UNIVERSITÀ
DEGLI STUDI
FIRENZE

DIPARTIMENTO
DI CHIMICA
"UGO SCHIFF"

DOTTORATO DI RICERCA IN
SCIENZE CHIMICHE

Il Coordinatore

Collegio dei Docenti del Dottorato di Ricerca in Scienze Chimiche

Verbale della riunione del 19/02/2015

Il Collegio dei Docenti del Dottorato di Ricerca in Scienze Chimiche si riunisce nella Biblioteca lato organica del Dipartimento di Chimica "Ugo Schiff" alle ore 12.30 del 19/2/15 con il seguente ordine del giorno:

1. Comunicazioni
2. Approvazione verbale
3. Richieste sospensione corso di Dottorato
4. Richieste valutazione compatibilità corso di Dottorato con altre attività
5. Richieste attività didattica integrativa
6. Esclusione dal corso di Dottorato
7. Convenzione di co-tutela
8. Didattica anno 2015
9. Varie ed eventuali

Il numero legale viene raggiunto alle ore 12.35

Sono indicati con P i presenti con G gli assenti giustificati.

Baglioni Piero	
Bencini Andrea	
Bianchi Antonio	P
Bonini Massimo	P
Brandi Alberto	P
Capperucci Antonella	P
Cardini Gianni	P
Cincinelli Alessandra	G
Costagliola Pilario	P
Dei Luigi	G
Del Bubba Massimo	G
Felli Isabella	G
Fragai Marco	P
Fratini Emiliano	P
Giorgi Rodorico	G
Goti Andrea	P

Dottorato di Ricerca in Scienze Chimiche
Prof. Andrea Goti, Coordinatore
Via della Lastruccia, 3/13 – 50019 Sesto Fiorentino (FI), Italy
Phone (direct): +39 055 4573505; fax: + 39 055 4573531; e-mail: andrea.goti@unifi.it
P.IVA | Cod. Fis. 01279680480

Guarna Antonio	
Lo Nostro Pierandrea	P
Mandò Pier Andrea	G
Marrazza Giovanna	P
Menichetti Stefano	P
Messori Luigi	G
Minunni Maria	G
Mordini Alessandro (ICCOM-CNR)	P
Occhiato Ernesto Giovanni	P
Papini Anna Maria	P
Procacci Piero	G
Salvini Antonella	P
Sessoli Roberta	G
Smulevich Giulietta	P
Sorace Lorenzo	P
Udisti Roberto	

Rappresentanti dei dottorandi:

Presiede la seduta il Prof. Andrea Goti
Assume le funzioni di segretario verbalizzante il Dott. Roberto Di Camillo

1. Comunicazioni

- I dottorandi devono eleggere i due nuovi rappresentanti in sostituzione di Lorenzo Poggini e Federica Scaletti che hanno terminato il terzo anno di corso
- i dottorandi hanno comunicato che stanno organizzando il PhD-Day[6], che dovrebbe tenersi il 27 maggio 2015
- gli esami finali del XXVII ciclo sono in corso di svolgimento: le due Commissioni che hanno già esaminato i dottorandi previsti hanno generalmente mostrato grande apprezzamento del lavoro svolto

2. Approvazione verbale

Viene messo in approvazione il verbale del 15/01/2015.
Approvato all'unanimità

3. Richieste sospensione corso di Dottorato

Miriam Marconi, dottoranda del XXVI ciclo (tutore Roberto Udisti, titolo tesi "Ricostruzione di record paleoclimatici e paleoambientali dalla composizione geochimica di carote di sedimenti marini. Progetti internazionali ANDRILL e HOLOCLIP"), ha chiesto la

sospensione dal dottorato per maternità con gravidanza a rischio dal 28/1/2015 fino a tre mesi dopo la data effettiva del parto (data presunta del parto 25/7/2015).
Approvato all'unanimità

Pamela Ferrari, dottoranda del XXX ciclo (tutore Rodorico Giorgi, titolo tesi "Fading dei coloranti moderni: studio dei meccanismi di reazione e di possibili soluzioni attraverso la sintesi di nuovi prodotti per la loro conservazione"), ha chiesto la sospensione dal dottorato per per poter assolvere al servizio civile regionale ai sensi dell'art. 17 comma 10 del D.R. 670/2013 Regolamento del Dottorato dal 25/2/2015 al termine o interruzione dello stesso (periodo previsto 1 anno).
Approvato all'unanimità

Elena Lenci, dottoranda del XXIX ciclo (tutore Antonio Guarna, titolo tesi "Sintesi orientata alla diversità di glico- e/o peptidomimetici come modulatori dell'interazione proteina/proteina"), ha chiesto la sospensione dal dottorato per motivi di studio per poter frequentare il Tirocinio Formativo Attivo dal 26/2/2015 alla conclusione del corso (data presunta 31/7/2015).
Approvato all'unanimità

Stefania Mirabella, dottoranda del XXIX ciclo (tutore Francesca Cardona, titolo tesi "Sintesi di ammino e imminozuccheri per la decorazione di biomateriali"), ha chiesto la sospensione dal dottorato per motivi di studio per poter frequentare il Tirocinio Formativo Attivo dal 14/2/2015 alla conclusione del corso (data presunta 31/7/2015).
Approvato all'unanimità

4. Richieste valutazione compatibilità corso di Dottorato con altre attività
Chiara Ruberto, dottoranda senza borsa del XXIX ciclo (tutore Lorenzo Giuntini (INFN); co-tutore: Pier Andrea Mandò, titolo tesi "Creazione di mappe di distribuzione elementale mediante l'uso della fluorescenza a raggi x (XRF)"), chiede la valutazione della compatibilità con lo svolgimento di attività lavorativa retribuita come tutore per la Scuola di Scienze Matematiche, Fisiche e Naturali, corso di Laurea in Diagnostica e Materiali per la Conservazione e il Restauro essendo risultata vincitrice del bando Tutor 2015. Il bando prevede 600 ore complessive di tutoraggio con un minimo di 10 ore settimanali. Il tutore e co-tutore sono favorevoli all'accoglimento della richiesta.
Approvato all'unanimità

Sono stati ampiamente dibattuti i limiti di impegno previsto entro i quali sia lecito concedere a dottorandi il nulla osta per svolgere attività non congruenti a quelle previste nell'ambito del progetto di ricerca del dottorato. Unanimemente viene considerato che il limite più grande sia dovuto all'attuale normativa, che non consente l'estensione del periodo di dottorato e dello

status di dottorando oltre i tre anni canonici. A questo proposito Giulietta Smulevich e Anna Maria Papini propongono di predisporre una richiesta da inoltrare al MIUR e in cc alla CRUI per chiedere che come in altri paesi europei, venga consentito un prolungamento del periodo di dottorato oltre i tre anni con mantenimento dello status di dottorando, soprattutto nel caso in cui i dottorandi siano coinvolti in attività formative non conformi alle normali attività di ricerca.

