APPEL A PROJETS EQUIPEX / CALL FOR PROPOSALS

2010

Acronyme du projet / Acronym

DOCUMENT SCIENTIFIQUE B / SCIENTIFIC SUBMISSION FORM B

Acronyme du projet/ Acronym of the project	**SENS**	
Titre du projet en français	RMN de Surface Exalté par Polarisation Dynamique Nucléaire	
Project title in English	Surface Enhanced NMR Spectroscopy by Dynamic Nuclear Polarisation	
Coordinateur du projet/Coordinatorof the project	Nom / Name : Lyndon EMSLEY Etablissement / Institution : CNRS Laboratoire / laboratory : CRMN Lyon Numéro d'unité/unit number : FRE3008	
Aide demandée/ Requested funding	Tranche 1/Phase 1 1 996 248 € TTC	Tranche 2/Phase 2 567 191 € TTC
Champs disciplinaires / disciplinary field	X Santé, bien-être, alimentation et biotechnologies / health, well-being, nutrition and biotechnologies X Urgence environnementale et écotechnologies / environnemental urgency, ecotechnologies X Information, communication et nanotechnologies / information, communication and nantechnologies ☐ Sciences humaines et sociales / social sciences X Autre champ disciplinaire / other disciplinary scope	
Domaines scientifiques/ scientific area	Sustainable Development, Materials, Catalysis, Surface Science, Nanoparticles, Structural Biology	

Affiliation(s) du partenaire coordinateur de projet/ Organization of the coordinating partner

Laboratoire(s)/Etablissement(s) Laboratory/Institution(s)	Numéro(s) d'unité/ Unit number	Tutelle(s) /Research organization reference
Centre de RMN à Très Hauts Champs à Lyon	FRE 3008	CNRS / ENS-Lyon / UCBL

Affiliations des partenaires au projet/Organization of the partner(s)

Laboratoire(s)/Etablissement(s) Laboratory/Institution(s)	Numéro(s) d'unité/ Unit number	Tutelle(s)/Research organization reference
Entreprise(s) / company	**Secteur(s) d'activité/activity field**	**Effectif/ Staff size**

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RESUME / SUMMARY

(2 pages maximum)

This project concerns the acquisition of a high-field solid-state (800 MHz) DNP accessory for the Centre de RMN à Très Hauts Champs à Lyon. This equipment will be one of the very first to be installed in the world, as soon as it becomes available in 2011.

As complexity constantly increases, molecular level characterization of materials (whether molecular, inorganic, nano-structured or biological) is today often the key barrier to further developments in many areas. Nuclear magnetic resonance (NMR) spectroscopy (often in conjunction with diffraction methods) is the method of choice for this type of characterization whenever it is possible, but many modern materials are below the sensitivity limit of detection for NMR. The sensitivity enhancement provided by DNP (factors up to several hundred) leads to reductions in experimental times of between *three to five orders of magnitude*. This changes completely the type of molecular, biological or materials systems that could be studied by NMR. High-field high-resolution DNP systems capable of providing these enhancements in a Laboratory environment have only been available commercially since last year. The performance of these systems (so far at 400 MHz) is outstanding, and already is the center of a plethora of new developments in NMR spectroscopy that were previously considered inconceivable. There are currently only two commercial 400 MHz systems installed in the world (Berlin and Lausanne). There are none in France.

We propose the acquistion of a 527 GHz DNP accessory for the 800 MHz wide-bore NMR spectrometer at the CRMN Lyon. The CRMN Lyon is a National and European user facility, and the new equipment would automatically be made available as a demonstration platform to the broadest possible trans-disciplinary user community through the infrastructure. This will be the source of immediate innovations in materials science, catalysis, nanotechnology and structural biology.

To date, most previous DNP NMR experiments have been focused on biological systems. While the system will be open to, and used by, biological scientists, we are particularly interested in the novel possibility that DNP yields to characterize surfaces and surface species central to modern sustainable chemistry, through catalysis and nanosciences. The detailed projects described herein are thus primarily aimed at developing Surface Enhanced NMR Spectroscopy (SENS). We propose to develop and demonstrate that SENS experiments are a straightforward and general method for probing the surface sites of a variety of support materials, such as mesoporous silicas and particulate alumina. This has the potential to completely revolutionise approaches to the detailed characterization of the structure and dynamics of surface species, thereby driving the development of new high performance materials.

