

**Presentation of funded projects in 2008 for
 Program: « Green Chemistry and Processes for a
 sustainable development »**

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Program: « Green Chemistry and Processes for a sustainable development »

Edition 2008

Projec Title	BIOPOLYCAT - Catalytic systems for the ring-opening polymerization of novel monomers derived from the biomass via an original polymerization process
Abstract	<p>In light of the depletion of fossil feedstocks and to help address the global environment concerns, increasing attention should nowadays be paid to polymeric materials such as polyesters synthesized from monomers derived from readily renewable natural resources (biomass) within green and sustainable chemistry. Synthetic polyesters are versatile polymers exhibiting good thermo-mechanical and physical properties, which make them leading candidates for, in particular, biomedical applications (e.g., tissue repair and regeneration, controlled and sustained drug or gene delivery vehicles) but also as recyclable substitutes to plastic commodities (e.g., packaging, films,...). However, the limited number of existing polyesters derived from the currently available monomers can not substitute the whole range of thermoplastics. Therefore, developing polyesters from the biomass is of double and highest interest. Efforts must be paid also to develop highly effective, environmentally friendly catalyst systems for the preparation of these biomass-derived polyesters. We thus propose herein an academic, industrially-orientated research project which consists in 1) the design and synthesis of novel cyclic monomers as new chemicals derived from biomass, and 2) the use and development of original catalytic systems for ring-opening polymerization (ROP) including 2a) organic, 2b) organometallic and 2c) bifunctional "dual" ones. This will be done using a combined experimental and theoretical approach.</p>
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ANR Funding	554 013 €
Beginning & duration	01/12/2008 - 36 months
Reference	ANR-08-CP2D-01-01

Program: « Green Chemistry and Processes for a sustainable development »

Edition 2008

Projec Title

BIOPSIL - Ecofriendly transition metal catalytic systems based on renewable biopolymeric support and ionic liquids: Efficient, recyclable and reusable heterogeneized homogenous catalysts

Abstract

Organometallic catalysis is an important player for the development of new sustainable process in industry. About 85% of the present chemical processes are run using a catalyst. Out of these about 75% are run based heterogeneous catalysis due to their advantages of easy separation from product streams and of their recycling and reuse. On the other hand, homogeneous catalysts are appreciated in terms of their activity and selectivity. However these catalysts, which associate a transition metal and a ligand designed to fine tune the properties of the catalyst are more expensive. Recycling and reuse of these important catalysts become thus pertinent both from environmental and economical reasons. To solve this problem, we propose to develop novel catalytic materials, which combine both the advantages of homogeneous (high activity and selectivity) and heterogeneous catalysis (easy product/catalyst separation, recycling and reuse of the catalyst). This new catalytic materials will associate a biopolymer issued from the biofeedstock (chitosan, alginate) as support and a multiple layer of ionic liquid (preferably biodegradable) in which the homogeneous catalyst will be dissolved. To obtain efficient catalysts, a particular attention will be paid to the conditioning of the biopolymers (beads, scaffolds, fibers, membranes and to their structure (meso or microporosity). Moreover, to prepare fully biodegradable BioPSIL materials, biodegradable ILs will be designed and associated to the biopolymer support. The global biodegradability of the BioPSIL materials will be evaluated. In order to have a better understanding of the properties, which are responsible of the efficiency of the BioPSIL catalysts, a study on the interactions between IL/transition metal catalyst/support will be undertaken. The novel BioPSIL catalysts will be evaluated in four catalytic reactions: the "Tsuji-trost" reaction which is a leading reaction for the construction of C-C bond, the hydrogenation of nitrophenols, the C-P bond formation, which is a powerful catalytic method to access the valuable phosphine ligands and the olefin metathesis which is an inescapable reaction in organic synthesis and polymer science. These four reactions are catalyzed by transition metal complexes (palladium or ruthenium), which are costly and toxic. Thus, both from an environmental and economic point of view, the recycling and the reuse of the catalyst are main issues. Furthermore, these reactions display different features (basic, neutral conditions, liquid, gaseous reagents, palladium and

ruthenium catalysts...), which will enable to evaluate the scope and limitation of the novel catalytic materials that will be developed. The study will consist in the evaluation of the BioPSIL materials in a model reaction in order to determine the best biopolymer conditioning for a high conversion and an efficient recycling and reuse of the catalytic system. The impact of catalytic parameters (metal dosage, IL content, ...) and the impact of operating parameters (substrate concentration, agitation or flow velocity,) will be investigated. Among the criteria for the evaluation of the catalytic systems TOF, conversion, yield will be considered but also the stability of the materials (metal leaching) and the recycling and reuse of the catalytic system (long-time activity...).

Afterwards, the reaction will be extended to other substrates and/or reagents to evaluate the scope and limitations of the reaction under these new catalytic reactions.

Partnership

CNRS - LCMT- Polymères - UMR 6507
CNRS - LCMT-Soufre et Phosphore - UMR 6507
Centre commun ARMINES - LGEI - Ecole des Mines d'Alès

**Coordinator
ANR Funding
Beginning
& duration
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367 259 €
01/12/2008 - 36 months
ANR-08-CP2D-02-01

Program: « Green Chemistry and Processes for a sustainable development »

Edition 2008

Projec Title	BMZ-MCRS - DEVELOPMENT OF NOVEL MULTICOMPONENT REACTIONS FOR RAPID AND ECO-COMPATIBLE SYNTHESIS OF MEDICINALLY RELEVANT HETEROCYCLES
Abstract	Multicomponent reactions (MCR) are processes in which three or more reactants are combined in a single chemical operation to produce products that incorporate substantial portions of all the components. They are by definition sustainable chemistry and constitute a gateway to the ideal organic syntheses in which the target molecule is made from readily available starting materials in one simple, safe, environmentally acceptable and resource-effective operation. As an enabling technology, the development and application of multicomponent reactions are now an integral part of any major medicinal research unit. Our group at "Institut de Chimie des Substances Naturelles" has been actively involved in this burgeoning area and has acquired basic know-how in this field. In collaboration with Targeon, an emerging biopharmaceutical company that develops targeted therapies in oncology, we intend to further develop the "substrate design" approach" for the design of novel MCRs that match the criteria of green chemistry, but also directly target the pathogenic macromolecules for the development of bioactive compounds.
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ANR Funding	598 474 €
Beginning & duration	01/12/2008 - 48 months
Reference	ANR-08-CP2D-03-01