5. Richieste attività didattica integrativa

Daniele Frosini, XXVIII ciclo, chiede l'autorizzazione a svolgere attività di didattica integrativa per 15 ore complessive, consistente in assistenza al laboratorio del corso di Chimica Analitica Ambientale - Componenti Inorganici presso il Corso di laurea in Scienze Chimiche di cui è titolare il Prof. Roberto Udisti. Il tutore è favorevole ed il Consiglio di Corso di Laurea ha già approvato. Il Coordinatore propone di rilasciare il nulla osta per la presentazione della richiesta di assegnazione presso il Consiglio di Dipartimento in Chimica.
Approvato all'unanimità

Fabio Giardi, XXX ciclo, chiede l'autorizzazione a svolgere attività di didattica integrativa per 15 ore complessive, consistente in assistenza al laboratorio del corso di Chimica Analitica Ambientale - Componenti Inorganici presso il Corso di laurea in Scienze Chimiche di cui è titolare il Prof. Roberto Udisti. Il tutore è favorevole ed il Consiglio di Corso di Laurea ha già approvato. Il Coordinatore propone di rilasciare il nulla osta per la presentazione della richiesta di assegnazione presso il Consiglio di Dipartimento in Chimica.
Approvato all'unanimità

Laura Caiazzo, XXX ciclo, chiede l'autorizzazione a svolgere attività di didattica integrativa per 15 ore complessive, consistente in assistenza al laboratorio del corso di Laboratorio di Chimica Analitica II presso il Corso di laurea in Chimica di cui è titolare la Dr.ssa Rita Traversi. Il tutore è favorevole ed il Consiglio di Corso di Laurea ha già approvato. Il Coordinatore propone di rilasciare il nulla osta per la presentazione della richiesta di assegnazione presso il Consiglio di Dipartimento in Chimica.
Approvato all'unanimità

6. Esclusione dal corso di Dottorato

Ai sensi dell'art. 18 comma 2 e art. 19 del D.R. 670/2013 Regolamento del Dottorato, il Collegio dei docenti propone al Rettore l'esclusione dal corso di Dottorato di Mohammadhamed Ardakani, iscrittosi al XXIX ciclo del corso di dottorato ma mai presentatosi né avendo mai risposto ai messaggi inviati di posta elettronica, per i motivi di cui al punto c, comma 1, art. 19 del citato Regolamento, ovvero assenze ingiustificate e prolungate.
Approvato all'unanimità

7. Convenzione di co-tutela
È pervenuto il testo della convenzione per la co-tutela in ingresso di Guglielmo Fernandez Garcia, dottorando dell'Università di Rennes, con Federico Totti tutore presso l'Università di Firenze. Viene messo in approvazione il testo della convenzione di co-tutela (Allegato 1).
Approvato all'unanimità

8. Didattica anno 2015
In Allegato 2 sono riportati i corsi attivati per l'anno 2015, ovvero tutti quelli precedentemente proposti ai dottorandi eccettuati i due che non hanno raggiunto il numero minimo di dottorandi richiesto.

9. Varie ed eventuali
Il coordinatore presenta delle proposte di modifica che intende presentare per incentivare i dottorandi ad una partecipazione più attiva a seminari e corsi e ad una maggiore familiarità con l'uso della lingua inglese. Anche in seguito ad altri interventi vengono individuate come azioni adeguate la presentazione delle ricerche dei dottorandi in lingua inglese in sede di colloqui per il passaggio al III anno e l'incentivazione di discussione della letteratura scientifica come verifica di acquisizione delle conoscenze dei corsi seguiti.

Anna Maria Papini riporta al Consiglio le informazioni raccolte nel corso della riunione dei delegati Erasmus delle Scuole, organizzata dal Prorettore alla Didattica Anna Nozzoli. Ai fini di aumentare la visibilità internazionale del nostro Ateneo, nell'ambito del programma Erasmus+ iniziato lo scorso anno, è auspicabile che i dottorandi che quasi sempre effettuano periodi all'estero, partecipino al Bando Erasmus+ Traineeship che uscirà entro la fine di Aprile pv. Questo per permettere ai dottorandi di avere lo status Erasmus nel corso del periodo svolto all'estero e ottenere crediti formativi, che la Scuola ha già definito in 1 ECTS/25h di attività di laboratorio. Le partenze possono avvenire da settembre 2015 con rientro entro settembre 2016. L'Ufficio Relazioni Internazionali della Scuola di Scienze sta approfondendo le possibilità di finanziamento tramite i fondi Erasmus+. A.M. Papini in qualità di Delegato Erasmus della Scuola di SMFN e della Chimica è disponibile a collaborare con gli studenti per la predisposizione delle pratiche.

Non essendoci altri argomenti in discussione la seduta termina alle ore 13.30.

Il Segretario Verbalizzante — Il Coordinatore
Dott. Roberto Di Camillo — Prof. Andrea Goti

ALLEGATO 1

UNIVERSITÀ DEGLI STUDI DI FIRENZE

and

LE CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE

and

UNIVERSITE DE RENNES 1

International Phd Agreement for the Project

"Computational study of Single Molecule Magnets: from the isolated molecule to the deposition on surface"

BETWEEN:

(1) **UNIVERSITÀ DEGLI STUDI DI FIRENZE**, whose address is at P.zza S.Marco, 4 - 50121 Firenze, Italy(da aggiungere qualcosa sulla loro falsa riga? (hereinafter referred to as "**Firenze University**");

(2) **LE CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE**, a scientific and technological public establishment, (hereinafter referred to as ***"CNRS")***, having its registered office at 3 rue Michel Ange, 75794 PARIS Cedex 16, France, N° SIREN 180089013, APE CODE 7219Z, represented by its President, M. Alain FUCHS, having given signatory power for this agreement to, Mrs Clarisse DAVID, Déléguée Régionale Bretagne - Pays de la Loire, Parc Alcyone, 1 rue André et Yvonne Meynier CS26936 35069 RENNES Cedex, France.

(3) **UNIVERSITE DE RENNES 1**, a French public entity qualified as scientific, cultural and professional located at 2 rue du Thabor – CS 46510 – 35065 RENNES Cedex, France, n° SIRET 193 509 361 00013, APE code APE 803Z, represented by its President, Mr Guy CATHELINEAU (hereinafter referred to as "**Rennes 1 University**"),

CNRS and Rennes 1 University acting both on their behalf and on behalf of the laboratory "Institut des Sciences Chimiques de Rennes", UMR 6226, (hereinafter referred to as the "Rennes Laboratory"), directed by Mr Jean-Luc ADAM.

The aforesaid organizations are hereinafter referred to individually as "Party" and collectively as "the Parties"

WHEREAS

(A) Considering the Franco-Italian University created further to the signature in Florence on the sixth of October 1998 by the French and Italian Foreign Affairs Ministries, and the Ministries responsible for Higher Education, and on the Italian side, considering the law of the 26th of May 2000, n 161, and on the French side considering to the French code of education, and notably its articles L123-7 and L612-7, considering the French decree of 6 January 2005 amended by the decree of 7 august 2006 concerning the international joint supervision of doctorates between French and foreign higher education institutions and the decree of 7 august 2006 regarding doctoral studies.

(B) The Parties wish to formalize the funding and conduct of an international Phd thesis, to enable the Student to carry out the Project and submit to RENNES 1 University the related thesis for examination. The Parties further acknowledge that the Project is intended to lead to academic publications relating to the results of the Studentship in furtherance of the Student's career.

(B) The Parties each further acknowledge that in the course of the Studentship the Parties may be exposed to proprietary and commercially valuable information or materials of the other Party. The Parties recognize the importance of holding in confidence such information or materials.

1. DEFINITIONS

In this Agreement the following expressions shall have the following meanings:

1.1 "Arising Intellectual Property" means any Intellectual Property Rights (IPR) arising from and developed in the course of the Project by any of the Parties;

1.2 "Background Intellectual Property" means Intellectual Property Rights controlled or owned by any Party prior to the date of the commencement of this Agreement or generated by any of the Parties

independently of the Project and controlled or owned by that Party and to which the Party has the necessary rights;

1.3 "Intellectual Property Right" (IPR) means any patent, registered design, copyright, database right, design right, trade mark, application to register any of the aforementioned rights, trade secret, right in unpatented know-how, right of confidence and any other intellectual or industrial property right of any nature whatsoever in any part of the world;

1.4 "Student" means Guglielmo Fernandez Garcia;

1.5 "Project" means the research project entitled "*Computational study of Single Molecule Magnets: from the isolated molecule to the deposition on surface*" to be undertaken by the Student, as detailed in in the 3.1 section of this Agreement;

2. Adminsitration

THE PROJECT

2.1 Registration

Mr Guglielmo Fernandez Garcia fulfils all conditions required for his registration for a joint supervision doctorate in both universities. The registration will be made after the signature of this PHD agreement. The duration of the research work is anticipated to last three years and a registration will be made every year in both universities.