1. ENVIRONNEMENT SCIENTIFIQUE ET POSITIONNEMENT DU PROJET D'EQUIPEMENT / SCIENTIFIC ENVIRONMENT AND POSITIONING OF THE EQUIPEMENT PROJECT

(4 pages maximum)

The development of more efficient catalysts in terms of activity, selectivity, and stability is one of the key challenges today because of the need to optimize the use of resources within the context of a more sustainable development. The mechanisms governing conversion of atmospheric CO_2, or the removal of (micro) pollutants are all based on chemical catalysis. Determining, understanding and characterizing the chemical species involved in catalysis is one of the foremost challenges to environmental and analytical science today.

This research proposal concerns the acquisition of revolutionary new equipment that will allow the structural characterization by state-of-the art solid-state DNP-NMR spectroscopy of new generations of heterogeneous catalysts, involved in key reactions of modern chemistry and designed for sustainable processes (clean processes/green chemistry).

It is estimated that catalysts are involved in 90% of all man-made chemical processes worldwide, with a large fraction of these processes involving heterogeneous catalysts. Catalysis is one of the pillars of modern society, as it is a key technology employed for converting natural resources into fuels, food, and basic and fine chemicals. The by products of these industrial reactions (e.g. CO_2, NO_2, metals…) are the major source of man-made environmental pollution today. The development of more efficient and cleaner chemical processes is necessary in order to guarantee future sustainable development. This is for instance possible through the reduction of the number of chemical steps, better use of resources, or the incorporation of more environmentally friendly processes.

In the search for more efficient chemical processes, one key approach consists in having a precise understanding of the structure of the active sites of the catalyst. This enables structure-activity relationships to be deduced and allows for the rapid and intelligent development of catalysts with improved properties. Spectroscopic methods are particularly interesting because they can provide information on the electronic states and the structures of the active sites, which in turn provide molecular information and allow for a possible rational improvement of the catalysts. Within this goal, infrared (IR), Raman, solid-state NMR, UV-Vis and X-ray absorption (XAS) spectroscopies along with other surface science and molecular modeling techniques have been extensively used.

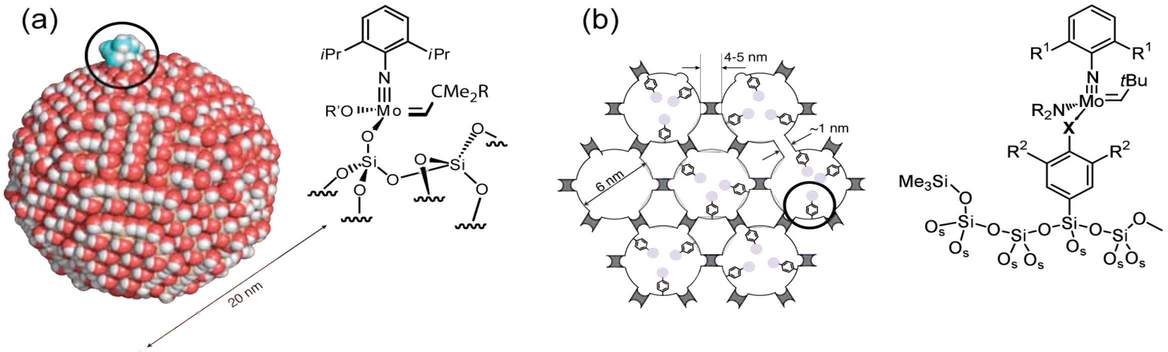

Figure 1: Schematic representation of typical complex modern materials, here surface organometallic catalysts. (a) Mo-based catalysts obtained by grafting a molecular compound onto on a silica support. Using this approach, the molecular compound reacts with SiOH ligands of the oxide support. Mono- or bis-grafted species are obtained, which may lead to specific interactions between the metal and the support. (b) Schematic diagram of the pore and channel network for meso-structured functionalized hybrid materials together with one targeted Mo catalyst. This approach combines the use of hybrid materials with surface organometallic chemistry. It allows notably a better control of the site density and the possibility to control the chemical nature of the binding ligand.