Program: « Green Chemistry and Processes for a sustainable development »

Edition 2008

Projec Title **CAPROCELL - Pure cellulose production from wood by an environmentally friendly process using catalysed hydrogen peroxide**

Abstract

Cellulosic pulps for paper production are obtained after wood delignification. The production of bleached fibres requires an additional bleaching step in order to remove coloured residual lignin. Cellulosic fibres are mainly used to produce white paper for printing applications. Only a small amount is used, after purification, for pure chemical cellulose production. This last application offers a great added value and has today a growing interest due to the opportunities offered by the cellulose regarding the synthesis of polymers and derivatives originating from the biomass, a renewable raw material. The use of cellulose in chemical application is limited due to the cellulose contamination with hemicelluloses, its lack of reactivity linked to the cellulose fibrous structure and its too large degree of polymerisation. Thus, beneficial properties in the papermaking process become handicaps for pure, reactive and molecular mass modulable cellulose production. The preliminary bleaching step necessary to these applications is difficult. Oxygenated reagents such as oxygen or hydrogen peroxyde are now applied in alkaline medium in substitution to usual chlorinated agents (chlorine, chlorine dioxide) responsible for the production of toxic organochlorinated compounds. However, the combination of oxygen and hydrogen peroxide treatments is not sufficient to fully complete the bleaching. As a consequence, some chlorinated agents are still largely used. This project aims at developping a catalytic bleaching process using hydrogen peroxide. This new process will enhance the residual lignin degradation and will remove major part of the hemicelluloses while enabling to get reactive celluloses with a variable degree of polymerisation. This new environmentally-friendly process would be implemented in parallel to the current bleached kraft pulp production line. 2 academic laboratories, the LGP2 and the DCM will drive this project with 2 industrial partners linked to the H₂O₂ production and the bleached kraft pulp production. Recent studies showed that transition metallic complexes, especially copper, exhibit a catalytic action on H₂O₂ reactions in alkaline medium with cellulosic pulp. The bleaching is strongly improved but the carbohydrates (cellulose and hemicelluloses) react also more, leading to higher oxydation and solubilisation of hemicelluloses and to a larger cellulose depolymerisation. Consequently, this catalytic process has a low selectivity towards the residual lignin. Nevertheless, this drawback could become an advantage regarding the production of

pure cellulose for chemical application. Indeed, the production of these high added value products requires a very efficient bleaching but also the hemicelluloses dissolution in order to get a highly reactive and partially depolymerised cellulose. The modification of the complex chemical structure (i.e the ligand), should modify the copper complex activity to adjust the carbohydrates degradation intensity, leading to celluloses suitable for cellulose derivative production used in textile, packaging, cosmetics, food additives... Several complexes such as Cu-polypyridinyl for instance, with different affinities towards carbohydrates will be studied and then applied on lignocellulosic substrates. The purpose is to develop an entirely environmentally friendly industrial process without chlorine for pure and reactive cellulose production. This is made possible because H₂O₂ is used, the effluent is burnt and the caustic soda is regenerated in the kraft recovery system.

Partnership

Grenoble INP - LGP2 - UMR 5518
UJF - DCM - UMR 5250
Arkema - CRRA
Confidentiel-Entreprise

**Coordinator
ANR Funding
Beginning
& duration
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ANR-08-CP2D-04-01

Program: « Green Chemistry and Processes for a sustainable development »

Edition 2008

Projec Title | **CO2 GREEN - Carbon dioxide as a green carbon source in transition metal catalyzed synthesis**

Abstract

This submitted project take place in the joint call of the Academy of Finland and the ANR. Utilizing renewable resources is a prerequisite for a sustainable organic chemistry industry. Depletion and increasing costs of fossil resources have led to search for new alternative carbon raw materials and technical solutions for chemical industry. One easily available green renewable carbon source to substitute fossil ones is carbon dioxide (CO₂) which has the advantages to be naturally abundant, inexpensive, non-flammable and non toxic. When properly catalyzed, carbon dioxide reacts with different substrates to produce valuable products. Because CO₂ is the most oxidized form of carbon, the biggest obstacle in the utilization of carbon dioxide as green-feedstock is its low energy level. Consequently only few industrial processes utilize CO₂ as a raw material. So conversion of CO₂ into a more reactive form is needed and it requires the use of catalysts to overcome high kinetic barriers stabilizing CO₂ molecule.

To achieve this goal catalytic reduction of CO₂ appears as a convenient way. Most commonly the reduction can be carried out by an electrochemical or a photo-catalytic process using transition metal catalysts. For obvious reasons simple CO₂ reduction products as CO can be then used further in various industrially important processes like carbonylation, Fisher-Tropsh or hydroformylation reactions. It should be underlined that hydroformylation of alkenes, with carbon monoxide and hydrogen, an industrially important reaction of carbon monoxide, is actually one of the best commercial examples of homogeneous catalysis using transition metal complex catalytic activation. In this context it has been recently demonstrated that reduction of CO₂ can be combined with hydroformylation. The research programme that we propose consists of an academic and fundamental search for effective ways to combine reduction of CO₂ with other catalytical processes. The ultimate goal is to replace CO as a feedstock with environmentally more benign CO₂ by designing new molecular catalysts (friendly metallic catalytic species) and innovative catalytical chemical pathways. Several approaches will be considered, especially those involving the use of the 1st row transition metal elements, the ionic liquids or the development of photochemical processes...