In Rennes 1 University, the registration shall be made within the Doctorate school Sciences de la Matière.

In Firenze University, the registration shall be made within the doctorate school of Scienze Chimiche.

The student's registration is made in RENNES 1 university as main institution (first location) and Firenze university as second location.

2.2 Fees

The Student will pay his registration fees to the University of RENNES 1

Insurance will be provided to the student by both universities according to the rules in force in each country.

Health insurance for Mr Fernandez Garcia Guglielmo is provided in France by the French social security system and in the foreign country by social regime applicable in the partner university

The Student shall subscribe at its own costs to insurance for any other risk not covered by the insurance provided by the universities according to the law.
The Student shall subscribe to a health insurance according to the law of the countries of both universities.

2.3 Accommodation and financial help for the student

The accommodation and financial help conditions for the student, if any, will be defined later.

3 Thesis

3.1 Research Works

The study carried out is entitled "*Computational study of Single Molecule Magnets: from the isolated molecule to the deposition on surface* "

The Thesis supervisors will be:

- In France in Rennes Laboratory, by Dr. Boris LE GUENNIC of Rennes Laboratory
- in Italy in Firenze University, by Dr. F. Totti of the Department of Chemistry "U.Schiff",

The study shall be conducted:

During the First year, from December 1st 2014 to November 30th 2015, in Firenze University, and Firenze University warrants that it shall recruit the Student directly during that period
During the second year, and during the first six months of the third year, from December 1st 2015 to May 31st 2017, in Rennes Laboratory, and CNRS warrants that it shall recruit the Student directly during that period,
Then the last six months of the third year, from June 1st 2017 to November 30th 2017, in Firenze University, and Firenze University warrants that it shall recruit the Student directly during that period.

3.2. Thesis drafting

The thesis shall be written in English

An abstract shall be written in French and in Italian.

3.3. Thesis oral examination

The thesis will be defended at: RENNES 1 university

This imperatively requires, on the French side, the review of the work by two external examiners, the opinion of the Head of the School concerned by the PhD based on the reports provided by the external examiners, and the prior authorization for the viva by the President of the University of Rennes 1.

The award of the PHD shall be made with a diploma delivered by both universities.

The language used for the thesis oral examination shall be English; it shall also include an oral summary in French and in Italian.

The jury shall be equally composed of members from both countries.

The two thesis Supervisors shall participate to the thesis oral examination but shall not be appointed president of the jury. The jury shall be composed according to the prevailing rules in both countries and shall be approved by the President of Rennes 1 University and the "Rettore" of Firenze University.
The Jury shall include members of both universities and external members. The thesis jury will comprise a maximum of 8 members. The president of the Jury shall be appointed by the Jury and shall write a thesis oral examination report signed by each member of the Jury.

The travel and accommodation fees for the members of the Jury participating to the thesis defence shall be paid by RENNES 1 university as first institution (where the scholarship fees are paid).

3.4. Attribution of the diploma

Following the successful thesis single defence, the doctor's degree shall be attributed by both Universities (double diploma). The diploma shall mention the specialization or field, the title of the thesis, the international joint supervision, the names and titles of the members of the jury and the date of the thesis defence.

Rennes 1 University shall award to Guglielmo Fernandez Garcia the title of: « Docteur de l' Université de Rennes 1 / Mention : Chimie» according to french rules in force.

Firenze University shall award to Guglielmo Fernandez Garcia the title of: "Dottore di Ricerca in Scienze Chimiche according to Italian rules in force.

TITRE 4 – Intellectual Property

4.1 All the results obtained by one Party prior to this agreement shall remain the exclusive property of the Party owning it (or, where applicable, the third party from whom their right to use the results has derived.)

4.2 Results pertaining to the field of the Study but not directly resulting from works carried out in the context of the present contract shall belong to the party having obtained them. All right, title, and interest in and to such results shall vest in and be the sole property of the respective Party or Parties who created or devised them.

4.3 Subject to any existing third party obligations, each Party grants the other Parties as necessary a royalty-free, non-transferable, non-exclusive, license to use its Background Intellectual Property only in the frame and for the purpose of undertaking the Project excluding any commercial exploitation of such Background Intellectual Property.

4.4 Subject to agreement by the Parties, all right, title, and interest in and to Arising Intellectual Property shall vest in and be the sole property of the respective Party or Parties who created or devised such Arising Intellectual Property.

The owning Party shall be free to undertake and continue at its own expense the application, prosecution and abandonment of any patent related to such results.

In case of results obtained by the Rennes Laboratory, the CNRS and Rennes 1 University jointly owns the results in accordance with the agreements executed between them.

4.5 Any Arising Intellectual Property jointly developed between the Parties shall be jointly owned between such Parties. Ownership of said jointly owned Arising Intellectual Property shall be shared between the Parties in proportion to their respective intellectual and financial contribution.

The Co-Owner Parties of the patentable Joint New Knowledge shall decide whether the latter shall be subject to patent applications filed/registered in their joint names and shall designate the Party from amongst them which shall be responsible for accomplishing the filing/registration formalities and for maintaining the patent in force. The expenses relating to filing/registration, obtaining and maintaining the new patents in force under co-ownership arrangements shall be borne by the Co-Owner Parties according to their share of ownership as set forth hereinabove

Should a Co-Owner Party waive its entitlement to file/register, continue with a registration procedure or maintain one or several new patents in force either in France or abroad, it shall inform the other Co-Owner Parties in due time so that the latter may file/register in their own names, and continue with the procedure for registering or maintaining said new patents in force, at their own expense and for their own benefit. The desisting Party undertakes to sign, or have signed, any and all documents required to enable the other Co-Owner Parties to become sole co-owners of the new patent(s) in question for the relevant country(ies).

A Co-Owner Party shall be deemed to have relinquished its rights over a new patent sixty (60) days following receipt of a registered letter with acknowledgement of receipt requesting it to give its decision in this respect, sent by the Co-Owner Party responsible for accomplishing the formalities relating to filing/registration and maintaining the patents in force, as referred to in the first paragraph of this Article.

It is hereby stipulated that the waiving Party shall not be able to claim any compensation as regards the use of the new patent(s) in question in the relevant country.

Each Co-Owner Party shall be personally responsible for any compensation for its inventors.

Title 5 Secret, Communication

5.1 The publication, reproduction, transfer, distribution and storage of the thesis shall be made in each country according to its rules in force.

5.2 The Parties each undertake to use reasonable endeavours to keep confidential and not to disclose to any third party (other than an Affiliate) or not to use other than for the purpose of the Project any information in any form directly or indirectly belonging or relating to the other Party, its Affiliates, its or their business or affairs, disclosed by one Party (the “Disclosing Party”) and indicated expressly as being “confidential” by a written legend on the information or when orally disclosed confirmed as being confidential within 15 business days (“Confidential Information”) and received by another (the “Receiving Party”) pursuant to or in the course of the Project.

5.3 Each of the Parties undertakes to use reasonable endeavours to disclose Confidential Information belonging to any of the other Parties only to those of its officers, employees, students, agents and contractors, (and those of its Affiliates) to whom and to the extent to which, such disclosure is necessary for the purposes contemplated under this Agreement and to ensure that all such personnel are bound by the same terms of confidentiality as those contained herein.

5.4 The Receiving Party shall not during a period of two (2) years after the termination of this Agreement, use Confidential Information for any purpose other than performance of the Project and in accordance with the terms of this Agreement.