Over the last few years, we have shown how solid-state Nuclear Magnetic Resonance (SSNMR) spectroscopy can be applied to gain a detailed understanding of the active sites of grafted organometalic catalysts,[1] supported gold nanoparticles[2] or hybrid mesoporous materials.[3] Further improved chemistry in the field of heterogeneous catalysis will come as a result of a joint effort from synthesis working hand in hand with advanced multi-dimensional NMR characterization.

The sensitivity of NMR poses the major limitation to the structural characterization of surface species. Even when using highly porous nano-particles having high specific surface area (925 m^2/g for the pore channel materials described in Figure 1), the concentration of NMR active nuclei often remains low (typically below 1 mmol/g for ^1H and 0.01 mmol/g for ^{13}C in natural abundance), requiring many hours or even days to accumulate simple one-dimensional ^{13}C NMR spectra with reasonable signal to noise ratios. This often prevents the acquisition of multi-dimensional correlation spectra, thus severely limiting the characterizing power of SSNMR. NMR sensitivity is thus one of the key barriers to further progress in many areas of surface chemistry. One way to deal with this sensitivity issue, and which we widely exploited in the past for the characterization of grafted species, is to synthesize specifically carbon-13 or nitrogen-15 labeled compounds. This requires however complex additional synthetic procedures (for systems which are often already non-trivial to make) and cannot constitute a general approach. Indeed, that we have resorted to this approach in the past illustrates the crucial role played by NMR characterization in catalyst development.

In the past few years dynamic nuclear polarization (DNP) has made great progress, and the technique, which was originally developed for low magnetic fields,[4-6] has been shown to be applicable in high magnetic fields.[7,8] For DNP the samples are doped with free radicals and the unpaired electrons are polarized by micro-wave (MW) irradiation. Griffin *et al.*[9-11]

have demonstrated signal enhancement factors (ε) of up to ~400 in cross-polarization (CP) MAS ^{13}C and ^{15}N spectra of frozen solutions of proteins in a D_2O/H_2O/glycerol mixture at temperatures below 90 K, using stable radicals such as TEMPO,[12] or TOTAPOL[13] as the source of polarization. Saturation of the EPR transitions of the radicals leads to polarization enhancement of nearby protons, and subsequent spin-diffusion leads to uniformly enhanced polarization of most protons in the sample. This polarization can then be transferred to other nuclei (such as ^{13}C, ^{15}N, or even ^{14}N[35] or ^{2}H,[36] by cross polarization).

Because it provides dramatic sensitivity enhancement, solid-state Dynamic Nuclear Polarization (DNP) NMR is currently emerging as a powerful tool to study samples are available in limited amounts and previously inaccessible to NMR studies.[7] Impressive DNP enhancements have been observed in biological samples such as amyloid fibrils,[14] or membrane proteins.[15,16]

DNP NMR instrumentation is highly complex, and the technology involving continuous wave gyrotron microwave sources has only recently become commercially available.[8] The impressive gains in signal demonstrated for SSNMR experiments on biomolecular systems suggests that DNP will gain a more widespread acceptance in the next several years.[7] Therefore, the development of new applications for DNP SSNMR spectroscopy are of great importance. We anticipate that there will be great interest within the NMR and inorganic chemistry communities in the characterization of inorganic and hybrid materials by DNP SSNMR spectroscopy.

To the best of our knowledge, so far the technique has not previously been applied successfully to inorganic or hybrid materials.

2. DESCRIPTION SCIENTIFIQUE ET TECHNIQUE / TECHNICAL AND SCIENTIFIC DESCRIPTION OF THE ACTIVITIES

2.1. ORIGINALITE ET CARACTERE NOVATEUR DU PROJET D'EQUIPEMENT/ORIGINALITY AND INNOVATIVE FEATURE OF THE EQUIPEMENT PROJECT

(2 pages maximum)

Solution and solid-state NMR spectroscopy have found widespread application in diverse fields such as biochemistry, synthetic chemistry, physics and medicine. Currently, NMR spectroscopy is limited to samples which contain a high concentration of nuclear spins due to the intrinsic insensitivity of the technique. As a result of this, the development of methods, which can enhance the signal of NMR experiments, and broaden the applications of NMR spectroscopy, are of great importance. In the past two years high field DNP SSNMR systems have become available from commercial manufacturers. Recent high field DNP SSNMR studies have demonstrated that impressive signal enhancements (ε_H) of ^{1}H SSNMR experiments by factors of ca. 50-100 are possible.[7] This foreshadows a more widespread adoption of DNP SSNMR in next several years suggests that DNP NMR spectroscopy will become a burgeoning research area, notably for samples which are available only in very limited amounts like surface species.

