JOURNÉE SCIENTIFIQUE
DE L'INSTITUT DES SCIENCES MOLECULAIRES
Vendredi 5 Juillet 2013

[Université Bordeaux 1]
Domaine du Haut-Carré
Espace Agora
http://www.ism.u-bordeaux1.fr/

[9h00 - 9h30] ---- Accueil et café de bienvenue
[9h30 - 10h00] ---- Ouverture de la journée
[10h00 - 11h00] ---- Communications orales - 1ère partie
[11h00 - 12h00] ---- Conférence invitée de Pascal Kintz
Toxicologie médico-judiciaire :
le cheveu révélateur

[12h00 - 13h00] ---- Buffet
[13h00 - 15h00] ---- Session posters
[15h00 - 16h00] ---- Communications orales - 2ème partie
[16h15] ************** Remise des prix, clôture de la journée
New binaphthyl-type iodanes for asymmetric synthesis

Cyril Bosset, Laurent Pouységü* and Stéphane Quideau*

Université de Bordeaux, Institut des Sciences Moléculaires (CNRS-UMR 5255), 351 Cours de la Libération, 33405 Talence cedex
and Institut Européen de Chimie et Biologie, 2 Rue Robert Escarpit, 33607 Pessac cedex, France

Thanks to their mild oxidizing properties, hypervalent iodine(III) and (V) reagents, referred to as $\lambda^3$- and $\lambda^5$-iodanes, have proved their efficiency on a wide range of chemical transformations.\(^1\) Mainly used for oxidation of alcohols (IBX, Dess-Martin periodinane), they can also perform several oxygen transfer reactions such as sulfide oxidation, $\alpha$-hydroxylation of ketones and hydroxylative phenol dearomatization reaction (HPD reaction). Our team particularly focuses on this HPD transformation that allows the conversion of 2-alkylphenols into the corresponding so-called ortho-quinols, with the creation of a stereogenic center at the ortho-position of the starting phenol. However, efficient asymmetric versions of this reaction are still lacking.

Previous investigations carried out in our laboratory led to the development of a substrate-controlled asymmetric dearomatization reaction, which has been successfully applied to the synthesis of natural products.\(^2\) We are currently developing a reagent-controlled oxygen transfer strategy\(^3\) using chiral alkoxy iodonaphthyles and related $C_2$-symmetric structures. Different versions of these molecules have been synthesized to study both steric and electronic effects of substituents towards iodine oxidation. A wide range of oxidants (peracids, peroxides, persulfates,…) have then been tested to perform the oxidation of the iodine atom but only dimethyldioxirane (DMDO) was efficient. Moreover, this oxidation step was unexpectedly selective since the generated iodanes were all pure iodine(III) compounds, as evidenced by $^{13}$C NMR spectroscopic analysis.

These novel $\lambda^3$-iodanes have been used with success in HPD reactions such as in the conversion of 2-methylnaphthol into the ortho-quinol 1. Enantioselectivities are so far up to 53 %.


ScCO$_2$ assisted impregnation of drugs into polymeric fibres: 
*in situ* study by high pressure FTIR microscopy

M. Champeau, $^{a, b}$ J-M. Thomassin, $^b$ C. Jérôme, $^b$ et T. Tassaing$^a$

$^a$ Institut des Sciences Moléculaires, UMR 5255 CNRS, Université Bordeaux I, 351 cours de la Libération, 33405 Talence Cedex, France

$^b$ Center for Education and Research on Macromolecules, Université de Liège, Bâtiment B6a, B-4000 Liège, Belgique

In the last years, supercritical carbon dioxide (scCO$_2$; $P_c=7.4$MPa $T_c=31^\circ$C) has become an interesting alternative to traditional organic solvents for polymer processing and, among it, for impregnation process of polymeric matrix with molecules such as drugs or dyes. Indeed, thanks to its solubility in some polymers, scCO$_2$ can increase their free volume and temporally swell them. Moreover, scCO$_2$ can solubilize different molecules and carry them inside the polymer matrix. The high diffusivity of scCO$_2$ makes the process easy and fast. In this context, infrared spectroscopy is an effective tool to characterize the thermodynamic behavior of polymer-CO$_2$ systems and to study the polymer impregnation thanks to scCO$_2$. Near and mid-FTIR (Fourier Transformed InfraRed) spectroscopy and ATR-IR (Attenuated Total Reflectance InfraRed) are the two main technics generally used. However, both of them have drawbacks. On the one hand, FTIR spectroscopy is more adapted to liquid and/or large samples (cm$^3$) [3]. On the other hand, ATR-IR spectroscopy requires shaping of the samples into films in order to ensure a good contact between the polymer and the crystal [4].

In order to allow the in-situ analysis of microscopic polymer samples (~ 5-500µm) without the need to change their shape, we have developed a new and original method. The experimental setup consists in a FTIR microscope coupled with a high pressure cell that enables to work up to 15MPa and with a controlled temperature.

This project aims at impregnating various polymer fibers with drugs using scCO$_2$. Thanks to the newly developed technic, we can determine not only the swelling and the CO$_2$ quantity adsorbed in the matrix but also the evolution of drug loading with time.

Rotational (de-)excitation of HCN in collisions with He

O. Denis Alpizar, T. Stoecklin, P. Halvick, and M. L. Dubernet

Université de Bordeaux, ISM, CNRS UMR 5255, 33405 Talence Cedex, France
Université Pierre et Marie Curie, LPMAA, UMR CNRS 7092, 75252 Paris, France
Observatoire de Paris, LUTH, UMR CNRS 8102, 92195 Meudon, France

Hydrogen cyanide (HCN) is among the most abundant organic molecules in the interstellar medium. The rotational emission lines of HCN are considered to be a major tracer of dense molecular gas (star-forming molecular clouds) in luminous and ultraluminous infrared galaxies. Different observations suggest that the vibrational excitation of HCN, at least in the bending motion, deserves to be considered in the collisions mechanism. Such transitions can be calculated using the rigid bender average approximation but it seems important to check if the results given by this approximation are reliable by comparing with the exact results. What makes the exact treatment even more necessary is the recent detection of HCN l-type transitions in hot planetary nebula as it involves nearly degenerate levels. We present a new theoretical method to treat atom-rigid bender inelastic collisions at the Close Coupling level (RBCC) in the space fixed frame. The coupling between rotation and bending is treated exactly within the rigid bender approximation and we obtain the cross-section for the rotational transition between levels belonging to different bending levels.

A four-dimensional potential energy surface representing the interaction between He and HCN subjected to bending vibrational motion is first presented. The global minimum is found to be with the H atom pointing towards helium for an intermolecular separation of 7.94 \(a_0\). The corresponding well depth is 30.35 cm\(^{-1}\). The quality of the new potential has been tested by performing two comparisons with previous theoretical and experimental works. The rovibrational energy levels of the He-HCN complex for a rigid linear configuration of the HCN molecule have been calculated. The transitions frequencies are found to be in good agreement with the experimental data. We performed close coupling calculations of the rotational de-excitation of rigid linear HCN in collisions with He and observed a close similarity with the theoretical data published in a recent study.

With this potential energy surface we then compare the effects of the vibrational bending of HCN using the rigid bender averaged approximation or the RBCC approach. We discuss the validity of this approximation and of the previous studies based on rigid linear HCN.

References
Sondes AFM à nanotubes de carbone fonctionnalisés pour la biotechnologie

Matthieu Meillana, Bernard Bennetau, Luc Vellutini, Marie Degueil, Karine Heuzé, Thierry Buffeteau, Gwénaëlle Le Bourdon, Colette Belin, Sophie Marsaudon, Jean-Luc Pellequer, Michaël Odorico

a ISM, UMR 5255-CNRS, 351 cours de la Libération, 33405 Talence Cedex, France.
b CBMN, UMR 5248, CNRS, Allée de St Hilaire Bât B14, 33600 Pessac, France
c CEA, iBEB, Service de Biochimie et Toxicologie Nucléaire, 30207 Bagnols sur Cèze, France

Les avancées dans le domaine des biotechnologies sont étroitement liées au développement des techniques d'analyse par mesures de force et tout particulièrement la microscopie par force atomique (AFM) 1,2. Le projet BIONANOTIP (ARN P2N 2010-2014; porteur B. Bennetau; C2M) s'inscrit dans cette thématique; il a pour objectifs de développer de nouvelles approches pour la construction des surfaces des biocapteurs, le greffage des récepteurs sur ces surfaces sans dégradation de leurs propriétés biologiques et la mesure des interactions ligands/protéine à l'échelle de la molécule unique.

L'immobilisation des biomolécules sur des SAMs a été réalisée à l'ISM (groupe C2M) qui possède depuis déjà plusieurs années une bonne expertise dans ce domaine3. Afin de mesurer les interactions moléculaires de l'ordre du piconewton (10⁻¹² N) et d'augmenter la résolution spatiale des pointes AFM, des nanotubes de carbone (CNTs) ont été fixés, ou générés in situ par dépôt chimique en phase vapeur. Les CNTs ont été ensuite biofonctionnalisés selon un protocole de trempage original mis au point par le CBMN afin d'obtenir une modification chimique sélective de l'extrémité de la pointe. L'efficacité de la biofonctionnalisation est actuellement en cours :
- en utilisant des nanoparticules recouvertes de biomolécules qui serviront de marqueurs pour la microscopie électronique à balayage
- au LIRM (CEA), par spectroscopie dynamique de force (DFS) 4 pour caractériser les forces d'interaction entre le récepteur immobilisé sur la SAM et le ligand greffé sur le CNT.