5.5 The obligations contained in this Clause 5 shall survive the expiry or termination of this Agreement for any reason but shall not apply to any Confidential Information which:

is publicly known at the time of disclosure to the Receiving Party;

after disclosure becomes publicly known otherwise than through a breach of this Agreement by the Receiving Party, its officers, employees, agents or contractors;

can be shown by reasonable proof of the Receiving Party that it reached its hands otherwise than by the Disclosing Party including being known to it prior to disclosure, or being developed by or for it wholly independently of the Disclosing Party or being obtained from a third party without any restriction on disclosure on such third party of which the recipient is aware, having made due enquiry:

is required by law, regulation or order of a competent authority (including any regulatory or governmental body or securities exchange) to be disclosed by the Receiving Party, provided that, where practicable, the Disclosing Party is given reasonable advance notice of the intended disclosure and provided that the relaxation of the obligations of confidentiality shall only last for as long as necessary to comply with the relevant law, regulation or order and shall apply solely for the purpose of such compliance; or

is approved for release, in writing, by an authorized representative of the Disclosing Party.

5.6 Subject to the provisions of Clause 4.8, no Party shall disclose or publish information in Arising Intellectual Property without the consent of the other. Such consent shall not to be unreasonably withheld or delayed.

5.7 In accordance with normal academic practice, all employees, students, agents or appointees of the Parties (including the Student) and any other persons who work on the Project shall be permitted, following the procedures laid down in Clause 6.3, to publish Arising Intellectual Property or discuss Arising Intellectual Property in internal seminars, and to give instructions within Firenze University and the Laboratory on questions related to such work.

5.8 All proposed publications (including, but not limited to, scientific publications, patent applications and non-confidential presentations), shall be submitted in writing to the other Parties for review at least thirty (30) days before submission for publication or before presentation, as the case may be. A Party (the "Requesting Party") may require the deletion from the publication, any of the Requesting Party's Confidential Information or Background Intellectual Property or an amendment to the publication through which the Requesting Party's Confidential Information or Background Intellectual Property is disguised to the satisfaction of the Requesting Party. The Requesting Party may also request to delay the publication, if, in their reasonable opinion, the delay is necessary in order to seek patent or similar protection to Arising Intellectual Property. Any delay imposed on publication shall not last longer what is reasonably necessary for the Requesting Party to obtain the required protection; and shall not in any case exceed a period of six (6) months from the date of receipt of the proposed publication by the Requesting Party. Written notification of the requirement for a delay in publication must be received by the other Party within thirty (30) days after receipt of the proposed publication.

5.9 Each Party agrees that any publication in a scientific/academic journal shall give due acknowledgement to the financial and/or intellectual contribution of all those involved in accordance with standard scientific practice.

TITRE 6 - AMENDMENT - TERMINATION

6.1 This agreement shall enter into force retroactively on December 1st 2014, upon signature by the duly authorized representatives of the Parties and shall terminate at the end of the PHD program.

6.2 This agreement may be modified and terminated by means of an amendment signed by the duly authorized representatives of the Parties.

6.3 The Parties shall endeavor to reach an amicable arrangement in the event of any disputes arising out of the interpretation or the performance of this Agreement

Failing this, the dispute shall be submitted to a commission composed of 3 members: one appointed by the president of the French university, one appointed by the president of Florence University, the president of such commission shall be appointed by the parties by common agreement.

If no amicable arrangement is settled within 10 days after the first notice:

If the complainant is Firenze University, the Parties agree to submit the matter to the French courts and the contract shall be ruled by French law

If the complainant is the CNRS or Rennes 1 University, the Parties agree to submit the matter to the Italian courts and the contract shall be ruled by Italian law

This Agreement has been signed by the duly authorized representatives stated below.

For and on behalf of Università degli Studi di Firenze

Signature: _____ Date: _____

Name:

Title:

For and on behalf of Université de Rennes 1

Signature: _____ Date: _____

Name:

Title:

For and on behalf of LE CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE

Signature: _____ Date: _____

Name: Clarisse David

Title: Déléguée Régionale

The Thesis Supervisors:

Dr. Boris LE GUENNIC

Signature: _____ Date: _____

Dr. F. Totti

Signature: _____ Date: _____

The Director of the Doctorate school Sciences de la Matière of Rennes 1 University:

Jean-François CARPENTIER

Signature: _____ Date: _____

The PHD Student:

Guglielmo FERNANDEZ GARCIA

Signature: _____ Date: _____

ANNEX 1 THE PROJECT

A Multiscale Computational approach for the study of lanthanide based Single Molecule Magnets on surface.

Abstract: In this research project is proposed the development of a computational multiscale method, integrating QM and MM techniques, for the description of lanthanide based Single Molecule Magnets on surface. During the MM set up, both experimental and computational data were used as references. The aims are to identify the possible conformers on surface, to understand the variation of the magnetic properties and to study quantitatively the self-assembly phenomena. The techniques employed ranges from MD dynamics with *ad hoc* parametrized of Force Fields, periodic-DFT and post Hartree-Fock methods.

Introduction to the project: the "single molecule magnets" (SMM) are a class of metallorganic compound showing a magnetic hysteresis with a finite blocking temperature of the magnetization [1]. This phenomenom is due to the high magnetic anisotropy of the metal center, resulting in a low relaxation rate between the two directions of the magnetization vector. The interest in these kinds of systems is given by their potential in the design of new generation materials. Indeed, with a "bottom up" approach, it is possible to employ the particular molecular properties of the SMMs to project model systems for data storage devices or spin valves, for example. The kinetic of the inversion of the magnetization, a crucial factor for the future applications, is determined by both thermal energy and *"spin tunneling"* phenomena (spin population passing through the barrier dividing the two directions of the magnetization, given by quantum tunneling): the less is the rate of these processes and the better is the efficiency of the SMM. As showed in [2], the dipolar interactions between complexes self-assembled on surface leads to a quenching of the "spin tunneling" effects. Indeed the study of the SMMs physisorbed or chemisorbed on a metallic surface, like Au(111) or Cu(111), becomes really important. Therefore it is necessary to develop new theoretical and computational tools, since the prediction of the behaviour of these systems is of great interest for the fine tailoring of new materials. Among the most promising molecules for this purpose are listed different complexes of the lanthanide's group, as La, Dy, Yb and polynuclear complexes as the *so-called* Fe_4. From an experimental point of view it is possible to study these systems with techniques as XMCD, XPS and UPS, STM or TOF-SIMS. All of this morphological and spectroscopical information need a rationalization not always trivial. Furthermore these techniques often require a huge cost in terms of resources and time.
The computational and theoretical approach has proved to be a useful tool to fully understand the properties we are interested in and to make easier the design and interpretation of the experiments: since the magnetic properties are determined by the electronic structure, the natural tool is the Density Functional Theory (DFT). Even if with the DFT it is possible to study systems even with high dimensionality, it is prohibitive the study of large scale (both temporal and spatially) phenomena as self-assembly on surfaces. Indeed even the *ab initio* dynamics of a single molecule on surface requires prohibitive calculations wall-time. So it is necessary a multi-scale approach, employing different level of approximations, to gain a complete view on the behaviour of the single molecule magnets on surface. While DFT and post-Hartree-Fock static calculations are suitable for the description of magnetic properties, we can obtain information on the large scale behaviour (both qualitative and quantitative) with the study of Classical Dynamics (in the theory of Molecular Mechanics, MM). In the latter the interaction between the atoms is described with classical effective potentials called Force Fields (FF) and the time propagation is made via the integration of the Newton equation. With this method is possible to drastically increase the speed of calculations by applying a larger approximation. A general Force Field for metal complexes is not available, due to the nature of the metal-ligand interaction. However nowadays are applicable codes, as HESS2FF [3], to extract from DFT frequency calculations the parameters for *ad hoc* potentials to describe a given complex. These potentials must to be added to an already available Force Field, as GAFF [4], in a computational package.
In this research project it is proposed to study, via integrated QM and MM techniques, lanthanides