Partnership	Univ. Joseph Fourier Grenoble 1 - DCM/CIRE - UMR 5250 Finland\University of Joensuu - JoY/CC
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Beginning & duration	01/12/2008 - 36 months
Reference	ANR-08-CP2D-05-01

Program: « Green Chemistry and Processes for a sustainable development »

Edition 2008

Projec Title **CRAZYPOLYSACCHARIDES - Screening of active enzymes without a priori on polysaccharides collection with known and unknown structures**

Abstract

Polysaccharides are the most abundant and the most diverse renewable materials found on earth and in the oceans. Except polysaccharides used traditionally in food and non-food industry, the structure and the functionality of most of them are unknown and unexplored. Structural analyses of complex polysaccharides benefit strongly from the use of polysaccharides depolymerising enzymes: glycoside hydrolases (GH) and polysaccharides lyases (PL). The enzymes have the advantage to produce discrete series of oligosaccharides which characterisation is determinant to resolve the parent polysaccharides structures. In addition, these oligosaccharides may have functional properties (e.g. biological) and could be used as precursors for chemical synthesis. Finally, enzymes are very useful tools for industrial biorefinery processes. GH and PL have been classified as a function of the reaction they catalyse (about 160 E.C. number) and by sequence homology (110 GH families and 18 PL families, CAZY classification). With the numerous genomic programs undertaken these last years, there is an exponential production of gene sequences. However, one may stress that despite this huge amount of genes elucidations, the pace for discovery of new GH and PL remains constant. The new sequence data allow the expansion of the existing enzymes families (E.C. and CAZY) but not the discovery of new catalytic functions. The function of most of the GH and PL genes remains putative, based on sequence/structure homologies or remains unknown. There are many collections of micro-organisms (i.e. bacteria) that can be grown on artificial medium. The capacity of these micro-organisms to produce and to degrade polysaccharides is mostly unexploited. In this context, we propose to design and implement a medium throughput screening platform for assessing GH and PL activities on a collection of polysaccharides substrates having known and unknown structures. We envision miniaturised incubations of polysaccharides with bacterial extracts or putative recombinant GH and PL. The detection will be achieved by mass spectrometry, which offers the experimental advantage of minute amount of material necessary and allows access to structural data of the degradation products. At the end of the project we will have discovered new GH and PL activities which will allow, in term, i) to determine the structure of less known or unknown polysaccharides, ii) to produce oligosaccharides having original structure and properties and iii) to enrich notably the catalogue of enzymatic tools.

Partnership	CNRS - Roscoff (Végétaux marins et biomolécules) UMR 7139 INRA - BIA UR 1268 CEVA IFREMER - Labo. de Biotechnologies et Molécules Marines Univ. de la Méditerranée - AFMB - UMR 6098 CNRS - LAMBE - UMR 8587
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ANR Funding	511 258 €
Beginning & duration	01/12/2008 - 36 months
Reference	ANR-08-CP2D-06-01

Program: « Green Chemistry and Processes for a sustainable development »

Edition 2008

Projec Title | **DOMINO-CO - Allylation / carbonylations domino reactions : concept and applications**

Abstract

The synthesis of elaborated organic molecules often results in large wastes production due to the multitude of reagents involved and the elevated number of purifications procedures that are necessary to isolate pure compounds. This has of course a strong negative environmental impact and is in addition often the source of extra costs compared to simpler procedures. The use of catalytic reactions is in many cases a good tool to reduce this impact as the transformations can be very selective and straightforward. In particular, catalytic reactions performed in a domino sequence represent an interesting way of research to counterbalance this problematic of solvent, time and atom wasting. Domino reactions are transformations that give rise to the formation of two or more bonds in a one pot procedure. The fast elaboration of organic molecules is thus made with limited purification procedures and solvent wasting.

The use of carbon monoxide as co-reagent in a domino reaction has several additional advantages. At first, it's noteworthy that a large scope of carbonyl containing derivatives is accessible from the carbon monoxide source. All these functions are of synthetic interest and involved in retrosynthetic schemes. Moreover, in addition to this versatility, the carbon monoxide molecule is entirely incorporated in the final product, this results in an improved atom economy for the overall procedure. Finally, carbon monoxide is a raw material widely available for large scale synthesis now accessible from renewable carbon containing sources. For this CP2D call to projects, our two research groups have merged and coordinated their expertises in the area of carbonylation reactions in one hand and domino transformations for organic synthesis in another hand. This collaboration has given birth to a project which deals with the elaboration of domino transformations involving carbonylation and allylic alkylation steps for an improved atom, step and solvent economy. The originality of our concept is based the on the synthesis of stabilized carbanions or allylic esters from the CO source followed by an allylic alkylation step. The two palladium catalysed steps are performed in a domino type sequence for an improved atom, solvent and catalyst economy. To initiate the project and validate the concept, the domino reactions will be set up with simple starting materials. In order to further improve the atom economy of this family of domino transformations, an original approach using an alkoxycarbonylation / allylation procedure is proposed. This methodology is advantageous since no base is needed for the

allylation step and the loss of the allylic leaving group is limited to a molecule of CO₂ instead of a salt. Then, in order to increase the status of our methodologies, we have planned to apply these procedures for the synthesis of molecules of biological interest, including asymmetric syntheses due to the expertise of both groups in this field. To fully complete this project, we also propose a mechanistic study based on in situ high pressure IR and NMR studies of the palladium intermediates. The thus collected spectroscopic data are precious to fully understand the role of the palladium source in the two combined reactions as well as to bring some clues to issue of catalytic reactivity that can be encountered during the project.

Partnership

Ecole Nat. Sup. de Chimie de Lille - UCCS - UMR 8181
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**Coordinator
ANR Funding
Beginning
& duration
Reference**

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485 036 €
01/12/2008 - 48 months
ANR-08-CP2D-07-01

Program: « Green Chemistry and Processes for a sustainable development »

Edition 2008

Projec Title | **ENZYPRO - Enzymatic synthesis of natural label esters in supercritical fluids**

Abstract

Today, most of the esters including aromatic ones are produced by chemical synthesis processes which entail some drawbacks in terms of cost (high temperature, number of stages, post-treatment steps...) and environmental impact (use of organic solvents for instance). In this project we propose to develop a new sustainable synthesis method for esters. The interest of this new method can be highlighted in three points. Firstly, the reaction will be catalysed by enzymes thus improving process cost (lower temperature, reduced number of stages) and the process performance (enhanced selectivity). Secondly, the enzyme will be immobilized on a membrane support and the reaction will be carried out in a continuous enzymatic membrane reactor. The immobilized enzyme will be thus re-used and reaction and separation will be integrated. Consequently, the overall performance of the process will be improved. Finally, supercritical carbon dioxide will be chosen as solvent in order to protect environment and to simplify product/solvent separation steps. The scientific novelty is linked to the design and the performance of this new continuous enzymatic membrane reactor in supercritical CO₂. No existing process presents the specification of this new ambitious process. Thus, the integration of the three technologies (enzymatic catalysis, continuous membrane reactor, use of supercritical CO₂) in a single apparatus is original.