Références
(2) Müller, D. J.; Dufrène, Y.F., Nature Nanotechnology, 2008, 3, 261 - 269
Dendritic functionalization of core-shell magnetic nanoparticles for biotechnology

L. Mitcova, H. Rahma, T. Buffeteau, G. Le Bourdon, M. Gaboyard, T. Duluc, B. Bennetau, Luc Vellutini, K. Heuzé

a Institut des Sciences Moléculaires, Université Bordeaux 1, CNRS UMR 5255, Bâtiment A12, 33405 Talence Cedex, France.
b Ademtech SA., Parc Scientifique Unitec, 4 Allée du Doyen Georges Brus, 33600 Pessac, France.

Modern biological sciences depend on the methods developed through biotechnology. In this area, protein immobilization is of high interest. The development of site selective methods of protein immobilization onto supports has enabled the fabrication of various functional protein microarrays and biosensors. Chemically, physically and biologically mediated methods of protein immobilization are well described in the literature.(1) However, the development of novel methods that would ensure protein integrity and functionality after their immobilization is required since proteins represent complex chemical structures. Moreover, proteins can adhere and adsorb on most surfaces through a variety of mechanisms resulting in non-specific protein bonding.(2)

In this work we proposed to obtain stable, water-dispersible, functionalized organic-inorganic nanohybrid material which will ensure selective, site specific protein immobilization. For this purpose superparamagnetic core-shell iron oxide nanoparticles (MNPs) were functionalized with maleimide functional group. In order to multiply the number of functional groups on the MNPs’ surfaces, MNPs were functionalized with dendritic coupling agent, thus enhancing their sensitivity in comparison with MNPs functionalized with a linear analogue. In order to induce a good dispersion in aqueous medium hydrophilic components were introduced in the dendritic structure’s backbone, such as poly(ethylene glycol) (PEG) chains or/and poly(amidoamine) (PAMAM) chains. Also, the PEG chain is considered to be one of the most inert chemical groups towards non-specific protein adsorption.(3) Dendritic structures were grafted onto MNPs via convergent approach. According to this approach first the structures are synthesized and characterized and only after that grafted on MNPs’ surface. Finally, maleimide functionalized MNPs were prepared and the dendritic effect was confirmed. These MNPs are stable in time and at temperature up to 100 °C and manifest a good dispersion in aqueous medium and in polar solvents.

References

A la découverte de la reconnaissance moléculaire
dans les containers photo-actifs

C. Mongin,a D. Bassani,a et B. Bibala

a Institut des Sciences Moléculaires, CNRS UMR 5255 - Université Bordeaux 1
351, Cours de la Libération, 33405 Talence (France)

La synthèse efficace1 de containers moléculaires fonctionnalisés et photo-contrôlables est encore un défi en chimie supramoléculaire. Dans cet objectif, nous avons conçu une nouvelle famille de récepteurs moléculaires de type cage incorporant un motif 9,10-diphénylanthracène. En effet, ce dérivé polyaromatique peut être oxydé de façon réversible en positions 9 et 10, pour former l’endo-péroxyde correspondant (Fig. 1). Cette modification dans la structure moléculaire n’a encore jamais été exploitée pour contrôler l’accès des molécules invitées aux containers moléculaires.

Nous présenterons donc la synthèse optimisée de ces nouveaux containers exploitant la réactivité contrôlée des triazines ainsi que la reaction de métathèse par effet gabarit2,3 puis les résultats sur la modulation de la cage en fonction de stimuli extérieurs (dioxygène, lumière, température…).

Références
(1) Rendements élevés, peu d’étapes, économie d’atome
(2) Blotny, G. Tetrahedron 2006, 62, 9507-9522
Viabilisation du recyclage de composites à renfort carbone et matrice thermodurcissable

M. Princaud\textsuperscript{a}, G. Sonnemann\textsuperscript{a}, S. Pompidou\textsuperscript{b}, N. Perry\textsuperscript{c}, C. Aymonier\textsuperscript{d}

\textsuperscript{a} Univ. Bordeaux, ISM, UMR 5255, F-33400 Talence, France.
\textsuperscript{b} Univ. Bordeaux, I2M, UMR 5295, F-33400 Talence, France.
\textsuperscript{c} Arts et Metiers ParisTech, I2M, UMR 5295, F-33400 Talence, France.
\textsuperscript{d} Univ. Bordeaux, ICMCB – CNRS, UPR 9048, F-33608 Pessac, France.

À l’origine développés pour des applications hautement techniques dans l’aéronautique et le spatial, l’usage des composites à renfort carbone et matrice thermodurcissable s’élargit depuis plusieurs années aux industries de l’automobile et des sports et loisirs. Toutefois, le choix du composite dépend parfois moins de ses performances techniques, que de critères esthétiques ou de l’image de haute technicité qu’il véhicule. Il en résulte ainsi un surdimensionnement des propriétés des constituants (en particulier, de la fibre de carbone) par rapport à la fonction du produit. En outre du point de vue environnemental, il a été montré que dans la mise en œuvre du composite, c’est la production de la fibre de carbone qui est la plus impactante. Une réponse économique et environnementale à ces inadéquations consiste donc à viabiliser le développement de composites à renfort recyclé.

Ainsi le recyclage du composite en fin de vie, même limité à la seule récupération des fibres, pourrait permettre de diminuer certains impacts anthropiques en réduisant les matières premières nécessaires à sa production (produits pétroliers essentiellement). En outre, ce recyclage du renfort peut être élargi aux déchets de production (fibres ou prépregs inutilisés, chutes de pièces composites, etc.). Les concepteurs seraient alors à même d’équilibrer coût et efficacité énergétique par la production de matériaux dits de seconde génération (p. ex. destinés d’abord à des pièces non-structurelles).

Toutefois, viabiliser cette filière de recyclage nécessite de palier les réticences des utilisateurs en les assurant de ses bienfonds technique, économique, environnemental et législatif. Ainsi, après avoir rappelé ces différents contextes, le recyclage des composite par solvolyse de la matrice par de l’eau en conditions supercritiques, ainsi que la mise en œuvre de semi-produits de seconde génération attractifs, seront présentés. Un premier bilan économique et environnemental de cette filière sera enfin dressé.

Références (extrait)
DEVELOPMENT OF MICROWELL ARRAYS: STUDYING THE METABOLIC RESPONSES OF SINGLE MITOCHONDRIA

Venkata Suresh Vajrala\textsuperscript{a}, Emmanuel Suraniti\textsuperscript{a}, Anne Devin\textsuperscript{b}, Michel Rigoulet\textsuperscript{b}, Stéphane Arbault\textsuperscript{a} and Neso Sojic\textsuperscript{a}

\textit{a} University of Bordeaux1, Institute of Molecular Sciences, CNRS UMR5255, NSYSA group, ENSCBP, 33607 Pessac, France.
\textit{b} University of Bordeaux Segalen, CNRS, IBGC UMR5095, 33077 Bordeaux, France.

Mitochondria play a central role in cellular respiration, ageing process and also in the onset of degenerative diseases. These duties are performed by the collections of mitochondria (within a cell) that are heterogeneous, dynamic, and subject to fusion and fission to form a network\textsuperscript{1}. Since the valuable information regarding mitochondrial physiology is missing during averaged analysis of a large population of these organelles, development of methods to probe the properties of individual mitochondria simultaneously at single organelle level is, therefore, a challenge for analyticians. In this context, we developed microwell array platforms based on fiber optic\textsuperscript{2} and PDMS micro-structuration\textsuperscript{3} that allow the screening of a large number of individual mitochondria simultaneously using fluorescence microscopy.

We used either a chemical etching procedure to create a high-density array of femtoliter (fL) containers from optical fiber bundles, or puncturing method to create milli to micrometric wells in PDMS- polymer thin layers. Mitochondria organelles were entrapped in these wells and independently imaged via reflecting optical signals. We developed experimental techniques which are required for the immobilization of mitochondria and also the screening of whole population and individual responses within those populations using optical fiber based microwell arrays and PDMS wells.

We studied the endogenous NADH (auto-fluorescence) variation of populations of individual mitochondria under activation with EtOH (substrate) and inhibition with Antimycin A (respiratory inhibitor). Statistical studies of mitochondrial NADH value distributions evidenced three different kinds of responses within the mitochondrial population, the metabolic performance being not related to the size of the mitochondrion. This individual mitochondrion analysis approach is now extended to the monitoring of different mitochondrial metabolic parameters, including mitochondrial membrane potential\textsuperscript{4} (oxidative phosphorylation activity) and oxidative stress markers for the detection of superoxide radical ($\text{O}_2^-$)\textsuperscript{5}.

References

(3) E.Suraniti \textit{et al. Anal. Chem.} \textit{(DOI: 10.1021/ac400494)}.
JOURNÉE SCIENTIFIQUE
POSTERS
Field Desorption : une technique d’ionisation complémentaire pour l’étude de matériaux organiques

C. Absalon\textsuperscript{a}, P. Castel\textsuperscript{a} et C. Mouche\textsuperscript{a}

\textsuperscript{a} ISM – CESAMO, UMR 5255, Université Bordeaux 1

L’analyse en spectrométrie de masse de polymères synthétiques et de macromolécules organiques et organométalliques est majoritairement réalisée à l’heure actuelle par Maldi ou ESI. Dans le cas des polymères notamment, l’analyse Maldi permet en effet d’apporter des informations cruciales aux polyméristes telles que la détermination des bouts de chaîne, la masse molaire moyenne et la distribution. Cependant, dans certaines situations : polymères ou molécules peu polaires, il s’avère délicat d’obtenir l’ionisation des composés recherchés.