complexes as La(TrenSal)[1] [5], $Tb(Pc)_2$[2] or $(Dy(hfac)_3PyNO)_2$[3] on metal surface as Au(111) or Cu(111). The first step will be the set up of an ad hoc FF and the testing of its quality, starting with well characterized systems from an experimental and computational point of view, as the double decker complex $Tb(Pc)_2$ [6]. Since the interaction of the compound with the surface is driven by π-stacking and given the symmetry of the complex, this system can be considered as a good reference system. It will be then necessary to test the modified FF on a series of benchmark systems (isolated molecule, crystalline structure, etc.): the model must reproduce both experimental (*e.g.* cell parameters) and computational data (*e.g.* root mean square deviation with QM structures). Moreover it will be also checked the capacity in the reproduction of both geometrical and energetic predictions of a less approximated method, as DFT. The following step will be the extension of the method to more complex systems. Indeed in situations like the La(TrenSal) on surface, the surface-complex interaction and the assembling process might be not so trivial as for double-decker systems: the complex is in fact "round-shaped" (resulting in a more variable dynamics and more conformational minima) and the surface-complex interaction changes with the substituent on the ligands (indeed we will study different functionalization as aliphatic chains with thiol termination, phenyl groups and also the bare molecule). Another important example is the antiferromagnetically coupled $(Dy(hfac)_3PyNO)_2$ dimer: this SMM, evaporable and luminescent, exhibits a peculiar "butterfly-like" hysteresis, possibly given by the weak antiferromagnetic coupling between the metal centers. While the complex in solid state is fully characterized [7], the studies on surface are the subject of a collaboration between the LAMM (LAboratory of Molecular Magnetism) of the University of Florence and the ISCR/CSM (Istitut des Sciences Chimiques de Rennes/Chimie du Solide et Matériaux) of the University of Rennes 1. Hence the method proposed in this research project may become an useful tool in the ongoing studies of more complex systems like $(Dy(hfac)_3PyNO)_2$.

The second step will be to apply the model for the dynamic of a single molecule on a metal surface (made with the LAMMPS program [8]), for the identification of the most probable conformers. Indeed it is not always trivial to achieve this from a DFT optimization and without a too expensive *ab initio* dynamics. However it is important to keep in mind that the MM structures are obtained via an approximated method: for the evaluation of the fine structural parameters, as the metal-ligand distance, a refinement of the structure will be necessary via DFT optimization of the new conformers. Once obtained the geometries it is possible to move to the *ab initio* calculation of the magnetic properties. Indeed the interaction with the surface may change the electronic structure, while for potential applications the SMM behaviour must be retained when molecules are in contact with the metallic substrate. In this project we will employ periodic-DFT (with Quantum Espresso, SIESTA and VASP) and post-HF calculations (with MOLCAS) in comparison. The best approaches for computation on lanthanide-based systems are post-HF methods, where the calculation involve also excited configurations and then the Spin-Orbit interaction is added in a perturbative fashion. With this approach it is possible to calculate directly and with high accuracy the spin hamiltonian terms (experimentally measurable). However *post*-HF approaches are unaffordable for calculations on surface and in such cases we will recur to periodic-DFT calculations with pseudopotentials, evaluating each time the difference between the two methods. Indeed we will compare calculations on three systems, to estimate the effect of the surface on the electronic structure: the isolated molecule, the conformer obtained via MM and refined via QM (as described above), and the structure extrapolated from the surface. In the latter system, the electronic effects are decoupled from the geometrical ones induced by the surface. The comparison between different results should give an important insight on the characteristics of these SMMs.

In addition to the calculation of magnetic properties of a single molecule on surface, we will study also massive systems as the monolayer and thick film, varying the surface density to understand the process of organization on surface. In this case we will employ the Molecular Dynamics

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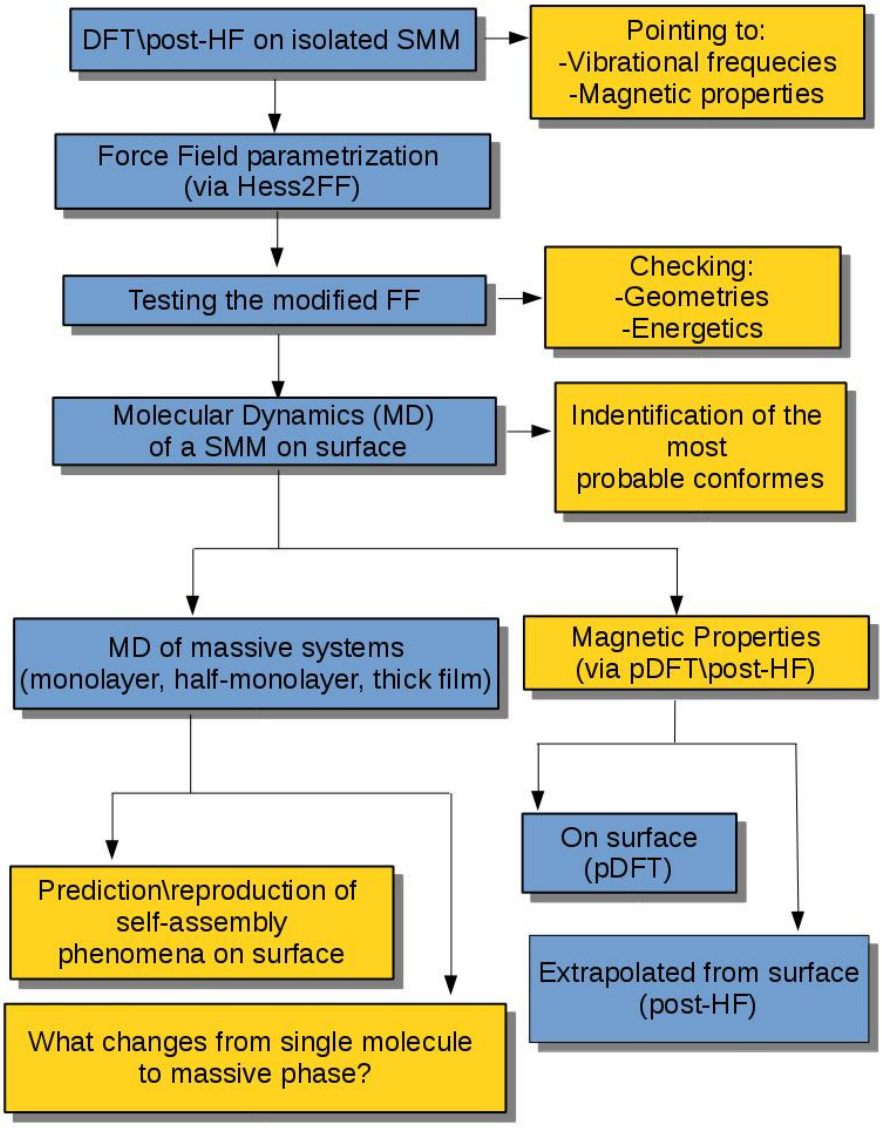
[1] With TreSal= tris-((2-hydroxybenzlidene)aminoethyl)-amine

[2] With Pc=phthalocyaninates

[3] With hfac=hexafluoroacetylacetone and PyNO=pyridine-N-oxide

method. Indeed we aim at reproducing, as well as predicting the self-assembly process, always exploiting experimental data as STM images provided by other members of the reasearch team. The Molecular Dynamics trajectory will be analyzed to understand the modifications the single molecule underwent up to the massive phase, for example studying the angle between the magnetization vector and the normal at the surface. The prediction of self-assembly is one of the main challenge for the Molecular Dynamics, since a classical Force Field model is the only approachable method for the study of such a large scale. This part of the study will be both qualitative (direct analysis of the trajectories) and quantitative, for example recurring at parameters as the "degree of crystallization" [9]. However the classical Molecular Dynamics may show a poor sampling of the phase space and a low probability in passing high energy barrier. Indeed we plan to employ more advanced techniques as Replica Exchange Methods (to improve the sampling) or Metadynamics (to overcome high energy barriers). In conclusion in this research project the development of an integrated QM and MM multiscale method is proposed, to give a wide access to several important properties of lanthanides complexes adsorbed on a surface, always in comparison between different levels of approximation and experimental data.