This new process will be applied for the synthesis of esters that have a high interest for cosmetic or food applications. It is worth noting that, with this new synthesis method, produced compounds will be able to obtain a natural label which enhances their interest.

In order to develop and optimize this new sustainable process, a pilot plan will be designed and built and experimental and modelling studies will be performed. Experimental research will focus on three points: research of adequate commercial enzymes to catalyse specific reactions of industrial interest, development and optimisation of an enzymatic membrane, study and optimization of the process of ester synthesis in the enzymatic membrane reactor using supercritical CO₂. Modelling and simulation of the process will help to improve the optimization of the system. Finally the new optimized process will be compared to the classical chemical one in terms of energetic balance, cost of the process and product quality. The interest of the new process as regards sustainable questions will be finally checked.

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Beginning & duration	01/12/2008 - 36 months
Reference	ANR-08-CP2D-08-01

Program: « Green Chemistry and Processes for a sustainable development »

Edition 2008

Projec Title | **ERISS - Innovative strategies of elaboration of liquid propellant used for the international space station propulsion**

Abstract

The project proposed concerns the lookout for a new strategy of a liquid propellant's elaboration, by intensification of Raschig process, which comes within the framework of sustainable development. It incorporates the overall synthesis steps, extraction and purification. It aims to replace a factory of industrial production. The future unit intends mainly to fabricate ultra pure propellants for the aerospace industry, as well as hydrazines of life science interest (pharmaceutical ingredients, cosmetics...). This work is carried out in a private partnership in the framework of an industrial research.

The benchmarks and the innovations sought concern several points:

1. At the synthesis level : by decreasing of the starting materials' amounts, which requires a new analysis of the reaction mechanisms and the introduction of an innovative technology in chemical engineering, by using micro-liquidizers and micro-reactors. This technology

is incontrovertible to assure the feasibility of the reactions conducted in extreme exothermic conditions (multiple-injection). Moreover, in a globalise market subjected to fluctuations, the microsystems adapt permanently the unit's size to the production volumes.

2. At the isolation level : by the lookout for a new extraction and purification's procedures, which should be selective, multiple-function and allowing energy gain, reactants saving and a drastic simplification of unitary operations, which the project evaluates to be around 70%.

3. Maintain the discriminative character of the current process concerning the competition ("Green" chemistry conducted in aqueous solutions which does not involve any organic solvent).

In opposition to the cryogenic couple H₂/O₂, the liquid stored propellants are incontrovertible for long-term space missions. Thus, the AVT (Automated Transfer Vehicle), elaborated by EADS Space Transportation and which transports 6 tons of propellants, will be used for supplying the International Space Station (ISS) and for its propulsion during the homing head (30 km/year). In worldwide, needs and demands are growing with the Space European Agency projects' development (AVT evolution) and with the NASA ones ("Constellation"), which anticipate crew exploration vehicles and freighters (conceived to support the human activity on low orbit, the International Space Station and installing of a

new moon base in 2018). New emergent powers have increasingly access to space exploration, which intensifies these markets (India, China, and Brazil).

"Hydrazines et Procédés" laboratory had acquired, during the last years, an international acknowledged (NASA, Defence Energy Center Support/DESC...) experience and knowledge in the field of chemistry of Nitrogen/Nitrogen interactions within the framework of pharmaceutical chemistry and cosmetics as well as for rocket propulsion. This expertise is supported by a synergy between the two laboratory teams : the mechanistic and synthesis team and the thermodynamics of multiphases systems team. The result of this interaction facilitates the control of the overall process chain starting from the reactants up to the pure product (chemical engineering). The LHP (Laboratoire "Hydrazines et Procédés") underlies the conception of several prototypes of industrial pilot plants and production units for many industrial groups in the field of pharmaceutical or aerospace research. The LHP cooperates with several national organisms (CNES, DGA and DCN) and had an asset of 30 patents, 50 publications and 100 international communications.

Partnership

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ANR Funding**

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**Beginning
& duration**

01/12/2008 - 36 months

Reference

ANR-08-CP2D-09-01

Program: « Green Chemistry and Processes for a sustainable development »

Edition 2008

Projec Title **EXPENANTIO - Towards green synthesis of chiral molecules: innovative experimental and theoretical approaches for understanding molecular basis of lipase and esterase enantioselectivity**

Abstract

There is an increasing demand for stereochemically pure compounds and a concomitant necessity to develop green chemistry. Our project is totally consistent with these two objectives, as its aim is: 1) to tightly combine environment-friendly experimental and theoretical novel methods for better understanding the molecular features that control enantioselectivity of lipases and esterases, in order to help in finding rational methods for improving enantioselectivity of these enzymes, 2) to use fundamental results obtained during the project, for the eco-conception of lipase-catalyzed production of optically pure alcohols, being important intermediates in asymmetric synthesis, for insuring at short term an efficient future exploitation of this work program.

By using innovative molecular modelling approaches, we will look for structural explanation for enantiopreference originating from differences phenomena, which have been little studied until now: differences in accessibility to the active site for enantiomers, "imprinting" effects on the active site afforded by substrates mimicking products, steric hindrance afforded by solvent molecules, changes in substrate and protein internal entropy upon substrate binding and changes in solvent molecule entropy upon substrate binding. Experimental approaches will be conducted in parallel to validate these theoretical results. First, rational computer-guided enzyme modification, using site-directed mutagenesis will be performed and kinetic and thermodynamic parameters of wild-type and modified lipase and esterase-catalyzed stereoselective reactions will be experimentally measured. As soon as substrates are volatile enough, reactions will be carried out in continuous solid/gas reactors, in which the enzyme at a solid phase is percolated by a carrier gas, containing gaseous substrates and additional non-reactant molecules, when needed. This system allows fixing independently and easily thermodynamic activities of the different species present in the vicinity of the enzyme, and obtaining as a consequence "intrinsic" kinetic and thermodynamic parameters of enzymes and "intrinsic" effect of non-reactant molecules. These parameters are useful for better understanding enzyme/substrate/solvent interactions defining enzyme selectivity.