Une autre technique d’ionisation : la désorption de champ (FD Field Desorption) peut alors se révéler particulièrement efficace. Cette technique a la particularité de permettre une ionisation extrêmement douce : on observe principalement des ions M\textsuperscript{+} et peu de fragments sont formés. Cette technique bien qu’ancienne\textsuperscript{1} connaît à l’heure actuelle un regain d’intérêt en raison de l’adaptation de sources FD sur des systèmes Tof et Ft-ICR et en raison de la mise au point d’un couplage : Lifdi (liquid injection field desorption/ionization) facilitant la mise en œuvre pratique de cette technique\textsuperscript{2}.

Cette étude porte sur la comparaison dans différents cas concrets des spectres Maldi et FD. Une attention particulière sera apportée à l’étude des polymères et la comparaison des données obtenues avec les 2 techniques d’ionisation. Nous détaillerons également l’intérêt de la FD dans le cas de polymères peu polaires (Polystyrène, Polyéthylène…).

Références

Gas adsorption and reactions on solids: in-situ study by thermal analysis and infrared spectroscopy

F. Benevides\textsuperscript{a}, G. Le Bourdon\textsuperscript{a}, J. Jolly\textsuperscript{c}, C. Pradere\textsuperscript{b}, J. Mascetti\textsuperscript{a}, L. Servant\textsuperscript{a}, J.C. Batsale\textsuperscript{a}, B. Pavageau\textsuperscript{c}

\textsuperscript{1}Institut des Sciences Moléculaires, UMR 5255 CNRS Université Bordeaux1, 351, Cours de la Libération, F-33405 Talence Cedex, France
\textsuperscript{2}Labaratoire Transferts Ecoulements Fluides Energétique, UMR 8508 CNRS, Esplanade des Arts et Métiers, F- 33405 Talence Cedex, France
\textsuperscript{3}Rhodia Laboratoire du futur (LOF), UMR 5258 CNRS, 178, avenue du Docteur Schweitzer, F-33608 Pessac cedex, France

We investigate in-situ gas adsorption on porous materials by combining infrared spectroscopy with infrared thermography. A model chemical reactor designed for Diffuse Reflectance Infrared Fourier Transform (DRIFT) allows us to clearly evidence the adsorbed species and to study the surface species formation and evolution, according to the temperature and the surrounding atmosphere (Fig 1). Infrared thermography is used to detect the heat flux coming from the sample surface (Fig 2) during gas adsorption (exothermic process). Heat transfer models (including losses by convection and conduction) are developed in order to evaluate the heat source and estimate the gas adsorption heat. By combining thermal analysis and spectroscopic information, key parameters for gas capture are characterized.

This approach allows us to better understand the mechanisms controlling the gas-surface interaction and may be used for studying heterogeneous catalytic systems and the fixation of CO\textsubscript{2} by solids (1), which is one of the most promising methods for its capture.

Références

Organic fluorescent nanoparticles as “ultra-bright” one- and two-photon emitters for (bio)imaging purposes

T. Bsaibessa, E. Genin, I. Gosse, E. Campioli, F. Terenziani, L. Cognet, M. Blanchard

*ISM, Univ. Bordeaux 1, France,*
*GIAF, Parma University, Italy*
*LP2N, Univ. Bordeaux 1, France*

Two-photon-excited fluorescence (TPEF) has gained widespread popularity in the biology community due to the advantages it provides in microscopic imaging. Among various probes, semiconductor quantum dots have been shown to provide a particularly powerful approach to luminescent nano-objects for bioimaging including TPEF. However, these inorganic systems suffer from several drawbacks such as toxicity, blinking and raise a number of questions with respect to environmental issues. With this in mind, we have developed fully-organic molecular-based luminescent nanoparticles showing exceptional one- and two-photon brightness. To this aim, novel triphenylamine-based dipolar dyes (1) were designed and used to prepare aqueous suspensions of fluorescent organic nanoparticles (FONs) via the precipitation method (2). The obtained spherical nanoparticles (30-60 nm in diameter) are fluorescent in aqueous solution (Fig.1) and exhibit extremely high one- and two-photon brightness (up to 10^8 M^-1 cm^-1 and 10^6 GM). The emission color of these nano-aggregates can be tuned from green to yellow, red and NIR by playing on the molecular structure and taking advantage of environment and local field effects. The use of these FONs as probes for biphotonic *in vivo* imaging was investigated on *Xenopus laevis* tadpoles. When using FONs made from an octupolar dye, the formation of microagglomerates (2-5 µm scale) was observed, with subsequent lethal occlusion of the blood vessels. At opposite, the nanoparticles of a dipolar dye allowed acute imaging of blood vessels, thanks to their suitable size and giant brightness, while no toxic effect was observed (Fig.2). The present study that engineering of FONs made from dipolar dyes can lead to ultrabright, biocompatible nanoparticles allowing acute bioimaging. These nano-objects represent promising alternative to quantum dots for bioimaging purposes.

![Fig. 1. Wide-field fluorescence image of NIR emitting FONs freely diffusing in solution. An excitation laser at 568nm was used (ab. 500W/cm^2). The photoluminescence was collected by a high NA objective (x60, 1.4NA) and sent to an EMCCD camera after passing through a longpass filter with a cutoff at 633nm. Bright spots correspond to in-focus individual nanoparticles. A short integration time of only 10ms is used such that most diffusing nanoparticles appear as nearly diffraction limited spots. Some out of focus nanoparticles are barely distinguishable in the background. Scale bar 5mm](image1)

![Fig.2. Green-emitting FONs suspension under UV lamp (left), observation by TEM of the nanoparticles and TPEF image (green signal) of blood vessels of a living *Xenopus laevis* tadpole (stages 48-52) after intra-cardiac injection of green-emitting FONs (right). Excitation at 820 nm. The red color corresponds to the endogenous SHG signal (410 nm) that arises from muscle tissue, while green corresponds to the TPEF signal generated in vivo by the FONs (460-590 nm). Scale bar = 100 µm.](image2)
Development of an Affinity-Based Proteomic Strategy for the Elucidation of Proanthocyanidin Biosynthesis

Hélène Carrié, Dong Tien Tran, Sabrina Rousseau, Denis Deffieux*, and Stéphane Quideau*
Univ. Bordeaux, Institut des Sciences Moléculaires (CNRS-UMR 5255) and Institut Européen de Chimie et Biologie, 2 rue Robert Escarpit, 33607 Pessac Cedex, France

Proanthocyanidins (PAs, Figure 1), also known as condensed tannins, are oligo/polymeric chains of flavan-3-ols. These polyphenolic flavonoid secondary metabolites are ubiquitously found in plants.¹ They are biosynthetically produced through the flavonoid pathway, one of the best studied biochemical pathways in plants. However, the last steps leading to the formation of Pas remain unclear. The exact nature of the starter and extension units, as well as whether or not a dedicated enzyme (i.e., a “proanthocyanidin synthase”) is involved in the coupling process, remains unknown. In this context, the discovery of any novel enzyme involved in PA biosynthesis by proteomic analysis would certainly supply valuable information regarding the mechanistic nature of this oligomerization process. The recent availability of the grapevine genome sequence has boosted efforts towards the proteomic analysis of tissues from various parts of this plant. However, despite outstanding progress in electrophoretic and chromatographic techniques coupled to mass spectrometry-based proteomics, the quantitative resolution and identification of all proteins in a given proteome is not feasible due to the complexity of the resulting extracted proteome (more than 700 proteins can be found just in grape skin). In order to reduce such complexity, we have developed flavanoid-based probes designed for investigating Pas biosynthesis. Those probes are based on the emerging chemical proteomic technology, activity- and affinity based protein (ABPP) originally developed by Cravatt and Bogyo²-³, which is particular well suited for the proteomic analysis of grapevine tissues. Two flavanols, (+)-catechin and (−)-epicatechin, presumably engaged in the oligomerization process leading to PAs, were selected for the design of these probes.⁴

To evaluate the suitability of these probes, we selected leucoanthocyanidin dioxygenase (LDOX) an enzyme implied in the last steps of the flavonoid biosynthesis pathway. This enzyme is capable to bind selectively with (+)-catechin and (−)-epicatechin and constitutes therefore an appropriate model enzyme for this proof-of-concept study.⁴,⁵

Références

New chiral iodanes for asymmetric oxygenation reactions

Romain Coffinier, Laurent Pouységuy* and Stéphane Quideau*

Université de Bordeaux, Institut des Sciences Moléculaires (CNRS-UMR 5255), 351 Cours de la Libération, 33405 Talence cedex
and Institut Européen de Chimie et Biologie, 2 Rue Robert Escarpit, 33607 Pessac cedex, France

Interest in hypervalent iodine(III) and (V) reagents, also referred to as $\lambda^3$- and $\lambda^5$-iodanes, is mainly due to their useful oxidizing properties, combined with their commercial availability and benign environmental character compared to heavy metal-based oxidizing agents. Both $\lambda^3$- and $\lambda^5$-iodanes have proven their efficiency in a wide range of chemical transformations. Recent developments in hypervalent iodine chemistry have concerned the elaboration of chiral iodanes for reagent-controlled asymmetric transformations and especially oxygenation reactions.