Schematic representation of the project



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ALLEGATO 2

2015- Febbraio **C. Analitica CHIM01 1 Ilaria Palchetti** ilaria.palchetti@unifi.it **Dr.ssa Galarini** (seminario) **Nanomaterials and other environmental emerging contaminants: the analytical approach Course description**: The course will cover the analytical approach to the determination of some emerging contaminants like engineered nanomaterials, microorganisms and prions. Prions are infectious particles composed of a protein in a misfolded form, which are responsible for several fatal neurodegenerative diseases also in human, and which are claimed to be contaminants at the horizon. Moreover, special emphasis will be devoted to the analysis of veterinary pharmaceutical residues with a seminar of an expert in the field. **Nanomateriali ed altri contaminanti ambientali emergenti: l'approccio analitico Descrizione del corso:** Il corso si propone di introdurre il problema ambientale e l'approccio analitico alla determinazione di alcuni contaminanti emergenti quali ad esempio i nanomateriali, alcuni microorganismi, ed i prioni. Inoltre, speciale enfasi verrà attribuita alla determinazione di residui di farmaci veterinari con l'intervento di un esperto del settore. **Periodo**: Febbraio **Numero di studenti**: -- **Metodo di valutazione**: lettura critica e discussione di un articolo scientifico sugli argomenti del
corso **Chim. Fisica CHIM02 1 Chim. Fisica CHIM02 , CHIM/01 (CHIMICA ANALITICA), IND/22 (SCIENZA E TECNOLOGIA DEI MATERIALI)**
Dr. Maurizio Muniz-Miranda maurizio.muniz@unifi.it **Nuovi Materiali Nanostrutturati per Applicazioni Catalitiche, Ambientali e Biomediche Descrizione del corso:** La ricerca di nuovi materiali nanostrutturati è una esigenza urgente nello studio di reazioni catalitiche eterogenee, nella rilevazione e rimozione di inquinanti ambientali e in applicazioni biomediche, come "drug delivery" e attività antibatterica. **Novel Nanostructured Materials for Catalytic, Environmental and Biomedical Applications"Course description**: The search for new nanostructured materials is an urgent need in the study of heterogeneous catalytic reactions, in the detection and removal of environmental pollutants and in biomedical applications, such as drug delivery and antibacterial activity. **Periodo**: Febbraio **Numero minimo di studenti per l'attivazione**: 2 **Metodo di valutazione**: *esame orale*

2 Dr. Santiago Sanchez-Cortes s.sanchez.cortes@csic.es **Instituto de Estructura de la Materia. CSIC. Serrano, 121. Madrid. Spain Nanobiospectroscopy: Bioanalysis and Sensitive Molecular Detection Course description**: Plasmonics is based on the interaction of light with materials in the nanoscale. The large local enhancements of the incident electromagnetic field in the proximity of nanostructured metals, as a consequence of the localized surface plasmon resonance (LSPR) have advanced applications in photonics, electronics and optical spectroscopy. In particular the course will be focused on the study of the Surface-Enhanced Raman scattering (SERS) ad Surface-Enhanced Fluorescence (SEF) techniques. This course will display potencial applications of SERS and SEF in biodiagnosis and, in general, molecular sensing at trace concentrations. The contents of the lectures will be specifically focused on important processes related to surface-enhanced optical spectroscopy, such as nanofabrication, functionalization and practical application in the detection of biomolecules and environmental pollutants. **Periodo**: Febbraio **Numero di studenti**: 6 **Metodo di valutazione**: esame orale o lettura critica e discussione di articolo scientifico (Referente, Dr. Alessandro Feis)
Chim. Inorganica CHIM03 1
Dr. Federico Totti totti.federico@unifi.it **Orbital Interactions in Chemistry Course description:** The course will cover the construction and the role of the molecular orbital interactions from the basis to their operative applications. The reactivity and spectroscopic properties for both organic and inorganic species will be then studied in this framework . The aim of the course, therefore, is to make the student able to sketch the electronic structure of the species under study in order to understand and to predict certain reaction and/or spectroscopic behaviours. **Interazioni Orbitaliche in Chimica Descrizione sintetica del contenuto del corso:** Il corso tratterà la costruzione e il ruolo delle interazioni orbitali molecolari dalla base alle loro applicazioni operative. La reattività e le proprietà spettroscopiche di specie organiche ed inorganiche saranno studiate contestulamente. L'obiettivo del corso è quello di mettere lo studente in condizione di delineare la struttura elettronica delle specie oggetto di studio al fine di comprendere e prevedere la loro reattività e le loro proprietà spettroscopiche. **Periodo**: Febbraio **Numero minimo di studenti per l'attivazione**: 2 studenti **Metodo di valutazione**: Colloquio

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Noemi Linares noemi.linares@ua.es Molecular Nanotechnology Lab University of Alicante, Alicante Spain **Sol-gel chemistry: Synthesis, characterization and applications of inorganic porous materials Course description:** The course will deal with the synthesis of different inorganic materials using sol-gel chemistry. A brief introduction of the sol-gel chemistry approach will be provided, together with a detailed explanation of the type of inorganic materials that can be synthesized, the most important methods employed in their characterization and also the wide range of applications that they cover nowadays. Sol-gel chemistry is typically used in combination with molecular and supramolecular templates, especially surfactants, to produce a wide variety of porous metal oxides. Both soft templates, such as surfactant and polymers and hard templates such as carbon and metal oxides and carbonates which can be burned-off or easily dissolved at a certain pH, have being extensively used to introduce controlled mesoporosity in a wide variety of solids. This is a simple and versatile strategy able to produce very complex and interconnected porous structures. Regarding the porous texture of these solids, they can be studied by a combination of different techniques such as, physical adsorption, mercury porosimetry, X-Ray diffraction or electronic microscopy, with each technique allowing the study of the porosity in a particular range. Finally, special attention will be paid to important applications of porous inorganic materials, which in the last years have become countless. Currently, they are frequently employed in catalysis; weather as catalysts or supports, adsorption, pollutant remediation, sensors, drug delivery systems, photocatalysis, batteries, solar and fuel cells. **Periodo**: seconda metà Febbraio **Numero minimo di studenti per l'attivazione**: 2 **Metodo di valutazione**: test risposta multipla. (Referente: Dr. Carmen Moreno Marrodan) **Chim. Organica CHIM06 1**

Prof. Dr. David Díaz David.Diaz@chemie.uni-regensburg.de **Click Chemistry: A Versatile Tool for Materials Synthesis and Biotechnology Course description:** Over the last decade, click chemistry has taken a spectacular growth and became a highly creative area of research. Although the foundation of click chemistry had initially an eye on drug discovery, its applications to materials synthesis and biotechnology have been a shocking success story. This course will first provide an introduction of the concept of click chemistry and its potential value as a universal chemical ligation strategy. Synthetic capabilities and limitations of this type of chemistry will be discussed, along with the different applications in a range of important materials science and biotechnology areas. **Click Chemistry: Uno Strumento Versatile per la Sintesi e la Biotecnologia dei Materiali Descrizione del corso:** Nell'ultimo decennio la "click chemistry" ha visto una crescita spettacolare, diventando un'area di ricerca altamente creativa. Sebbene lo sviluppo delle fondamenta della click chemistry sia stato inizialmente rivolto alla "drug discovery", la sua applicazione alla sintesi e biotecnologia dei materiali ha avuto una storia di straordinario successo. Lo scopo di questo corso e' principalmente quello di fornire un'introduzione al concetto di click chemistry ed al suo valore potenziale quale strategia universale di legatura chimica. Nel corso verranno discusse le potenzialita' sintetiche e le limitazioni di questo tipo di chimica, insieme con le differenti applicazioni in alcune aree di rilievo nella scienza e biotecnologia dei materiali.