Apart from these fundamental studies, microwave irradiation will be studied as an alternative activation method of selective lipase-

catalyzed reactions, promoting a reduction of energy costs. Stereoselectivity of native or modified enzymes will be investigated in details under microwave irradiation, in relation with other parameters having an influence on selectivity such as temperature, type of solvent, presence of water as co-solvent in the reaction medium. Besides, ionic liquids, whose effect on lipase and esterase stereoselectivity has already been mentioned, will be studied in the project. These media have been described "greener" than classical organic solvents, essentially for their low vapor pressure and their possible recycling at the end of a chemical or an enzymatic process. However, if one considers the real environmental impact of ionic liquids, the effect of their own synthesis on environment must be included. To that end, ionic liquids will be designed in our own laboratory, according to the principles of green chemistry, and then tested for their stability and ability to promote highly selective lipase-catalyzed reactions.

Promising reaction conditions and modified enzymes obtained, will finally be used to the green production of polyacetate and polypropionate, based on enzymatic acylation of 1,2,3-triols having a pseudosymetry in C2, and pseudo-ceramides, produced by lipase selective acylation of amino-alcohols with acyl donors such as methyl esters of myristic and stearic acids. Enantiomerically pure chiral alcohols will also be produced at pre-pilot (g) and pilot scale (kg) in solid/gas reactor, which furthermore enables reducing to zero the use of solvent encountered in liquid systems.

Partnership

CNRS - CNRS/LIENSs – BIEN - UMR 6250
 CNRS - CNRS/LIENSs –MAB
 CNRS UMR 6250
 CNRS - U3B - UMR 6204
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 ANR Funding
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 01/12/2008 - 48 months
 ANR-08-CP2D-10-01

Program: « Green Chemistry and Processes for a sustainable development »

Edition 2008

Projec Title | **FLUOSENSIL - Fluosensors based on task specific ionic liquids for quantification of heavy metals in water**

Abstract

The Executive European Directive 2000/60/EC (DCE/2000) and its national declensions aims at environmental restoration by 2015. More specifically, the concepts of « right chemical state » and « right ecological state » of water have emerged as a world concern. Indeed new regulations are a powerful impetus for the development of analytical tools devoted to environmental quality control. One of the difficulties is the wide dynamics of spatio-temporal scales involved in environmental quality control. Both localized area (such as polluted streams) and wide (typically several km²) catchments area are concerned. The temporal issue is also of importance. Environmental disruptive phenomena are generally transitory, implying time constraints for environmental quality control (necessary delayed measurements). Among the pollutants to detect, trace elements, especially the Heavy metals (lead, mercury, cadmium), are regarded as one of the major sources of pollution in the environment, since Present, even at low doses, a long-term toxicity. Within the framework of the DCE 2000/60/EC, the temporary values (DCE/2005/14) defining the "good chemical state of waters", go from 0,4 µg/l for the lead, 1 µg/l for the mercury and until 5 µg/l for the cadmium. These values can be considerably reduced in case of "very good quality waters": < 0,007 µg/l for the mercury and < 0,004 µg/l for the cadmium.

In this context, this project concerns the design and the implementation of an integrated, portable and inexpensive sensor in order to detect quantitatively and selectively heavy metals (lead, mercury, cadmium) with a sensitivity, consistent with the official norms required by the European Union. The water analysis will be conducted on small volumes and continuously with high-performance microsystems (typically of a few square centimeters) by using fluorescence as detecting method. The innovative approach that we propose is based on the immobilization of novel selective and sensitive molecular fluorescent sensors in an ionic liquid stationary phase allowing concentrating extraction of the heavy metals cations from a water phase.

In order to do that fluorescence molecular sensors in which the fluorescence is modified in the presence of cation will be designed and synthesized. By suitable molecular engineering, various fluorescent molecular sensors which are designed for selective detection of heavy ions (Pb²⁺, Hg²⁺ and Cd²⁺) with different functionalities will be synthesized.

-The fluorophore will be excited by fluorophores with Two-Photon

Absorption in order to enhance signal to noise ratio and therefore improve the sensitivity.

-The fluoroionophore will be incorporated in a ionic liquid phase. Such approach will allow in situ quantification of heavy metals traces in water with unprecedented sensitivity. The complexing and photophysical properties of the fluoroionophores will be studied at first in cuvettes in order to determine the characteristic of the molecular sensors in terms of sensibility, selectivity and extracting capacity.

The two phases will be further integrated in a microfluidic system and a microfluidics bench will be realized with fluorescence detection. The final goal is the development of a industrial prototype microfluidic system for in situ quantification of heavy metals traces in water with unprecedented sensitivity.

This project develops an innovative approach to achieve a new generation of sensor complementary to the existing electrochemical sensors and such a system may be extended to other pollutants metallic or organic (aluminium, pyralene ..).

Partnership

CNRS Ile-de-France EST - PPSM -UMR 8531
LSSOPN - UMR 7573
CNRS - CPM - UMR CNRS/UR1 6510
CEA- Labo. d'Electronique et de Technologies de l'Information
ELTA

**Coordinator
ANR Funding
Beginning
& duration
Reference**

Mme Isabelle LERAY (isabelle.leray@ppsm.ens-cachan.fr)
919 914 €
01/12/2008 - 36 months
ANR-08-CP2D-11-01

Program: « Green Chemistry and Processes for a sustainable development »

Edition 2008

Projec Title

HAMAC - Hybrids: Artificial Metalloenzymes for Asymmetric Catalysis

Abstract

Today, enantioselective catalysis is a crucial field for fundamental and applied chemistry. Despite three decades of intensive research, numerous catalytic processes have to be reconsidered in light of environmental and economic concerns. Enzymatic and homogeneous inorganic catalysis have been successfully used for such transformations but have to be improved to reach a broad use in industry. Today, the major need is to predict enantioselectivity mainly because supramolecular interactions are involved during the asymmetric reaction. These weak interactions have been optimized through evolution in metalloenzymes but are very hard to achieve in homogeneous catalysis. Then, the combination of biocatalysis and homogeneous catalysis specificities should allow the generation of very efficient catalysts.