Our team is notably interested in the hydroxylative phenol dearomatization reaction (i.e., HPD reaction) of 2-alkylphenols. The ortho-phenolic carbon center at which the hydroxylation takes place becomes stereogenic. Thus a chiral iodane reagent capable of controlling the absolute configuration of this center would constitute a valuable tool for organic synthesis, and in particular for the total synthesis of natural products whose elaboration is biosynthetically based on the HPD reaction. The classical examples are the many natural bicyclo[2.2.2]octenones that are elaborated by the [4+2] cyclodimerization of HPD-derived ortho-quinols.

In this context, we have been developing a reagent-controlled asymmetric induction strategy, which relies on the synthesis of new $C_2$-symmetrical Salen-like di-iodinated compounds. These structures could be obtained in a one step synthesis starting from various chiral diamines. Screening of oxidants revealed that only 3,3-dimethyldioxirane (i.e., DMDO) was able to mediate a clean and efficient oxidation of these Salen-like structures. This DMDO-mediated oxidation was selective and led only to $\lambda^5$-iodanes derivatives, which were isolated in high yields by simple filtration and unambiguously characterized by $^{13}$C NMR spectroscopic analysis.

The ability of these Salen-type $\lambda^5$-iodanes to induce asymmetry in HPD reactions, key step in the synthesis of natural ortho-quinol-derived [4+2] cyclodimers such as (+)-biscarvacrol, is being evaluated at this time. In this case, enantioselectivity up to 55% was obtained starting from carvacrol and increased up to 68% in the case of bisthymol from thymol.

---


Dinitrogene tetroxide $\text{N}_2\text{O}_4$ formed and trapped in a glass matrix by thermal poling treatment

T. Crémoux,\textsuperscript{a} Marc Dussauze,\textsuperscript{a} Evelyne Fargin,\textsuperscript{b} Thierry Cardinal,\textsuperscript{b} David Talaga,\textsuperscript{a} Frédéric Adamietz,\textsuperscript{a} et Vincent Rodriguez \textsuperscript{a}

\textsuperscript{a} Univ. Bordeaux, ISM, CNRS UMR 5255, F-33400 Talence, France
\textsuperscript{b} Univ. Bordeaux, ICMCB, CNRS UPR 9048, F-33600 Pessac, France

Polarized glasses are of great interest for a large range of applications going from photonic to biomaterials. In the past decade, researchers used thermal poling to induce Non Linear Optical (ONL) properties inside of glasses. Indeed, thermal polarization treatments permit to entrap a strong and stable electric field right below the anodic surface of a glass slice. This internal electric field is a consequence of a space charge layer induced within a cationic depletion layer. However to this day poling effects on glasses structure are not fully understood by scientific community. Poling effects depend on a wide range of parameters such as the glass composition, the working atmosphere, electrodes' nature, poling voltage and temperature.

In this work using, Energy Dispersive Spectroscopy (EDS), vibrational spectroscopies coupled with Second Harmonic Generation techniques, we have fully characterized the poling effects on a specific borosilicate glass. We have observed dinitrogene tetroxide $\text{N}_2\text{O}_4$ entities entrapped within the polarized glass matrix. Moreover, this study shows that formation mechanisms of $\text{N}_2\text{O}_4$ are linked to a complex coupling between the poling atmosphere and the glass structure rearrangements.

These results contribute to a better understanding of the poling mechanisms and effects regarding glasses composition which is necessary to progress towards possible applications.
Activité Optique Raman de cryptophanes optiquement purs

N. Daugey\textsuperscript{a}, T. Brotin\textsuperscript{b}, D. Cavagnat\textsuperscript{a} et T. Buffeteau\textsuperscript{a}

\textsuperscript{a} Groupe Spectroscopie Moléculaire – Institut des Sciences Moléculaires, Talence, France
\textsuperscript{b} Laboratoire de Chimie de LENS-LYON, Ecole Normale Supérieure de Lyon, Lyon, France

L’activité optique d’une molécule, ou d’une structure moléculaire, se traduit par une réponse spectrale différente à une excitation photonique polarisée circulairement gauche ou circulairement droite. Cet effet est en relation directe avec la chiralité de la molécule ou de la structure moléculaire. La mesure de l’activité optique d’une molécule chirale, associée à des calculs de chimie quantique, permet de remonter à leur configuration et/ou conformation absolue.

Plusieurs techniques permettent de mesurer l’activité optique d’une molécule : le Dichroïsme Circulaire Vibrationnel (VCD) dans l’infrarouge, l’Activité Optique Raman (ROA) dans le visible, et le Dichroïsme Circulaire Electronique (ECD) dans l’UV. Nous développons au sein du GSM la technique ROA, unique en France, matérialisée par notre instrument Chiralraman. Celle-ci s’avère un outil complémentaire indispensable de la technique VCD. En effet, cet instrument permet de mesurer simultanément le spectre Raman dépolarisé et l’Activité Optique Raman de 100 à 2500 cm\textsuperscript{-1} de molécules pures ou en solution (solvant organique ou aqueux).

Nous présenterons des exemples de mesure d’Activité Optique Raman sur les cryptophanes Cr(OMe)\textsubscript{6}, Cr(OMe)\textsubscript{9} et Cr(OMe)\textsubscript{12} en solution dans CDCl\textsubscript{3} et C\textsubscript{2}D\textsubscript{2}Cl\textsubscript{4}. La complexation ou non du solvant sera étudiée sur le Cr(OMe)\textsubscript{6}.
Rotational (de-)excitation of HCN in collisions with He

O. Denis Alpizar, a T. Stoecklin, a P. Halvick, a et M. L. Dubernet b, c

a Université de Bordeaux, ISM, CNRS UMR 5255, 33405 Talence Cedex, France
b Université Pierre et Marie Curie, LPMAA, UMR CNRS 7092, 75252 Paris, France
c Observatoire de Paris, LUTH, UMR CNRS 8102, 92195 Meudon, France

Hydrogen cyanide (HCN) is among the most abundant organic molecules in the interstellar medium. The rotational emission lines of HCN are considered to be a major tracer of dense molecular gas (star-forming molecular clouds) in luminous and ultraluminous infrared galaxies (1). Different observations suggest that the vibrational excitation of HCN, at least in the bending motion, deserves to be considered in the collisions mechanism (2). Such transitions can be calculated using the rigid bender average approximation but it seems important to check if the results given by this approximation are reliable by comparing with the exact results. What makes the exact treatment even more necessary is the recent detection of HCN 1-type transitions in hot planetary nebula as it involves nearly degenerate levels (3).

We present a new theoretical method to treat atom-rigid bender inelastic collisions at the Close Coupling level (RBCC) in the space fixed frame. The coupling between rotation and bending is treated exactly within the rigid bender approximation and we obtain the cross-section for the rotational transition between levels belonging to different bending levels.

A four-dimensional potential energy surface representing the interaction between He and HCN subjected to bending vibrational motion is first presented. The global minimum is found to be with the H atom pointing towards helium for an intermolecular separation of 7.94 Å. The corresponding well depth is 30.35 cm^{-1}. The quality of the new potential has been tested by performing two comparisons with previous theoretical and experimental works. The rovibrational energy levels of the He-HCN complex for a rigid linear configuration of the HCN molecule have been calculated. The transitions frequencies are found to be in good agreement with the experimental data. We performed close coupling calculations of the rotational de-excitation of rigid linear HCN in collisions with He and observed a close similarity with the theoretical data published in a recent study (4).

With this potential energy surface we then compare the effects of the vibrational bending of HCN using the rigid bender averaged approximation or the RBCC approach. We discuss the validity of this approximation and of the previous studies based on rigid linear HCN.

References
Total Synthesis of Bacchopetiolone via Hypervalent Iodine-Mediated Hydroxylative Phenol Dearomatization

Mourad Elassal, Laurent Pouységù* and Stéphane Quideau*

Université de Bordeaux, Institut des Sciences Moléculaires (CNRS-UMR 5255), 351 Cours de la Libération, 33405 Talence cedex
and Institut Européen de Chimie et Biologie, 2 Rue Robert Escarpit, 33607 Pessac cedex, France

The oxidative dearomatization of phenols has today become a popular reaction for the synthesis of complex natural substances.1 Hypervalent iodine compounds (i.e., iodanes) and metal-based (e.g., Pb(OAc)₄, Tl(NO₃)₃) reagents are efficient tools to carry out this type of reaction and notably allow the transformation of 2-substituted phenols into cyclohexa-2,4-dienone derivatives. In addition, the iodanes represent an attractive alternative to the use of toxic metallic compounds with the current awareness of the need to develop “green” chemical approaches. We are currently working on the synthesis of bacchopetiolone, a dimeric sesquiterpene that was isolated in 1991 from the aerial parts of Baccharis petiolata, a Chilean shrub commonly used in traditional medicine and known for its in vitro antimicrobial activity.2 The biogenesis of bacchopetiolone 1 has been proposed to proceed through a [4+2] cycloaddition of the bisabolane derivative 2, a so-called ortho-quinol which is obtained by hydroxylative phenol dearomatization (i.e., HPD reaction) of its natural phenolic precursor, the (R)-(-)-curcuphenol 3. Despite previous synthetic efforts carried out by others,3 no total synthesis of the naturally occurring ortho-quinol-derived [4+2] cyclodimer 1 has been reported so far.