Periodo: 23-27 Febbraio 2015. **Numero minimo di studenti per l'attivazione**: - **Metodo di valutazione**: L*ettura critica e discussione di articoli scientifici inerenti gli argomenti trattati nel corso. (*Referente: *Dr. Stefano Roelens)* **Fisica Applicata Fis07 1 Prof. Pier Andrea Mandò**/ pierandrea.mando@unifi.it **X ray spectrometries for the diagnostics of Cultural Heritage Course description:** The course will deal with the basic principles of compositional analysis of materials of interest in the field of Cultural Heritage, performed by means of X ray spectrometries (X Ray Fluorescence [XRF], PIXE [Particle-Induced X ray Emission]). A comparative examination of advantages and limitations of each technique will be made. A short description of the main instrumentation employed for this kind of analysis will also be given. **Spettrometrie X per la diagnostica dei Beni Culturali Descrizione del corso:** Nel corso saranno esposti i principi alla base delle analisi di composizione di materiali di interesse nel campo dei beni culturali, basate sull'utilizzo di spettrometria X (X Ray Fluorescence [XRF], PIXE [Particle-Induced X ray Emission]), con una disamina comparata dei vantaggi e dei limiti di ciascuna tecnica. Saranno brevemente descritte le principali strumentazioni utilizzate per queste analisi. **Periodo**: Febbraio **Numero minimo di studenti per l'attivazione**: 3 **Metodo di valutazione**: *Esame orale o lettura critica e discussione di un articolo scientifico inerente argomenti trattati nel corso.* **2**
Maria Elena Fedi fedi@fi.infn.it **Radiocarbon dating for Archaeology and History of Art Course description:**The course will first provide the schematic principles at the basis the method of radiocarbon dating, explain the sample preparation procedures, and the way measurements are performed using Accelerator Mass Spectrometry. Also discussed will be the recalibration that must be applied to the obtained results in order to correct for the simplified assumptions initially adopted, thus getting to a more accurate date. **Datazioni col radiocarbonio per l'archeologia e la storia dell'arte Descrizione del corso:** Nel corso saranno esposti i principi schematici alla base delle datazioni col metodo del radiocarbonio, le procedure di preparazione dei campioni, e quelle di misura con la tecnica della Accelerator Mass Spectrometry. Si discuteranno anche le correzioni di ricalibrazione che è necessario successivamente apportare ai risultati ottenuti, per tenere conto delle approssimazioni semplificate adottate inizialmente e arrivare a una datazione corretta. **Periodo**: Febbraio **Numero minimo di studenti per l'attivazione**: 3 **Metodo di valutazione**: *Esame orale o lettura critica e discussione di un articolo scientifico inerente argomenti trattati nel corso.*

Settembre C. Analitica CHIM01 1

Prof. Giovanna Marrazza giovanna.marrazza@unifi. **Recent advances in emerging techniques for food quality and safety Course description:** The availability of high-quality food with respect to nutrition, freshness and food safety is a major issue for customers and legal authorities. Smart monitoring of nutrients and fast screening of biological and chemical contaminants are some of the key evolving issues challenging the assessment of food quality and safety. Good traceability systems help to minimize the production and distribution of unsafe or poor quality products, thereby minimizing the potential for bad publicity, liability, and recalls. Advances in materials science and nanotechnology, electromechanical and microfluidic systems, protein engineering and biomimetics design are boosting sensing technology from bench to market. The course will highlight current and future trends in analytical diagnostic tools focused on the food industry and target analytes to support healthier nutrition. **Nuove tecniche analitiche per la qualità e la sicurezza alimentare**
Descrizione del corso: La disponibilità di cibo di alta qualità per quanto riguarda la nutrizione, la freschezza e la sicurezza alimentare è una problema importante per i consumatori e le autorità giudiziarie. Il monitoraggio dei nutrienti e lo screening veloce di contaminanti biologici e chimici costituiscono alcune delle principali questioni ancora aperte per la valutazione della qualità e della sicurezza alimentare. I sistemi di tracciabilità aiutano a minimizzare la produzione e la distribuzione di prodotti non sicuri o di scarsa qualità, permettendo da una parte di ridurre al minimo il potenziale per cattiva pubblicità e dall'altra di individuare l'eventuale responsabilità. I progressi ottenuti nel campo della scienza dei materiali, delle nanotecnologie, dell'elettromeccanica, dei sistemi microfluidici e dell'ingegneria biomolecolare hanno permesso di ottenere nuove tecnologie analitiche. Il corso metterà in evidenza le tendenze attuali e future degli strumenti analitici utilizzati nell'industria alimentare per selezionati analiti che aiutano ad avere una nutrizione più sana. **Periodo**: Settembre **Numero minimo di studenti per l'attivazione**: **- Metodo di valutazione:** lettura critica e discussione di un articolo scientifico inerente argomenti trattati nel corso. **Chim. Fisica CHIM02 1**
Pier Remigio Salvi piero.salvi@unifi.it **Aromaticity, antiaromaticity and Moebius aromaticity Course description:** Cyclobutadiene, benzene e cycloottatetraene as archetypal structures of conjugated cyclic molecules. Aromatic stability and antiaromatic instability. Isodesmic and homodesmotic reactions. Excited states of cyclobutadiene and benzene. Benzene photochemistry. Pentalene. Higher annulenic structures, from[10]-annulene to [18]-annulene. Porphyrins. Moebius structures of conjugated cycles and stability.

Aromaticità, antiaromaticità e aromaticità di Moebius Descrizione del corso: Ciclobutadiene, benzene e cicloottatetraene come archetipi di strutture coniugate cicliche. Stabilità aromatica e instabilità antiaromatica. Reazioni isodesmiche e omodesmotiche. Stati eccitati del ciclobutadiene e del benzene. Fotochimica del benzene. Pentalene. Strutture annuleniche superiori, dal [10]-annulene al [18]-annulene. Porfirine. Strutture di Moebius di cicli coniugati e loro stabilità. **Periodo:** Settembre **Numero minimo di studenti per l'attivazione:** 4-5 **Metodo di valutazione**: lettura critica e discussione di un articolo scientifico sugli argomenti del corso **Chim. Inorganica CHIM03** / **Fisica Fis01 1 Dr.ssa M. Fittipaldi** maria.fittipaldi@unifi.it **Dr. L. Sorace** lorenzo.sorace@unifi.it **Paramagnetic Resonance: Fudamentals and applications Course description:** This group of lectures is aimed at providing the basic concepts needed to use and analyze the information which can be obtained by Electron Paramagnetic Resonance spectroscopy, while presenting some case studies of application of the different variants of this technique in Chemistry, Physic, Biology and Material Science. The course is subdivided in two different modules, to be taught in September 2014 and September 2015. The two modules are independent on each other, but anybody interested in the second one -devoted to pulsed techniques- is strongly advised to follow also the first one, which is devoted to more general subjects. The course will focus on the following topics: *1^ module (September 2014) 2^ module (September 2015)* Introduction to pulsed EPR spectroscopy; The Density Matrix; The magnetization in the sequences of pulses: spin echoes. Application of ENDOR, ESEEM, HYSCORE e ELDOR-detected NMR spectroscopy to measure hyperfine interactions. Structural determination by using pulsed EPR and spin labels. **Fondamenti e applicazioni di Risonanza Paramagnetica Elettronica Descrizione del corso:** Scopo del corso è fornire le conoscenze necessarie all'utilizzo e alla comprensione delle informazioni ottenibili dalla spettroscopia di risonanza paramagnetica elettronica (EPR) nelle sue diverse varianti, presentando al contempo esempi applicativi in sistemi di interesse chimico, fisico, biologico e della scienza dei materiali: Il corso è suddiviso in due moduli, che verranno svolti a Settembre 2014 e Settembre 2015. Ogni modulo può essere svolto indipendentemente dall'altro, ma - se si intende seguire il secondo modulo, relativo alle tecniche impulsate - è consigliato seguire anche il primo,dedicato ad aspetti più generali. Il contenuto del corso sarà il seguente: *1^ modulo (settembre 2014 2^ modulo (settembre 2015)* Introduzione alla spettroscopia EPR pulsata. La matrice densità. La magnetizzazione nelle sequenze di impulsi: echi di spin; Spettroscopia ENDOR, ESEEM, HYSCORE e ELDOR-detected NMR per misurare interazioni iperfini. Determinazioni strutturali attraverso l'uso dell'EPR pulsata e spin labels. **Periodo**: Settembre **Numero minimo di studenti per l'attivazione**: 3 **Metodo di valutazione**: *esame orale o lettura critica e discussione di un articolo scientifico inerente argomenti trattati nel corso.*