Our strategy consists on the design of hybrid metal-based catalysts at the interface of the biology and the chemistry. The hybrid catalyst will be formed by an active site coming from the coordination chemistry and a protein host. The folding of the protein will modulate the selectivity of the reaction whereas the inorganic complex, achiral, will conduct the reactivity. The advantages of this "bio-inorganic" approach are outstanding. First, The possibility of dissociating the activity and the selectivity of the reaction will allow the generation of very specific catalysts. Second, the efficiency of catalysts will be greatly enhanced by the use of molecular biology and parallel synthesis for the complex fragment. Third, the weak interactions will be exploited to modulate the inorganic active site. Finally, the conditions for catalysis will fulfil the environmental requirements and follow the principles of green chemistry. Our objectives are focused on the design of hybrid catalysts for enantioselective oxidations, oxygen transfer reactions in particular. Today there are no efficient catalytic systems for the asymmetric transformations of alkanes, alkenes and sulfides. Our will is to propose a couple protein/complex in which the activity will depend on the complex affording then modularity for the catalysis. Aromatic hydroxylation will also be studied for the development of catalysts as treatment of HAP pollutants.

The key point of this project is the selection of the host/guest couple. Based on our recent work, two protein platforms will be selected.

The achiral inorganic complexes will be chosen from the pool of the bio-inspired catalysts developed since 10 years in the CRBio team

from LCBM laboratory. This approach implicates also fundamental aspects for these original catalysts. The parameters that influence the selectivity have to be determined. The structural parameters are then essential for the project and one partner has a worldwide recognition in this field. Thanks to protein crystallography, we hope to develop a method to shoot each step of the enantioselective reaction, leading to uncover the mystery of the asymmetric control. Optimization of these catalysts for high enantioselectivity is a major goal of the project. To do so, a site directed mutagenesis and screening for the mutants based on enantioselectivity will be undertaken.

Finally, the complementarities of the two laboratories CRBio/LCBM and LCCP/IBS into the enzymology, structural biology and bioinorganic chemistry should ensure the achievement of this project for the design of original artificial metalloenzymes.

Partnership

CNRS Alpes - LCBM -Equipe CRBio UMR 5249
CEA - IBS - LCCP - UMR 5075

**Coordinator
ANR Funding**

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**Beginning
& duration**

368 972 €

01/12/2008 - 36 months

Reference

ANR-08-CP2D-12-01

Program: « Green Chemistry and Processes for a sustainable development »

Edition 2008

Projec Title

HEXOSIC - Heat-Exchanger made of Silicon Carbide

Abstract

Bluestar Silicones, one of the worldwide leaders in silicones chemistry, proposes a R&D project, aiming to design new equipment for the transposition of batch to continuous processes. The safety and environmental issues linked to this type of chemicals, and the productivity targets as well require innovative technologies characterized by a fair corrosion resistance and high heat and mass transfer performances. A preliminary prototype of heat exchanger reactor made of silicon carbide plates has been developed by the LGC in collaboration with a SME specialist of SiC, Boostec. It has allowed to show the pilot feasibility with some reactions of industrial interest for a Bluestar Silicones. Now, it is necessary to pursue this effort and beyond the feasibility step to go on up to the design of an industrial reactor. It is expected that process intensification will lead not only to an enhancement of the operating conditions (better thermal control, efficient mixing) and of hazards management (hold-up decrease, strong thermal effusivity) but also to an increase of productivity (with the increasing reactants concentrations) and to a better selectivity with a better environmental impact (decrease of the solvent amount). It will be probably possible to imagine new chemical paths for new products. Some bottlenecks still remain in designing a reactor for silicones applications. First, since the products of the studied reactions are viscous, the reactor has to be operated under pressure because of the expected high pressure drop. This question has to be addressed through a specific design of the reactive channels and thanks to a particular way of brazing the SiC plates, that has to be developed by Boostec. Secondly, Bluestar Silicones would like to enlarge the applicability of this type of heat exchanger reactor to other exothermal reactions, that require a precise control of two-phase mixing and a good resistance to corrosion. This latter requirement is a typical feature of silicon carbide. Simultaneously, two ways of catalysis will be investigated : one homogeneous studied by the LGC and the other one being heterogeneous with a supported catalyst, studied by the LGPC, specialized in catalytic process engineering. The objective is to find the most suitable commercial catalyst (acquisition of kinetic data, deactivation,...) and to study the ways of catalyst deposition and the production of interfacial area inside the reactor. This research is also considered by Boostec as a challenge and an opportunity to prove the versatility of this type of technology. One attempt is to open the market of this SME. This project corresponds to a programme of innovative process development in order to design cleaner, safer and less consuming devices.

Partnership	BLUESTAR SILICONES France SAS (BSS) BOOSTEC Industries INPT - LGC - UMR 5503 CNRS - LGPC - UMR 2214
Coordinator	M. Kamel RAMDANI (kamel.ramdani@bluestarsilicones.com)
ANR Funding	796 635 €
Beginning & duration	01/12/2008 - 48 months
Reference	ANR-08-CP2D-13-01

Program: « Green Chemistry and Processes for a sustainable development »

Edition 2008

Projec Title	MESASCOLL - Chiral and recyclable mesoporous materials based on metallic nanoparticles for the asymmetric hydrogenation of arenes
Abstract	<p>The "MesAsColl" project deals with the development of "clean" and innovative asymmetric catalysts on mesoporous supports, leading to a sustainable and environment-friendly fine chemistry. The originality of the recyclable catalytic systems proposed lies in the confinement of metallic nanoparticles stabilized by optically active synthons into the pores of aluminosilicic mesoporous materials. Various approaches based on preparations in water under air are envisaged: i) the insertion of "pre-formed" colloids stabilized by chiral protecting agents ; ii) the "in situ" formation of nanoparticles in the presence of chiral stabilizing agents or their grafted analogues.</p> <p>The crucial step of this project lies in the evaluation of the new catalytic systems obtained in a target reaction, the hydrogenation of prochiral arenes in aqueous media under mild pression (1 bar H₂) and room temperature conditions. This reaction remains one of the last challenges of asymmetric catalysis and, to the best of our knowledge, there is no significant results in terms of asymmetric induction. An instructive example of industrial interest is the hydrogenation of a renewable biomass product, thymol, in (-)-menthol leading to the one-step formation of three chiral centers.</p> <p>This project results from the interaction of two research groups whose activities are centered on the development of selective and recyclable catalytic systems. The synergy of the intrinsic specificities of the mesoporous materials (Group of Dr. F. Launay, Paris) and of the nanoclusters (Group of Pr A. Roucoux, Rennes) is promising in terms of catalytic activity, chimioselectivity and asymmetric induction.</p>
Partnership	UPMC Paris 06 - SIEN - UMR 7142 LSCR -COS - UMR 6226
Coordinator	M. Franck LAUNAY (franck.launay@upmc.fr)
ANR Funding	418 842 €
Beginning & duration	01/12/2008 - 36 months
Reference	ANR-08-CP2D-14-01