We thus envisaged to apply our biomimetic SIBX-mediated HPD reaction to (R)-curcuphenol 3 for converting it into the desired (RR)-ortho-quinol 2, which was expected to homodimerize spontaneously.4 Treatment of 3 with SIBX, the stabilized version of the λ⁵-iodane 2-iodybenzoic acid (IBX),5 followed by an acidic hydrolysis, afforded the expected [4+2] cyclodimers as a clean 3:2 mixture of (RR,RR)-1 and its (RS,RS)-isomer, in a good yield of 69%. Current investigations are being carried out with home-made chiral iodanes with the aim of developing an asymmetric version of this HPD reaction.


Journée Scientifique de l’ISM
5 Juillet 2013
Espace Agora, Domaine du Haut-Carré, Talence
A Chemiluminescent Janus Rod Prepared by Indirect Bipolar Electrodeposition

Zahra Fattah, Jérome Roche, Patrick Garrigue, Dodzi Zigah, Laurent Bouffier and Alexander Kuhn

Université Bordeaux 1, ISM, ENSCBP, 16 Avenue Pey Berland, 33607 Pessac, France

Janus nano- and microparticles are of enormous interest because the multiple functionalities of these objects allow their application in various fields, from photocatalysis to drug delivery. Bipolar electrochemistry (BPE) is one of the few methods that can be used to synthesize such objects in a true bulk phase. This concept has been applied to deposit very different materials using either direct or indirect bipolar electrodeposition (IBED) in order to generate asymmetric objects, which are modified at one end either with a metal, an organic or inorganic layer, or a polymer moiety. In the present work we demonstrate that IBED is very appropriate for the toposelective modification of objects with inorganic complexes, which remain fully functional. Water-insoluble Prussian Blue (PB), Fe$^{III}_4$[Fe$^{II}$(CN)$_6$]$_3$, and related compounds have been deposited on a graphite rod. The presence of this inorganic layer efficiently promotes luminol chemiluminescence, which is revealed by the emission of a typical blue light at one end of the Janus object. This coordination compound has been used for many interesting applications in the field of analytical chemistry especially as a functional ingredient for chemical and biological sensors. These proof-of-principle experiments open up new perspectives for the straightforward generation of functionalized light-emitting objects. Such objects might find interesting applications either as sensors or catalytic swimmers, taking advantage of PB’s activity with respect to the decomposition of hydrogen peroxide, acting in this way also simultaneously as a chemical fuel for autonomous chemiluminescent swimmers.

Références
POROUS MATERIALS MADE FROM A PAPER MILL BY-PRODUCT AND THE LIFE CYCLE ASSESSMENT OF THEIR ENVIRONMENTAL IMPACTS

Amandine Foulet, Hervé Deleuze, Guido Sonnemann and Philippe Garrigues

Université Bordeaux 1, ISM-UMR CNRS 5255, The Life Cycle Group CyVi, 351 Cours de la Libération, F 33405 Talence, France

In the worldwide Kraft pulping process, the dissolved wood together with the spent pulping chemicals forms a liquid stream called black liquor containing organic matter such as degraded lignin. Everyday tons of Kraft black liquor are produced and merely used for energy production whereas it could be a source of biopolymers.

Kraft lignin valorization has been previously investigated in our research laboratory (1). The developed process allows the preparation of porous monoliths directly from black liquor by using a technique based on an emulsion-templated polymerization. Porosity is generated by using castor oil as porogenic agent and lignin is thermally crosslinked to form the solid polymeric network. The obtained material is a cylinder-shaped monolith showing a homogeneous macroporous structure (see Fig. 1&2).

Combining a vegetable oil with an industrial waste to prepare porous materials seems to be in line with the green chemistry principles (2). The validity of this assumption is being determined by a comparative life cycle assessment (LCA) which is a relative tool assessing the potential environmental impacts of a studied system (3). To draw up a relevant comparison, castor oil is replaced by a petrochemical, the 1,2-dichloroethane (DCA) which is consistent with the emulsification parameters. The resulting preparation technique allows to establish the recycling of all solvents used in the process including DCA, unlike castor oil. The early results showed that using a vegetable oil leads to a low potential impact on climate change but is less advantageous than using a petrochemical in most other environmental indicators studied.

Références

Design and synthesis of small molecules based on TIPS-triphenodioxazine core for n-type organic field-effect transistors

Guillaume GRUNTZ\textsuperscript{a}, Yohann NICOLAS\textsuperscript{a}, Lionel HIRSCH\textsuperscript{b}, Thierry TOUPANCE\textsuperscript{a}\textsuperscript{*}

\textsuperscript{a}University of Bordeaux 1, ISM-UMR 5255 CNRS, 351 Cours de la Libération, F-33405 Talence Cedex, France.
\textsuperscript{b}University of Bordeaux, Laboratoire de l’Intégration du Matériau au Système, UMR 5218 CNRS, ENSCBP, 16 Avenue Pey-Berland, 33607 Pessac Cedex, France.

For some years, the TIPS-Pentacene architecture has been studied and has showed very interesting properties for an efficient p-type organic semiconductor including charge transport and very good solubility [1]. This architecture led to a 2-D brick-layer arrangement of p-stacking [2] and mobility higher than 1 cm\textsuperscript{2}V\textsuperscript{-1}s\textsuperscript{-1} for solution-processable transistors [3]. In order to design soluble n-type materials, a recent strategy has consisted in lowering the LUMO energy level by the replacement of carbon and hydrogen atoms of TIPS-pentacene by nitrogen atoms [4-5]. Another concept has also been developed by replacing the pentacene core by the triphenodioxazine (TPDO) skeleton in order to stabilize the anionic form. Indeed, unlike the aromatic core of pentacene, triphenodioxazines exhibit a quinoid structure at the center of the pentacycle that is expected to enhance the stability of the anion. This TIPS-TPDO led to electronic mobilities that outperformed by two orders of magnitude those of TIPS-pentacene measured under similar conditions [6-7].

In order to increase the electron mobility of devices, electron-withdrawing groups were attached to the TPDO core and soluble TIPS derivatives have been synthesized. It resulted in lowering the LUMO energy level of the molecules and better n-type semi-conductors are expected.

Soft Heterogeneous Catalysis in Droplet-Based Microfluidics

Q. Jochyms\textsuperscript{1,2}, E. Mignard\textsuperscript{1}, J.-M. Vincent\textsuperscript{2}

\textsuperscript{1} Laboratoire du Futur, UMR 5258 CNRS-Rhodia, 178 Avenue du Dr. Schweitzer, 33608 PESSAC Cedex, France

\textsuperscript{2} Institut des Sciences Moléculaires, UMR 5255 Bâtiment A11, Université de Bordeaux 1, 33405 TALENCE Cedex, France

The aim of this project is to develop a new kind of catalyst with surfactant properties. By anchoring one or several fluorous tails to the ligand, the catalyst can be used at the interface of a non-miscible liquid-liquid system, i.e. where a phase including all reagents and products is dispersed in a fluorous oil containing the “surfactant catalyst”. The reaction would thus occur at the interface of the two fluids.

This new synthetic pathway could thus be seen as “soft heterogeneous catalysis” (SHC) by reference to other heterogeneous systems which use solid supports.\textsuperscript{1} Here the support is the interface of the emulsion thanks to the surfactant properties of the catalyst. Advantages of SHC include: control of the catalyst charge by playing with the size of the emulsion and the surfacic concentration, good heat transfer thanks to the inert oil (instead of solid with a poor heat transfer coefficient), separation of the catalyst from the product can be achieved by a simple decantation. Those points can be enhanced by using microfluidic devices instead of traditional process.

The well-known cycloaddition of Huisgen, catalyzed by Cu(I), will be used as a proof of concept for the SHC. This reaction is very effective but since Cu(I) is unstable, it will be introduced as Cu(II) and reduced \textit{in situ}. By a photosensitizer linked to the copper.\textsuperscript{2} The reduction is done via a photo electron transfer from the photosensitizer group to the copper-core, a N-ligand helping in the process of reduction and stabilizing of the new species.

The first step of the work is to add fluorous tails to the ligand without changing the efficiency of the catalyst. The second step will be to achieve reactions in droplet-based microfluidic devices. By this way, we will be able to generate model experimental conditions to fully characterize this new synthetic approach.

Références:


Synthetic approach to spirolides total synthesis

Jessica Labarre-Lainé, Redouane Beniazza, Ignacio Perinan, Alexandre Guthertz, Simon Grelaud, Valérie Desvergnes, Yannick Landais

Université de Bordeaux, Institut des Sciences Moléculaires, UMR-CNRS 5255, 351, cours de la Libération, 33405 Talence Cedex, FRANCE

Spirolides are macrocyclic imine phycotoxins produced by dinoflagellate Alexandrium Ostenfeldii and first isolated in the early 1990s. They can be concentrated in shellfish edible tissues and thus transferred to marine animals and humans causing poisoning. Spirolides induce rapid death by intraperitoneal injection (IC₅₀ = 7-9 mg/kg) to mice and have been shown to be a potent antagonist of nicotinic acetylcholine receptors. Therefore, total syntheses of spirolides as well as other phycotoxins are currently at the heart of an intense research activity. Fourteen different spirolides have been identified but to date no total synthesis of spirolides has been reported.

We propose an approach to the both bis-spiroketal south fragment and spiroimine north fragment of 13-desmethyl spirolide C. In particular, the approach to bis-spiroketal skeleton is based on a sila-Stetter reaction as the key step.