DNP NMR will allow characterization of previously inaccessible systems. This will lead directly to enabling breakthroughs in areas as diverse as nao-technology, catalysis and structural biology.

Here, we propose to acquire a high-field (800 MHz) Dynamic Nuclear Polarisation (DNP) system to place Lyon and France on the world map in advanced solid-state NMR technology. The research project will notably focus on the development of new DNP NMR methodologies for the structural investigation at the atomic scale of challenging inorganic or hybrid materials including heterogeneous catalysts. This equipment will be one of the very first DNP NMR instruments at 800 MHz worldwide (*possibly the first*) and will be unique in France. This acquisition will strengthen the position of the CRMN allowing local, French and European laboratories to access state of the art NMR equipment in one of the leading worldwide centers in NMR spectroscopy. Many local and French laboratories have shown their deep interest in the development of high field DNP NMR in the fields of materials and biological solids, and in the possibility to use of such equipment at the CRMN in Lyon.

In the short time since this call was published, the following laboratories have already written letters of support included in the annex : Michel Lacroix (Director, IRCELYON Lyon), Bruno Chaudret (Director, LCC Toulouse, Member of the French Academy of Sciences), Dominique Massiot (Director, TGE-RMN & Director, CEMHTI Orléeans), Geoffrey Bodenhausen (ENS Paris & EPFL Lausanne), Claude Berthier (Laboratoire National des Champs Magnétiques Intenses), Stefano Caldarelli (ISM2 Marseille), Florence Babonneau (ESPCI-Collège de France), Anja Böckmann (IBCP Lyon).

The project is also supported by the Institut de Chimie de Lyon, and the Institut Natioanal de Chimie du CNRS (see letters annexed).

In addition, we received letters expressing interest from the following key international scientists: Clare Grey (Head of Inorganic Chemistry, Department of Chemistry, University of Cambridge), Brad Chmelka (Materials Sciences, University of California, Santa Barbara), Ivano Bertini (University of Florence, Director of the European Integrated Infrastructure for Bio-NMR), Jean-Marie Basset (ESCPE-Lyon & KAUST, Director of the Catalysis Institute, Member of the French Academy of Sciences).

We also note that the preliminary results described in section 2.2 below were first presented in July at the EUROMAR meeting in Florence where more than 1200 attendees were present to hear more than 180 talks. The work generated much excitement, and was highlighted at the end of the conference in the summary session *as the only major breakthrough of the conference in theory and methods*.

The originality and innovative nature of this project is further highlighted by noting that the CRMN Lyon is currently the only group in the world that has so far carried out a successful surface enhanced NMR study of materials by DNP.

Although it is not the focus of this proposal, outstanding new perspectives are also expected in the field of biological solids, in which impressive DNP enhancements have already been observed in complex systems such as amyloid fibrils,[17] or membrane proteins.[16,18] With a group of 11 members now working at the CRMN on protein related projects, our laboratory is one the leading groups in Europe developing solid-state NMR of proteins and protein assemblies. A DNP system at 800 MHz will be a unique opportunity to explore new frontiers in this fast developing area and tackle increasingly complex biological assemblies. For example, in collaboration the IBS and the EMBL (Grenoble), DNP NMR will be used to tackle structural information, previously inaccessible by standard solid-state NMR techniques, in large complexes of virus nucleocapsid proteins.

