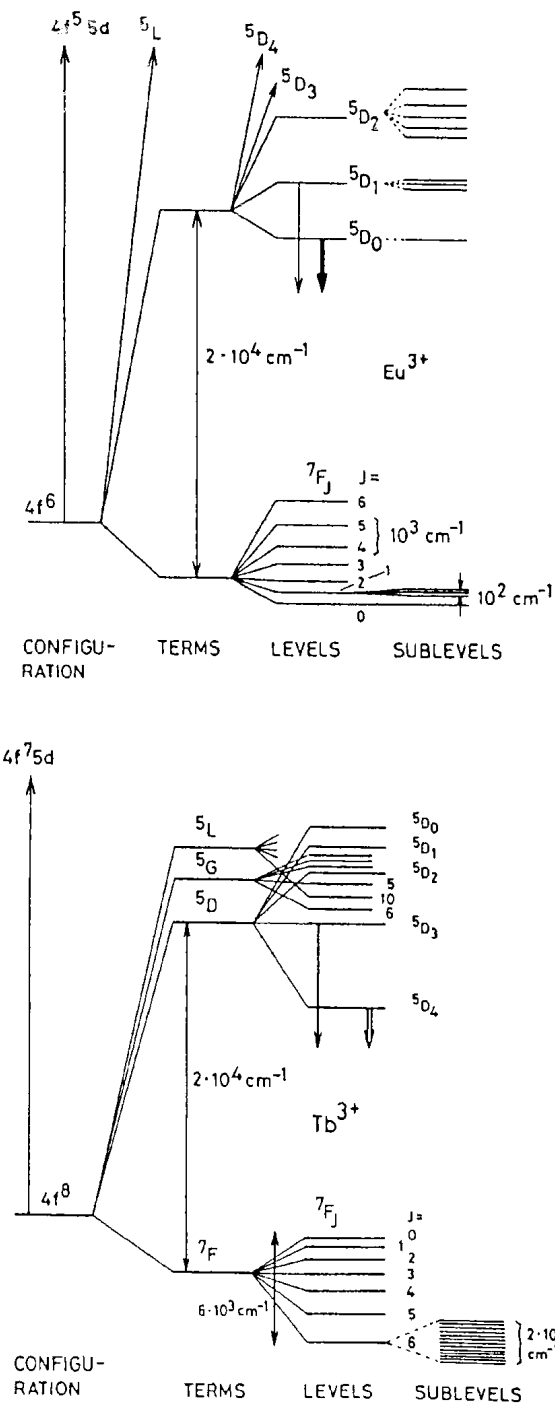


Figure 1 : Partial energy level diagrams for Eu^{III} and Tb^{III} .