Our strategy to reach north spiroimine will also be reported.

---

Free-Radical Carbo-alkenylation of Enamides and Ene-carbamates

Virginie Liautard, Clément Poittevin, Redouane Beniazza, Frédéric Robert, Yannick Landais

Université de Bordeaux, Institut des Sciences Moléculaires, UMR-CNRS 5255, 351, cours de la Libération, 33 405 Talence Cedex, FRANCE

Following our continuous interest in multicomponent processes,\(^1,2\) we recently studied the reactivity of enamides and ene-carbamates in the presence of free-radical species. Electron-deficient radical intermediates such as \(A\) (esters, ketones, amides, etc.) are known to add efficiently onto electron-rich olefins such as \(B\), to provide a new radical species that is then involved in reduction and atom-transfer reactions or oxidized into an iminium. The present work will show that based on the concept of matched polarity between the different partners, the electron-rich radical intermediate is able to react with a third component such as an electron-deficient olefin \(C\) to afford the carbo-alkenylation product with high levels of diastereocontrol in the cyclic series.

![Diagram of free-radical carbo-alkenylation](image)

Intermolecular additions of two functionalized carbon fragments across various cyclic and acyclic enamide and ene-carbamate \(\pi\)-systems thus allow introducing diversity and complexity on the olefinic backbone and offer a straightforward access to valuable intermediates for the total synthesis of alkaloids.

Références


Journée Scientifique de l’ISM
5 Juillet 2013
Espace Agora, Domaine du Haut-Carré, Talence
Aminoborane : new methodologies in the boron chemistry toolbox

Ludovic D. Marciasini a, Hélène Guerrand a, Thomas Gendrineau a, Melissa Jousseaume a, Nicolas Richy b, Mathieu Pucheault a* and Michel Vaultier a

aEquipe PHOENICS, ISM, Université de Bordeaux 1, 351 cours de la libération 33405 Talence cedex
bCPM, UMR CNRS 6510, Université Rennes 1, Campus de Beaulieu, 263 Avenue du Général Leclerc, F-35042 Rennes Cedex, France

Depuis les travaux de H. Brown sur la préparation et l’utilisation de composés du bore comme le borohydrure de sodium et sa découverte de l’hydroboration d’alcène et d’alcyne, la chimie du bore n’a cessé de s’enrichir. Au sein du laboratoire, plusieurs méthodologies sont développées visant la synthèse de composés arylboroniques à partir de différents substrats et utilisant comme agent de borylation un aminoborane. Ces composés sont des synthones très utilisés et appréciés en chimie organique de par la multitude de possibilités réactionnelles qu’ils offrent mais aussi de par leur faible toxicité. Cette synthèse utilisant des iodures d’aryles a été utilisée pour préparer, par réaction tandem de borylation/couplage de Suzuki-Miyaura, des biphényles dissymétriques (figure 1) (1).

Figure 1 : synthèse de biphényles dissymétriques par réaction tandem

Continuant la recherche de nouvelles méthodologies pour la création de liaison carbone-bore, l’utilisation de sels de diazonium en tant que substrats de départ a été étudiée. La grande réactivité de ces sels et des aminoboranes ont permis la synthèse d’esters arylboroniques dans des conditions très douces (figure 2) (2). Cette nouvelle technologie a également été implémentée en réacteur continu. Actuellement, l’utilisation de nouveaux catalyseurs de palladium sont à l’étude et ce pour la formation de liaison carbone-bore (3) mais aussi dans la déshydrogénation de complexe amine-borane.

Figure 2 : synthèse d’ester boronique à partir de sels de diazonium

Références
Etude par spectroscopies optiques d'acides phénoliques, d'anthocyanes et de tanins en solutions hydro-alcooliques

C. Martin, J.L. Bruneel, C. Belin, M. Jourdes, P.L. Teissèdre, P.P. Jobert et F. Guillaume

a ISM, UMR 5803 CNRS, Université Bordeaux, 351 cours de la Libération, Talence, 33405, France

b ISVV, UMR 1065, 210 chemin de Leysotte, Université de Bordeaux, Villenave d'Ornon 33883, France

c ATT, 99 avenue de la Châtaigneraie, Rueil-Malmaison F-92500, France

Remerciements: ces travaux sont co-financés par la région Aquitaine, la chambre de commerce et d’industrie de Bordeaux et le conseil interprofessionnel des vins de Bordeaux.
Ingénierie moléculaire pour la synthèse de chromophores pour les cellules solaires à colorant

J. Massin, a C. Olivier, a T. Toupance, a

a ISM U-Bordeaux 1, 351 cours de la libération 33405, Pessac, France

Depuis la mise en lumière par Graetzel et coll.1 de l’intérêt des cellules solaires à colorant (DSSC), la recherche de chromophores à la fois efficaces et robustes a fait l’objet de nombreux efforts. Dans ce contexte, les chromophores organiques présentant une structure de type « push-pull » se sont particulièrement illustrés avec des rendements de conversion photovoltaïques supérieurs à 10%.2 Cependant, un travail d’optimisation de ces colorants reste à effectuer pour améliorer les propriétés d’absorption dans le domaine du visible ou encore moduler les propriétés électroniques afin de changer la nature de l’électrolyte dans le dispositif (utilisation d’électrolyte à plus haut potentiel d’oxydation).

Dans ce but un travail d’ingénierie moléculaire a été réalisé sur deux séries de colorants. Notamment, nous démontrerons comment sur la première série nous avons optimisé les propriétés d’absorption des chromophores en modulant la nature de l’espaceur. Dans un second temps, nous décrirons comment nous avons fait varier la nature du groupement d’attache.

Références

(2) P. Wang et al., Chem. Mater., 2010, 22, 1915.
Dendritic functionalization of core-shell magnetic nanoparticles for biotechnology

L. Mitcova,a H. Rahma,a T. Buffeteau,a G. Le Bourdon,a M. Gaboyard,b T. Duluc,b B. Bennetau,a Luc Vellutini,a K. Heuzéa

a Institut des Sciences Moléculaires, Université Bordeaux 1, CNRS UMR 5255, Bâtiment A12, 33405 Talence Cedex, France.
b Ademtech SA., Parc Scientifique Unitec, 4 Allée du Doyen Georges Brus, 33600 Pessac, France.

Modern biological sciences depend on the methods developed through biotechnology. In this area, protein immobilization is of high interest. The development of site selective methods of protein immobilization onto supports has enabled the fabrication of various functional protein microarrays and biosensors. Chemically, physically and biologically mediated methods of protein immobilization are well described in the literature.(1) However, the development of novel methods that would ensure protein integrity and functionality after their immobilization is required since proteins represent complex chemical structures. Moreover, proteins can adhere and adsorb on most surfaces through a variety of mechanisms resulting in non-specific protein bonding.(2)

In this work we proposed to obtain stable, water-dispersible, functionalized organic-inorganic nanohybrid material which will ensure selective, site specific protein immobilization. For this purpose superparamagnetic core-shell iron oxide nanoparticles (MNPs) were functionalized with maleimide functional group. In order to multiply the number of functional groups on the MNPs’ surfaces, MNPs were functionalized with dendritic coupling agent, thus enhancing their sensitivity in comparison with MNPs functionalized with a linear analogue. In order to induce a good dispersion in aqueous medium hydrophilic components were introduced in the dendritic structure’s backbone, such as poly(ethylene glycol) (PEG) chains or/and poly(amidoamine) (PAMAM) chains. Also, the PEG chain is considered to be one of the most inert chemical groups towards non-specific protein adsorption.(3) Dendritic structures were grafted onto MNPs via convergent approach. According to this approach first the structures are synthesized and characterized and only after that grafted on MNPs’ surface. Finally, maleimide functionalized MNPs were prepared and the dendritic effect was confirmed. These MNPs are stable in time and at temperature up to 100 °C and manifest a good dispersion in aqueous medium and in polar solvents.

References

Tip-Enhanced Raman Spectroscopy of polymer-wrapped semiconducting single-walled carbon nanotubes


Université de Bordeaux, Institut des Sciences Moléculaires, CNRS UMR 5255, F-33400 Talence, France

Department of Chemistry, French Family Center, 124 Science Drive, Duke University, Durham, NC 27708, USA

Tip-enhanced Raman spectroscopy (TERS) is a powerful technique to investigate nanosystems since it allows chemical, structural, electronic and topographical information to be obtained with nanoscale spatial resolution (10-20nm typically). The enhancement of the Raman signal are thought to derive mainly from the occurrence of the electrostatic lightning rod effect and the excitation of surface plasmon resonances (SPR) at a metal (Au and Ag mainly) tip. In particular, SPR of metal nanostructures are very sensitive to the shape and dielectric properties, and the selected excitation wavelength must be adequate to excite this resonance and the nanomaterial under study.

We have selected polymer (PNES)-wrapped semiconducting single-walled carbon nanotubes (SWNTs) highly enriched (> 85%) with (6,5) chirality, for which nanotube-nanotube associative interactions are reduced. Here, we scrutinize Raman spectroscopic properties of these nanohybrids, discuss the experimental conditions and the instrument used to perform TERS and present our first TERS results on isolated individual PNES-[(6,5) SWNTs].