Several industrial partners have also shown their interest in using the DNP equipment and we already received formal letters of support from: IFP, Rhodia and Bruker. In addition, as mentioned in the letter of support from Bruker, the purchase of a high-field DNP equipment in the CRMN Lyon, will further reinforce the collaboration between our laboratory and the company. Notably, the 1.3 mm probe system represents a completely new development, which would not be possible without this order. *It will result in the creation of highly skilled jobs within the company over an enduring period, of at least 10 years, as well as in the academic and industrial laboratories that will acquire such systems*, as a direct result of the demonstration experiments that will be done in the context of the current project.

2.2. DESCRIPTION DU PROJET / DESCRIPTION OF THE PROJECT

2.2.1 PRESENTATION SCIENTIFIQUE DU PROJET/SCIENTIFIC PROGRAMME

(6 pages maximum)

Although NMR provides incredibly detailed information at the atomic level on structure and dynamics, essential for the characterization of the majority of molecules and materials that make up our everyday life, it suffers from one key weakness, which is that the NMR signal is very weak. This prevents NMR being used for characterization in many of the most exciting areas of modern science, in particular the study of surfaces and materials, or the study of large proteins. One approach to solving this problem involves finding alternative sources of polarization, to enhance the NMR signal. In this respect, in the past few years high-field Dynamic Nuclear Polarization (DNP) has made great progress.[7,8] Signal enhancement factors (ε) of up to ~400 (corresponding to a decrease of 160 000 in the experimental time!) have been reported for biological solids. This incredible increase in signal-to-noise from DNP is expected to open new possibilities not only in the field of biological solids but also in the field of materials, thus expanding the range of systems solid-state NMR spectroscopy can successfully tackle.

One very exciting application of DNP NMR is to the structural characterization of surface species, including heterogeneous catalysts. While NMR is indeed commonly considered as one of the best tools to access local information in terms of structure and dynamics of complex materials, here the low intrinsic sensitivity of surface entities makes NMR extremely difficult with standard approaches, even when dealing with highly porous materials. Through a collaboration between the CRMN, the C2P2 (CNRS - CPE Lyon - Université de Lyon) and the EPFL (Lausanne), which hosts one of the two 400 MHz commercial DNP accessories in Europe, we have recently demonstrated[19] that DNP technology could be used in an expeditious way for the characterization of surface species in organic-inorganic materials that were previously impossible to study by NMR.

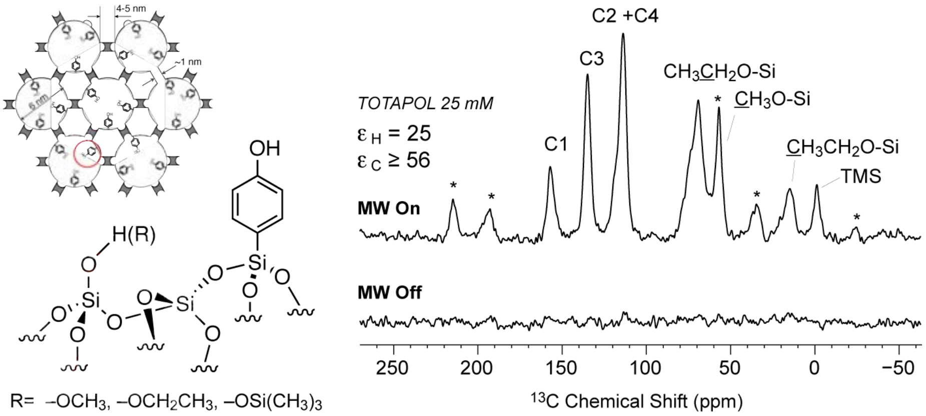

Figure 2: ^{13}C CP MAS spectra of the phenol-functionalized hybrid mesostructured materials with (top spectrum) and without (bottom spectrum) MW irradiation at 263 GHz to induce DNP.[19]

In that study, mesostructured materials (Figure 1b), functionalized with phenols or imidazolium units were investigated. We have shown how DNP could yield up to a fifty-fold increase in the NMR sensitivity of the organic functionalities of these hybrid silica materials as illustrated in Figure 2.[19] We were notably successful in recording two-dimensional (2D) ^{1}H-^{13}C correlation spectra within a couple of hours, which was inconceivable without polarization enhancement. The further development of new DNP SSNMR techniques for the characterization of the molecular structure and dynamics of these newly synthesized heterogeneous catalysts will be the focus of the proposal.