Program: « Green Chemistry and Processes for a sustainable development »

Edition 2008

Projec Title

MUSE - Ugi-Smiles Coupling : environmental friendly access to new pharmaceutical scaffolds and ligands for heavy metals

Abstract

The development of new multicomponent reactions represents an important stream of green chemistry in term of atom and step economy. We recently described a new 4-component reaction (4-MCR) between carbonyl compounds, amines, isocyanides and electron poor phenols (Ugi-Smiles couplings). The reaction is conducted at high concentration or neat, and water is the only side-product generated. In order to get a better understanding of this reaction and control the various parameters affecting the reactivity of phenols, we wish to make a theoretical study and describe the various transition steps involved in the reaction. The model will help us to rationalize the extension of this coupling to new phenol families. We will mainly focus our efforts working with heterocycles such as triazines, quinolines, acridines. Indeed, the amino substituted derivatives of these heterocycles possess important features dealing with their biological properties and their interaction with various metals. The choice of these systems will help us to better promote this chemistry. Apart from the one-step preparation of rather complex aminoheterocycles from the analogous hydroxy, one of the main features of this approach is link to the preparation of these compounds without any chlorinated reagent. Indeed traditional syntheses from the hydroxy requires its conversion to the chloroheterocycle before adding the amine. The adducts we can prepare will be studied according to two directions: in a first study, we will develop cascades involving [4+2] cycloadditions of triazines. Ugi-Smiles coupling of hydroxytriazines with a suitable alkyne as MCR partner allows us to design an Ugi-Smiles/[4+2] cycloaddition/ rétrocycloaddition sequence with formation of fused pyridines (pyrrolopyridines, naphthyridines) widely studied for their biological properties. A second study concerning these MCR adducts will focus on their behavior as ligands towards heavy metals. Ugi-Smiles coupling of heterocycles such as hydroxybipyridine or hydroxytriazolopyridine should afford new ligands. Their selectivity and affinity should be strongly affected by the nature of the 4-MCR partners. Thus several libraries will be prepared and their properties as ligands will be studied towards metals such as nickel, copper and lead. In the case of triazolopyridines, this study will be extended to the complexation of actinides in the presence of lanthanides due to the interest of these systems in nuclear waste treatment. This projet

will be studied in a collaboration between the "organic chemistry research group of ENSTA" leader for the study, the "theoretical chemistry group" of ENS Lyon and the "chemical engineering group" of ENSTA.

Partnership

ENSTA – DCSO - UMR 7652
ENS Lyon - Labo. de chimie UMR 5182
ENSTA - Laboratoire de Génie des Procédés

Coordinator

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ANR Funding

464 277 €

Beginning

01/12/2008 - 48 months

& duration

Reference

ANR-08-CP2D-15-01

Program: « Green Chemistry and Processes for a sustainable development »

Edition 2008

Projec Title	OUTREMER - Clean Process of Ultramarine Pigments Synthesis
Abstract	<p>The ultramarine pigments are industrial pigments widely used in plastics and paints. The recognized absence of toxicity of these pigments allows their use into food contact plastics as well as in cosmetics. The annual world production of ultramarine pigments is estimated at 40 000 t. Without any treatment, the world industrial manufacture of these pigments would release in the atmosphere 72 000 t/y of carbon dioxide (CO₂) and 24 000 t/y of sulfur dioxide (SO₂). The liquid effluents (sulphates, polysulphides and so on) also pollute the water course when not treated. Hence, to respect the environnement, this process requires substantial investments.</p> <p>The XXX company is one of the main worldwide manufacturer of ultramarine pigments. Concerned about the respect of our environment, this company invests in the reduction of the pollution. XXX already uses a very efficient SULFOX process to recover the sulfur dioxide in the form of sulfuric acid, and treats its liquid effluents. These constraints justify the search of other less polluting process. A collaboration between the XXX and the Laboratory YYY has enabled the deposit of a patent on a new process of synthesis of ultramarine pigments. This new method is principally characterized by the fact that, on the opposite to the present process, it does not produce any gaseous effluent (CO₂, SO₂), or liquid effluent.</p> <p>The presented program "Clean Process of Ultramarine Synthesis" (OUTREMER), proposes to promote this patent. Numerous scientific and technological obstacles have to be overcome before an industrial process can be developed.</p>
Partnership	Confidential-Enterprise Confidential-Research Institute
Coordinator	XXX
ANR Funding	726 427 €
Beginning & duration	01/12/2008 - 39 months
Reference	ANR-08-CP2D-16-01

Program: « Green Chemistry and Processes for a sustainable development »

Edition 2008

Projec Title	PENTOVAL - Biotechnological production of pentanoic acids from sidestreams of agrobiomass biorefineries
Abstract	<p>Like petrol, biomass is a complex mixture of molecules that only become valuable once they have been extracted, purified and transformed into industrially-pertinent products. In the context of future biorefineries, biomass refining will require specific technologies and processes that will not only be economically viable, but also environmentally friendly and sustainable. Faced with such strict criteria, it will be indispensable to develop uses for all biomass fractions, including pentoses. In this context, the PENTOVAL project aims to address pentose biorefining, notably through the development of biotechnological strategies that will allow (i) the extraction of pentose-rich hemicelluloses from agricultural coproducts and (ii) the bioconversion of pentoses into useful chemicals.</p>
Partnership	<p>INSA - LISBP - UMR INRA792/CNRS 5504 Finlande\VTT (Valtion Teknillinen Tutkimuskeskus, Biotechnology, food industry, pharmaceuticals) Finlande\CBL (Computational Biosci. Laboratory, Dept Biol, and Environmental Sci, Univ. Jyväskylä)</p>
Coordinator	M. Michael O'DONOHUE (michael.odonohue@insa-toulouse.fr)
ANR Funding	230 691 €
Beginning & duration	01/12/2008 - 36 months
Reference	ANR-08-CP2D-17-01