Références

Chemical studies of the oxidation of wine-related catechols and pyrogallols

Emilie PETIT, Rémi JACQUET, Denis, DEFFIEUX, Stéphane QUIDEAU

Université de Bordeaux, Institut des Sciences Moléculaires (CNRS-UMR 5255) and Institut Européen de Chimie et Biologie, 2 rue Robert Escarpit, 33607 PESSAC Cedex, France.
s.quideau@iecb.u-bordeaux.fr

Oxygenation is one of the crucial factors underlying the expression and evolution of the organoleptic properties of wine such as astringency, bitterness, colour and aroma. Numerous oxidations and subsequent transformations of wine remains a matter of much concern for oenologists and wine scientists. It is generally accepted that a fast and excessive oxygenation has rather deleterious effects, whereas a slow and continuous aeration can have a positive impact on the organoleptic profile of wine. In this context, the traditional aging of wine in oak barrels offers an adequate means to temper its aeration by allowing a slow penetration of oxygen through the wood (30-40 mg per year when using new barrels). The capacity of wine, especially heavy red wines, to absorb oxygen is very high, and can reach up to 800 mg/L. Once dissolved in wine, oxygen is thus progressively and rather rapidly consumed by various substrates.

In this context, phenolic compounds are among the primary reactants with oxygen or more precisely, with reactive oxygen species, such as the hydroxy peroxy radical and hydrogen peroxide generated by the reduction of O₂ with transition metal ions (e.g. Fe²⁺) at the acidic wine pH (3-4). Some authors have described the oxidation of catecholic flavanols such as catechin, but very few studies have addressed the oxidation of pyrogallolic C-glucosidic ellagitannins, oak wood tannins extracted by wine during aging in barrels.

In the presence of reactive oxygen species, catecholic and pyrogallolic species can lead to the formation of ortho-quinones and α-hydroxy-ortho-quinones. Then, these electrophilic entities can react with nucleophiles via either direct or conjugate addition reactions. In this context, we are currently studying the oxidation of C-glucosidic ellagitannins such as vescalagin and castalagin under different chemical and enzymatic oxidation conditions in the presence of wine nucleophiles. The result will be presented at the scientific day of ISM.

Références

Theoretical analysis of the dynamics of N$_2$ scattering on W(100) surface

R. Pétuya$^{a,b}$, P. A. Plötz$^{a,b}$, C. Crespos$^{a,b}$ and P. Larrégaray$^{a,b}$

$^a$ Université de Bordeaux, UMR 5255, F-33400 Talence, France
$^b$ CNRS, ISM, UMR 5255, F-33400 Talence, France

The dynamics of N$_2$ molecules scattered from a W(100) surface has been investigated by performing classical trajectories simulations in order to interpret experimental measurements of scattering angle distributions (1). The width of the angular distributions has been found to evolve non-monotonously with the translational energy of the impinging N$_2$ molecules. After a description of the theoretical model used in our simulations, an original interpretation is proposed to understand this rather puzzling behaviour. The shape and the position of the angular distributions are discussed together with other observables like the final translational energy distribution of the N$_2$ molecules.

Références

Synergic Modular Structures for Two-Photon Uncaging of Biomolecules

S. Picard, a E. Cueto Diaz, a E. Genin, a et M. Blanchard-Desce a

a Institut des Sciences Moléculaires, Equipe PHOENICS, Université de Bordeaux 1, CNRS UMR5255, Bâtiment A11, 351 cours de la Libération, 33405 Talence Cedex, France

Two-photon absorption (TPA) is a quantum process that allows the simultaneous absorption of two photons to reach an excited state (identical or different - depending on symmetry - from those attained by standard one-photon excitation). The investigation of TPA in organic compounds has attracted increased interest in the last years due to the many advantages it provides (highly confined 3D resolution, increased penetration depth in scattering media including tissues) of wide interest for applications in various fields.1

Caged molecules can be irreversibly activated by irradiation with light leading to photo-controlled release of a labile moiety.2 Ideally caged molecules are stable in the dark in operating conditions but allow efficient photorelease under excitation at suitable wavelengths (typically > 300 nm) and produce non-toxic by-products. Whereas a variety of uncaging molecules have been developed for one-photon photoactivation, two-photon uncaging is still in infancy, although it offers many promises for bioapplications (particularly neurosciences). These applications however requires the design of “biphotonic” efficient cages displaying very large two-photon uncaging action cross-section at suitable wave length (typically in the NIR region allowing improved penetration and reduced toxicity). In this context, we recently developed the design and synthesis of smart synergic nanodots combining photolabiles precursors and two-photon absorbers. That act as two-photon antenna then transferring their excitation energy to the uncaging module whose properties are retained. The synergic modular uncaging structure is built from a biocompatible platform developed by the group of J.-P. Majoral.3 The photolabile precursor is based on modified 2-nitroveratryl structure. The two-photon absorbers have been selected based on the expertise from the group4 as quadrupolar modules. Proof of concept has been demonstrated for uncaging of model acid compounds.

References

ENHANCED ELECTROGENERATED CHEMILUMINESCENCE IN THERMO-RESPONSIVE MICROGELS

F. Pinaud, L. Russo, S. Pinet, I. Gosse, V. Ravaine, N. Sojic

Institut des Sciences Moléculaires, 16 avenue Pey-Berland, 33 600 Pessac, France.

Electrogenerated chemiluminescence (ECL) is initiated by an electron transfer at the electrode surface and it ends with the light emission from an electronically excited states. In other words, the initiation of the phenomenon is an electrochemical step, whereas the analytical information is usually contained in the light signal. ECL systems are commercialized for more than 90 immunoassay tests. Strong amplification of ECL was also reported with Ru(bpy)$_3$$_2^+$-doped silica nanoparticles. Many efforts have been focused on the development of new ECL nanomaterials (NPs, carbon nanotubes, ultrathin films, etc). Stimuli-responsive microgels (typical diameter: 50-1000 nm) are swollen cross-linked polymer particles, which undergo volume phase transition upon application of a stimulus (temperature, solvent, solution composition, pH, etc). In the present work, we synthesized microgel NPs based on poly(N-isopropylacrylamide) (pNIPAM) copolymerized with a Ruthenium (Ru(bpy)$_3$$_2^+$ monomer) complex. We demonstrated that ECL can be used as transduction technique for the thermo-responsive microgel NPs. Increasing the temperature, the gel shrinks and the diameter decreases from 140 nm to 60 nm. At the same time, the ECL intensity is drastically enhanced. In these experiments we showed for the first time, a correlation between the swelling/shrinking and the ECL intensity amplification. The perspectives of this study, which shows an estimated ECL intensity increase of 3 orders of magnitude from a single dye to NP, are their applications in ultrasensitive bioassays.

Références

Controlling the third property of light: Towards photopolic materials

Debdas Ray, André Del Guerzo, Guillaume Raffy, Cheng-Che Chu, Lionel Hirsch, Dario M. Bassani

1 Institut des Sciences Moléculaires, CNRS UMR5255, Université Bordeaux 1, 33405 Talence
2 Laboratoire de l’Intégration du Matériau au Système, CNRS UMR5218, ENSCPB, 33607 Pessac

In recent years, the development of nanoscale molecular devices has emerged as a viable route to intelligent functional materials operating at the molecular level. For applications in solar energy conversion, the organization of the electron donating and electron accepting moieties is a prerequisite. Such organization, which can be attained by making use of supramolecular interactions, can lead to materials exhibiting controlled electron and energy transfer processes. A major feature of the self-assembly process is that individual components will spontaneously combine in a predetermined fashion due to the presence of complementary molecular recognition sites. Hydrophobic / hydrophilic interactions, metal ion coordination, π-stacking interactions, and hydrogen bonding have all been used successfully in the preparation of multi-component molecular edifices. An advantage of supramolecular architectures is their ability to accommodate geometries not easily obtained by conventional synthesis, such as proximal arrangements of distant orthogonal units. This can lead to interesting photochemical and photophysical behavior, such as the observation of additional electronic interactions, or the control of excited-state processes.

References

Breaking the symmetry of micro- and nanoobjects by bipolar electrochemistry

J. Rochea, G. Logeta, Z. Fattahb, D. Zigahb, L. Bouffiera and A. Kuhna

a Univ. Bordeaux 1, UMR 5255, ENSCBP 16 avenue Pey Berland, 33607 E-mail: jroche@enscbp.fr

Referring to the roman god Janus, depicted with two heads, Janus particles are defined as micro- or nano- particles owning two sides of different chemistry1. Since 2000, the number of publications about those objects is significantly growing each year due to their unique properties. Indeed, it has been demonstrated that they can be used as key-components in applications such as catalysis2, medical therapy3, detection4 or display technologies5. However, the synthesis of Janus particles is still challenging, and achieving a cost effective large-scale production remains an issue that slows down their industrial application. So far, a great majority of methods used to produce these particles breaks the symmetry by using a surface or interface6. This makes the preparation of large quantities rather difficult, because those processes involve a 2D reaction space, and thus, lead only to monolayer equivalents of material. We demonstrated that it is possible to use the concept of bipolar electrochemistry to generate anisotropy on conductive particles in the bulk phase7. In the presence of an electric field, a conductive object in solution becomes a bipolar electrode that acts simultaneously as an anode on one side and as a cathode on the other side. If the polarization is strong enough, this phenomenon allows driving simultaneously two different electrochemical reactions on the same object. If one adds, for example, a metal salt to a suspension of the particles, it becomes possible to reduce it selectively at one side of the objects to form an anisotropic particle. Furthermore, this technology allows tailoring the shape and the position of the deposited materials by controlling the applied electric field as well as the reactor configuration. We are currently working on i) improving the efficiency of these synthesis, in order to optimize the yield, as well as on the scaling up of the approach, and ii) increasing the versatility of the process in terms of particle materials, size and shape as well as the type of deposited material (metals, polymers, semiconductors, organic layers)8,9,10,11. This communication will present an overview of the different Janus particles obtained, like the ones depicted in the above picture, as well as the associated formation mechanisms.