Chim. Industriale - CHIM04 1

Prof. A. Salvini antonella.salvini@unifi.it **DESIGN AND SYNTHESIS OF NEW CONSOLIDANTS FOR THEIR USE IN WOOD CONSERVATION Course description:** In the past, several compounds and methods have been studied and used for the treatment of waterlogged wood. PEG (polyethylene glycol), at different molecular weights, is still today the most used compound for wood consolidation. However several problems appear consequent to the presence of PEG into wood, so the study of different consolidants is required. In the wood lifetime various agents alter the chemical structure of its main components. In detail, water and biological agents can favour hydrolysis reactions which cause the prevalent loss of hemicelluloses and cellulose, which represent the backbone of the ligneous structure. An important goal is the synthesis and characterization of some novel wood consolidants provided with a chemical structure similar to the wood, in order not to alter its aesthetic, mechanical and physical characteristics. **Progettazione e sintesi di nuovi consolidanti per il loro uso nella conservazione del legno archeologico imbibito Descrizione del corso:** In passato sono stati studiati diversi metodi e prodotti per il trattamento di legni archeologici imbibiti. Tra diversi consolidanti studiati i PEG (polietilenglicol), a diversi pesi molecolari, sono ancora oggi i prodotti più utilizzati nella conservazione del legno. Tuttavia sono numerosi i problemi che sono stati evidenziati negli ultimi anni imputabili alla presenza del PEG nel legno consolidato. Risulta quindi di grande importanza lo studio di nuovi prodotti dotati di maggiore affinità per il legno e capaci di rispettarne le caratteristiche chimico-fisiche. Nella vita di un manufatto ligneo vari agenti possono agire sui componenti principali del materiale legno modificandone la struttura chimica. In dettaglio, l'acqua e microorganismi possono favorire reazioni di idrolisi e causare la perdita di alcuni dei componenti principali come emicellulose e cellulosa. Obiettivo importante è la progettazione e la sintesi di nuovi consolidanti, caratterizzati da una struttura chimica affine ai componenti principali del legno, in modo da non alterare l'aspetto estetico, le proprietà fisiche e quelle meccaniche. **Periodo**: Settembre **Numero minimo di studenti per l'attivazione**: 3 **Metodo di valutazione**: *Esame orale o lettura critica e discussione di un articolo scientifico inerente argomenti trattati nel corso.* **Chim. Organica CHIM06 1 Prof. ANNA BERNARDI**

anna.bernardi@unimi.it **Dipartimento di Chim. Organica ed Industriale - Università di Milano**

Medicinal chemistry with carbohydrates: the influenza virus and the discovery of sialidase inhibitors Course description: 1. Introduction: the influenza virus; 2. Antiviral targets (HA, NA); 3. The viral sialidase (NA); 4. Design of sialidase inhibitors; 5. Synthesis of Tamiflu

Influenza virus is composed of a single-stranded RNA genome, enclosed within an outer lipoprotein envelope. The virions are studded with two different types of spikes, the hemagglutinin (HA) which mediates viral entry in the host cells, and the neuraminidase (sialidase, N) which

assists the release of viral progeny from the infected cells. Both of these surface glycoproteins are carbohydrate-recognizing proteins and play an essential role in the lifecycle of the virus within the host organism. Considerable effort has been devoted to the discovery of novel therapeutic agents against all types of influenza by targeting HA or N, and several reviews have been published. To date, the most successful drugs have arisen from targeting the sialidase function. Two influenza drugs, Zanamivir **1** (Relenza) and Oseltamivir **2** (Tamiflu), have emerged from structure-based drug discovery programs, which have provided one of the earliest examples of the application of structure-based drug design. The importance of these drugs has stimulated much interesting synthetic work that will be exemplified during the first 4 h of the course. In the following 4 h, participating students will give short presentations based on papers assigned during the first part of the course. 1. Introduzione: il virus dell'influenza; 2 Targets antivirali (HA, NA); 3. La sialidasi virale (NA); 4. Design di inibitori della sialidasi; 5. Sintesi del Tamiflu Il virus dell' influenza è composto di un genoma basato su un RNA single-stranded, racchiuso in un involucro di lipoproteine. I virioni sono decorati con due differenti tipi di "arpioni", l' emoagglutinina (HA) che media l'ingresso del virus della cellula ospite, e la neuraminidasi (sialidase, N) che assiste il rilascio del progene virale dalle cellule infettate. Ambedue queste glicoproteine di superficie sono protein che riconoscono carboidrate e giocano un ruolo essenziale nel ciclo di vita del virus all'inteno dell'organismo ospitante. Notevoli sforzi sono stati dedicati alla scoperta di nuovi agenti terapeutici contro tutti i tipi di influenza focalizzandosi su HA or N, e varie reviews sono state pubblicate. Ad oggi, i farmaci più efficaci sono stati ottenuti nel caso sialidasi. Due farmaci antiinfluenzali, Zanamivir **1** (Relenza) e Oseltamivir **2** (Tamiflu), sono emersi da *structure-based* programmi di drug discovery, che hanno fornito uno dei primi esempi di applicazione di *structure-based* drug design. L'importanza di questi farmaci ha stimolato una gran parte di interessante lavoro sintetico che sarà discusso durante il corso (4 ore) del corso. Nella seconda parte del corso gli studenti partecipanti faranno delle brevi presentazioni su lavori assegnati nel corso della prima parte. **Periodo**: Settembre **Numero minimo di studenti per l'attivazione**: 10 **Metodo di valutazione**: Discussione su un problema assegnato inerente argomenti trattati nel corso *(*Referente: *Dr. Gianna Reginato)*

Chimica dell'Ambiente e dei Beni Culturali CHIM12 1

Prof. Rodorico Giorgi giorgi@csgi.unifi.it **Nanotechnologies for the conservation of paper and parchment manuscripts Course description:** The conservation of paper and parchment manuscripts is one of the most difficult issues in conservation science, because biopolymers such as cellulose and collagen are susceptible to fast degradation, as a result of the combination of the environmental factors and the making-techniques, used during the century. In particular, manuscripts undergo degradation because they contain materials that catalyse the degradation reactions; this fact is added to the acidic pollutants from the environment and the intrinsic weakness of the organic-based materials.

The cleaning of these objects is also a very difficult topic. Water-based detergent systems offer several advantages, over organic solvents, for the cleaning of cultural heritage artifacts in terms of selectivity and gentle removal of grime materials, which are known to alter thereadability of the text.

Unfortunately, paper and parchment present specific characteristics that make the usage of water-based systems invasive. In order to avoid mechanical stress and to ensure a fine control (layer by layer) of grime removal, water-based cleaning systems can be confined into innovative

chemical hydrogels, specifically designed for cleaning water-sensitive cultural heritage artifacts. These lectures will focus on some of these aspects and the most recent contribution of nanotechnology to the development of innovative restoration methods will be described. **Periodo**: Settembre **Numero minimo di studenti per l'attivazione**: 6 **Metodo di valutazione**: Critical analysis and discussion about scientific publication in the field of paper and parchment manuscripts conservation