These remarkable (first worldwide) results in the field of materials open new, previously inconceivable, possibilities to investigate surface species in sophisticated systems of high fundamental and industrial relevance. In particular, this method selectively enhances the surface and surface species, without increasing the bulk signal which may otherwise the critical information coming from the surface. We believe this Surface Enhanced NMR Spectroscopy (SENS) approach is of particular significance.

The acquisition of a high-field DNP system will enable us to pursue our research effort in this very promising area and further reinforce the recognized expertise of our laboratory in the field of structural and dynamics characterization of catalysts and nanomaterials. Potential other applications in the future will concern, among others, the advanced structural investigation of new classes of increasingly complex heterogeneous catalysts in collaboration with the C2P2 (CNRS/CPE Lyon/Université de Lyon) and the ETH Zürich, or the investigation of metal-organic framework materials in collaboration with the IRCELYON (CNRS/University of Lyon).

We note that the project is inherently multi-disciplinary as it involves the synthesis and development of new heterogeneous organometallic catalysts (synthetic organometallic chemistry), the development of new methodologies for their characterization (NMR spectroscopy), and theoretical modeling of the catalyst structures (computational chemistry). Given the widespread industrial application of heterogeneous catalysts it is anticipated that there will be interest from both academic and industrial sectors in the results obtained from this project

We are currently the only Laboratory in the world working successfully in this area, aided notably by the fact that we had access to the demonstration facility in Lausanne. Many Laboratories would be interested in taking up these developments if the equipment were more widely available. Increasing the availability of DNP platforms will undoubtedly lead to the very rapid uptake of these methods (see, for example, the letters of interest in annex). Furthermore, since the 800 MHz DNP system will be integrated into our national and EU user facilities, we can guarantee that the system will be used to solve the most pertinent problems without delay as they arise, whether in catalysis, structural biology or elsewhere, as it will be accessible to the broadest possible community of users.

At a more detailed level, some of the specific objectives that we will develop on the road to widespread use of SENS, and which motivate acquisition of the system, are outlined *very briefly* as follows:

Optimal sample preparation strategies for surface enhanced NMR. Proper sample preparation is the key to obtaining large DNP enhancements in these materials. Therefore, further investigations into optimal methods for doping catalyst materials and pre-cursors will be conducted. In the preliminary experiments, the dry phenol functionalized silica samples were doped with radicals by incipient wetness impregnation[20] with a solution containing the radical species before filling the rotor. This appears to be an extremely promising approach, opening up the possibility to develop surface enhanced NMR spectroscopy. Many questions regarding this type of sample preparation however remain, such as the nature of the solvent (polar or apolar), the nature and concentration of the radical, the proportion of deuteration required in the solvent mixture or the effect of the presence in the solution of a cryoprotectant like Glycerol. Therefore, further DNP SSNMR experiments on silica particles wetted with different types of solvent and radicals will be conducted in order to address these issues. Notably, the choice of the solution containing the radical depends crucially on the material itself. For example, aqueous solutions do not enter the pores of passivated (hydrophobic) materials and would readily degrade the catalysts which will be investigated. We anticipate that “inert” solvents such as alkanes and toluene should be suitable for DNP SSNMR studies of the heterogeneous catalysts. We will also bear in mind that while for many materials it will not be a problem, reactivity of the radical with the metal complexes may be an issue in some cases. For most of the systems we propose to study, preliminary studies show that reactivity with TEMPO is relatively slow at room temperature, and will be much slower at DNP temperatures. This will be evaluated further. In cases where reactivity does become a problem, the use of more bulky radicals will be investigated. The results obtained here are anticipated to be broadly applicable and enable DNP SSNMR experiments to be applied to a wide range of inorganic and hybrid materials.