Références
Electrochemiluminescence Imaging at the Single Bead Level: New Approach to Investigate the ECL Mechanism

M. Sentic, M. Milutinovic, D. Manojlovic, S. Arbault, N. Sojic

 Université de Bordeaux, Institut des Sciences Moléculaires, ENSCBP, 33607 Pessac, France
 Faculty of Chemistry, University of Belgrade, 11000 Belgrade, Serbia

Electrogenerated Chemiluminescence (ECL) is a controllable form of luminescence where light emission is initiated by an electron-transfer reaction occurring at an electrode surface.[1] The most common system used for analytical purposes consists of the luminophore label Ru(bpy)$_3^{2+}$, or one of its derivatives, with a co-reactant such as tri-$n$-propylamine (TPrA) or 2-(Dibutylamino)ethanol (DBAE).[2-3] A microbead-based ECL system is commercialized by Roche Diagnostics Corp. for a number of assays with a particular focus on immunoassays. This assay uses magnetic microbeads decorated with probe molecules, such as antibodies or nucleic acids, to capture analyte molecules in a sample. Analyte presence is measured by attaching a sensing molecule, such as an antibody conjugated to a Ru(bpy)$_3^{2+}$ analog, and then generating ECL in a TPrA solution. The ECL mechanism involving TPrA with dissolved Ru(bpy)$_3^{2+}$ or with the ruthenium complex immobilized onto a bead is an active area of investigation.[4]

Figure 1. PL (A) and ECL (B) images recorded on a single 12-µm modified bead.

In the present work, we imaged the distribution of the ECL intensity at the level of single beads. Beads were functionalized with ruthenium labels and imaged by photoluminescence (PL) and by ECL under different experimental conditions. The combination of both PL and ECL imaging gives insight into the ECL mechanism involved in numerous bioanalytical applications.

References

Greffage de dérivés du cryptophane-A sur des surfaces SiO$_2$/Au

E. Siurdyban$^a$, T. Brotin$^b$, K. Heuzé$^a$, L. Vellutini$^a$ et T. Buffeteau$^a$

$^a$ Université Bordeaux 1, Institut des Sciences Moléculaires, 33405 Talence, France.
$^b$ Ecole normale supérieur de Lyon, laboratoire de chimie de l’ENS Lyon, 69364 Lyon, France.

Depuis la synthèse des premiers cryptophanes en 1981$^{(1)}$, de nombreux autres composés ont été élaborés et en particulier les dérivés hydrosolubles du cryptophane-A. Ces dérivés hydrosolubles, grâce à leurs cages lipophiles, ont montré une très bonne affinité pour la complexation de petites molécules neutres$^{(2)}$ ou d’espèces ioniques$^{(3)}$. Notre objectif est d’utiliser ces molécules comme sondes moléculaires pour la séquestration du césium et d’autres métaux toxiques. Ainsi, nous souhaitons greffer ces dérivés hydrosolubles sur des surfaces SiO$_2$/Au ou des nanoparticules cœur-écorce magnétiques (MNPs), afin de pouvoir extraire le césium d’un milieu aqueux. Dans ce travail, nous décrirons le protocole de greffage développé pour un cryptophane «modèle», le dérivé acide hexa-carboxylique cryptophane-A, sur des surfaces SiO$_2$/Au. Pour cela, la surface d’or va être fonctionnalisée par une monocouche autoassemblée (SAM) présentant des groupements amines terminaux. Ces fonctions amines seront utilisées pour immobiliser de façon covalente le cryptophane (Figure 1). Le greffage des cryptophanes sur les surfaces SiO$_2$/Au sera mis en évidence en utilisant la spectroscopie de réflexion-absorption infrarouge par modulation de polarisation (PM-IRRAS) (Figure 2).

Figure 1 : Schéma d’un dérivé du cryptophane-A greffé sur une surface SiO$_2$/Au (SAM-crypto)

Figure 2 : Spectre PM-IRRAS du greffage d’un dérivé du cryptophane-A sur une surface SiO$_2$/Au

Références

Synthèse de dérivés polyphénoliques pour étudier les interactions Polyphénol-Protéine par la technique de Résonance Plasmonique de Surface (RPS)

Tran Dong Tien\textsuperscript{a,b}, Daniela M. Delanno\textsuperscript{a,b}, Aude Watrelot\textsuperscript{c}, Denis Deffieux\textsuperscript{a,b,*}, Stéphane Quideau\textsuperscript{a,b,*}

\textsuperscript{a} Université de Bordeaux, Institut des Sciences Moléculaires (CNRS-UMR 5255)
\textsuperscript{b} Institut Européen de Chimie et Biologie, 2 rue Robert Escarpit, 33607 Pessac Cedex, France,
\textsuperscript{c} INRA UMR408 Sécurité et Qualité de Produits d'Origine Végétale, Domaine St Paul, 84914 Avignon Cedex 9, France

(dt.tran@iecb.u-bordeaux.fr, d.deffieux@iecb.u-bordeaux.fr; s.quideau@iecb.u-bordeaux.fr)

Les proanthocyanidines (PAs), également appelées tannins condensés, sont des oligo/polymères de flavan-3-ols.\textsuperscript{1} Ces composés polyphénoliques possèdent des propriétés physico-chimiques et biologiques importantes de part leurs pouvoirs astringents, anti-oxydants et anti-radicalaires.\textsuperscript{1,2} Ces effets biologiques sont en partie liés à la capacité d’interaction des polyphénols avec différentes protéines. Cette capacité d’interaction peut se faire de manière spécifique ou non-sélective en fonction des caractéristiques non seulement physico-chimiques mais aussi structurelles du polyphénol et de la protéine considérées. Récemment, nous avons montré que la Résonance Plasmonique de Surface (RPS) permettait de discriminer efficacement et rapidement les interactions spécifiques polyphénol-protéine, des non-sélectives.\textsuperscript{3}

Dans le but de développer et de valider la technique de Résonance Plasmonique de Surface appliquée à l’interaction polyphénol-protéine, nous avons conçu et synthétisé des dérivés polyphénoliques (la (+)-catéchine, l’(-)-épicatéchine et la proanthocyanidine B\textsubscript{2}) puis nous les avons fixés sur des “sensor chips” Biacore\textsuperscript{b}. Cette approche permet d’étudier non seulement la capacité d’interaction d’un polyphénol immobilisé sur différents types de “sensor chip” mais aussi d’étudier l’influence de la nature et de la localisation du linker sur un polyphénol vis-à-vis de son interaction avec une protéine donnée.

La modification des polyphénols sur différentes positions de la molécule et l’immobilisation de ces dérivés sur les “sensor chips” sont présentées dans cette étude\textsuperscript{4,8} La validité de cette technique permettra l’application à l’étude des d’interactions entre différents polyphénols et différents types de protéines (TopII\textsubscript{α}, BSA, streptavidine,...).

Références
(3) S. Quideau et al., ChemBioChem. 2009, 10, 2321 - 2324.
(4) S. Quideau et al., ChemBioChem. 2011, 12, 1193 - 1197.
(5) K. Ohmori et al., PNAS. 2004, 101 (33), 12002 - 12007.
(8) A. Sarkar et al., Bioconjugate Chem. 2011, 22, 1202 - 1209.
Mechanically-Interlocked Molecules via Barbiturate Templating

A. Tron, a P. Thornton, b H.-P. Jacquod de Rouville, a B. Kauffmann, b T. Buffeteau, a D. Cavagnat, a J. H. R. Tucker, c N. D. McClenaghan a

a Institut des Sciences Moléculaires, CNRS UMR 5255, Université Bordeaux 1, 33405 Talence, France. b School of Chemistry, University of Birmingham, Edgbaston, B15 2TT, Birmingham, United Kingdom. c Institut Européen de Chimie et Biologie, CNRS UMS 3033, Université Bordeaux 1, 33607 Pessac, France.

Over the past 30 years, interlocked structures have been developed and popularized using self-assembly harnessing non-covalent interactions including hydrogen bonding and aromatic stacking, between a guest and a macrocyclic host.1 Hydrogen bonds, with their inherent directionality, allow the binding of neutral molecules using multiple hydrogen bonds. One of the most successful receptors for complexation of neutral molecules is Hamilton’s barbiturate receptor,2 which in the current work is the unprecedented templating motif of choice for rotaxane formation.

This project focuses on the formation of interpenetrating structures via the formation of a neutral 1:1 inclusion complex (K_{ass} = 25000 M^{-1}) between a cyclic version of Hamilton’s receptor and a barbital (or extended barbital), shown in Figure 1. Subsequently, a [2]-rotaxane was realized via a “stopping” reaction from the preformed pseudo-rotaxane with an adapted thread, generating kinetically-inert, threaded architectures. This stopping strategy utilizes a copper(I)-catalyzed alkyn-azide 1,3-cycloaddition click reaction.3 This new architecture has been confirmed by 1D- and 2D-NMR studies of the rotaxane, thus adding to the small library of motifs for formation of mechanically-interlocked structures.

![Figure 1. X-ray structure of molecular host-guest complex (a) and crystal packing (b)](image)

Références