Program: « Green Chemistry and Processes for a sustainable development »

Edition 2008

Projec Title

SUSE - Sustaining carbonic esters synthesis with carbon dioxide feedstock

Abstract

Plant lipids are stored in subcellular structures called oil bodies. These structures, constituted by a neutral lipid core surrounded by a monolayer of phospholipids, are extremely stable; in particular, there is no fusion of lipid bodies in seeds, thanks to the presence, at the surface of these oil bodies, of hydrophobic proteins: oleosins. Vegetal oil extraction processes have a limited yield, and need mechanical and thermal energy to break up seeds (in particular for rape seeds), and organic solvents to extract oil from cakes. Knowing the structural basis of oil bodies stabilization by their integral proteins would help to optimize these processes, and to make them more environment friendly. Unfortunately, up to now the published structural data concerning oleosins are very poor: results on secondary structures are partial and conflicting, and there is no high-resolution structure. Then, very few patents concern oleosins, and they are not related to the objectives of this project. The present project brings four partners together: 1) Biochemists (AgroParisTech-INRA, Grignon 78) that product recombinant proteins from *Arabidopsis thaliana* oil bodies, study their interfacial properties, and solve three-dimensional structure of proteins using crystallography. 2) Chemists (ESPCI-CNRS, Paris) that synthesize amphipols since several years, and study their assemblies. 3) Molecular biologists specialized in seeds (INRA, Versailles) that can grow mutant plants lacking particular oleosins. 4) A group from Soleil synchrotron (Saclay 91) that performs synchrotron radiation circular dichroism (SRCD). 5) A group from CIRAD (Montpellier) with special experience on structure determination by NMR of plant proteins associated to lipids. To allow structural studies on hydrophobic proteins from plant oleosins, we will use original surfactants called amphipols (amphipile polymers). Two categories of amphipols will be used, random or blocky, the latter being more adapted to the solubilization of the long hydrophobic region of oleosins that allows insertion into oleosomes. Firstly, we will study using SRCD the secondary structure of oleosins in complex with amphipols. SRCD will also allow us to study the secondary structure of these proteins in oil bodies, either natural (wild-type or mutants) or reconstituted in vitro. Comparing the secondary structures of oleosins in different environments will allow to better understand how they stabilize oleosomes. Secondly, we will try to solve high resolution structures of oil bodies proteins, using either NMR (on proteins labelled with ^{15}N and ^{13}C) or protein crystallography (on

soluble fragments of oleosins, or on whole oleosins in complex with amphipols). Structural data provided by the present project will give insight on the functions of integral proteins from plant oil bodies. They should also help to improve oil extraction processes, and to identify new natural emulsifiers.

Partnership

CNRS - SYMCAT/uB (Inst. de Chimie Moléculaire de l'Univ. de Bourgogne - équipe Systèmes Hybrides : Milieux et Catalyseurs) UMR 5260

CNRS - MaNaPI/uB (Inst. Carnot de Bourgogne - équipe MATériaux NAnostrutturés: Phénomènes à l'Interface) UMR 5209

CHEMOD/UCBL (Labo. sci. Analytiques de l'Univ. Lyon 1 - équipe Chimiométrie/Modélisation Chimie Théorique) UMR 5180

Finlande\Academy of Finland - OU (dept. of process and environmental engineering, University of Oulu - group Mass and Heat Transfer Process Laboratory)

Finlande\Academy of Finland - AA (dept. of Chemical Engineering, Abo Akademi University - Laboratory of Industrial Chemistry and Reaction Engineering)

Coordinator

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ANR Funding

315 960 €

Beginning & duration

01/12/2008 - 36 months

Reference

ANR-08-CP2D-18-01

Program: « Green Chemistry and Processes for a sustainable development »

Edition 2008

Projec Title SOPOL - Solubilization of seed oil bodies integral proteins by amphipols: structural studies for valorization

Abstract

This project addresses basic issues in the design of reaction routes to benign carbonic esters taking advantage on a multi-disciplinary cooperation between Finnish and French research groups. For the purpose, carbon dioxide based methodologies are proposed for substituting those from phosgene and carbon monoxide feedstocks.

Increased use of carbon dioxide for the manufacture of chemicals offers opportunities in the direction of Sustainable Chemistry and Engineering. Carbonic esters are an important class of commodity chemicals that find applications in a variety of sectors. Nonetheless, their primary synthesis pathway still relies on the use of hazardous phosgene, one of the most acutely toxic substances used on industrial scale. The alternative route, the catalytic oxidative carbonylation of methanol, allows responding to the current demand in dimethyl carbonate. However, these technologies intrinsically limit the production due to engineering and safety constraints.

Therefore, substitution strategies are highly desirable in meeting the following criteria of the "12 Principles of Green Chemistry":

(1) waste prevention, (2) atom economy, (4) design of safer chemicals, (5) safer solvents, (7) use of renewable feedstocks, and (9) catalysis.

The project explores innovative hybrid catalysis for carbonic esters synthesis in shifting to carbon dioxide and alcohols co-reagents, the later opening new insight into biobased feedstocks. The chemical strategy is associated with reaction engineering design in processing the catalysts either in a fluid phase or as solids for the efficiency of the synthetic methodology. The ultimate aim is to promote the development of sustainable products and processes through the application of Ecodesign, Green Chemistry and Engineering principles. The benign by design approach will be implemented by using ecodesign tools, to reduce the life cycle impacts of CO₂-based chemical products and processes. Sustainability indicators will be evaluated, further developed and tested to assess and evaluate the impact of benign by design benefits.

Partnership

INRA - UMR CB 206 (UMR AgroParisTech INRA Chimie Biologique)
CNRS - ESPCI - UMR 7616
Synchrotron Soleil
INRA- DAP - DGB - UMR 1098

Coordinator	M. Thierry CHARDOT (thierry.chardot@grignon.inra.fr)
ANR Funding	399 965 €
Beginning & duration	01/12/2008 - 36 months
Reference	ANR-08-CP2D-19-01