Multi-dimensional correlations from surface species at natural isotopic abundance. Once basic procedures for preparing samples which allow for efficient DNP signal enhancements have been obtained, advanced SSNMR techniques will be developed and applied under DNP conditions. The structure of surface species before and after the grafting process will be characterized. In our first series of DNP NMR experiments on the phenol- and imidazolium-functionalized hybrid materials,[19] we have shown that through-space ^{1}H-^{13}C chemical shift correlation spectra could be recorded in relatively short experimental times at natural isotopic abundance, and that they provided useful information for the unambiguous characterization of these materials. We propose to apply 2D ^{1}H-^{15}N as well as ^{13}C-^{13}C correlation experiments, at natural isotopic abundance, to obtain further insight into the detailed structure of the materials. In parallel, the feasibility of developing new experiments for surface enhanced conditions by developing through-bond heteronuclear (INEPT) or homonuclear (INADEQUATE) type correlation experiments will be investigated. We also note that correlated chemical shift distributions potentially observed with 2D INADEQUATE type experiments, would lead to increased spectral resolution for the surface species, and access to structural studies of even more complex systems.

Surface Enhanced Proton NMR. Two-dimensional multiple quantum (MQ) ^{1}H–^{1}H spectroscopy has proved to be a powerful NMR technique to investigate structural information contained in ^{1}H–^{1}H dipolar couplings for a wide range of grafted surface organometallic catalysts.[21-23] However, under DNP conditions, proton one-dimensional spectra are dominated by the huge resonances of the solvent, which masks the signals of the species of interest. The feasibility of implementing either MQ filters or mobility filters to efficiently suppress the signals from the solvent and retrieve the enhanced proton NMR signals of the organic fragments will be investigated. If successful, this approach could be extended to two-dimensional experiments, under homonuclear decoupling[24,25] or constant-time acquisition[26,27] to further improve spectral resolution and information content.

Probing the Structure of the Silica Surface. In parallel, we propose to run DNP ^{29}Si SSNMR experiments in order to observe and characterize the silicon sites of the surface which are attached to the covalently bound organic fragments. It is well-known that solid-state ^{29}Si MAS NMR allows one to distinguish silicon atoms involved in siloxane bridges $(SiO)_4Si$ (denoted as Q^4 with a resonance at -110 ppm), single silanols $(SiO)_3SiOH$ (Q^3 = -100 ppm) and geminal silanols $(SiO)_2Si(OH)_2$ (Q^2 = -90 ppm). Silicon-29 T^3 sites, $(SiO)_3SiR$ where the silicon atom is attached to an organic moiety, also have specific well-documented chemical shifts.[28]

So far, however, using standard SSNMR technology, it is difficult to observe for example the silicon atoms linked to the phenol groups in the mesostructured materials likely because of its low concentration (1 site/nm^2, see Figure 4), so that the ^{29}Si CPMAS spectrum displays typically only a single broad resonance corresponding to the Q_4 and Q_3 species. The observation of the T^3 resonances by surface enhanced DNP ^{29}Si SSNMR will be a key objective of this project

In a more general way, in order to understand the reactivity of a solid support with an organometallic complex, the knowledge of the surface structure is essential (for example the concentration of silanols and siloxane bridges, types of silanols which can be either isolated, geminal, or vicinal, etc.). We propose to use ^{29}Si NMR in combination with DNP to characterize various types of solid supports, such as SBA-15 mesoporous silica or dehydroxylated silica treated at high temperatures (above 700 °C), and these silicas with grafted phenolic ligands. As an ultimate goal, silica/alumina (SiO_2/Al_2O_3) or alumina (Al_2O_3) solid supports will be investigated by ^{29}Si and ^{27}Al. There is currently interest within the catalysis community in studying the surface states of γ-Al_2O_3, which is one of the most commonly employed support materials for heterogeneous catalysts.[29] DNP ^{27}Al SSNMR could enable the more routine study of Al_2O_3 surfaces by preferential DNP enhancements of the ^{27}Al resonances of the surface sites.

Surface Dynamics Characterized by SSNMR. In addition to structural questions, very little is known about the dynamics of surface organometallic complexes or about the potential impact of molecular motion on catalytic reactivity and selectivity. However, it is very likely that a given substrate will interact differently with a rigid catalyst than with a more flexible one. For example, dynamics–activity relationships are well established for enzymes.[30] In a recent study, we reported preliminary investigations on the dynamics of grafted catalysts by means of solid state NMR.[31] Dynamical order parameters were evaluated for a series of eleven transition metal alkylidene complexes involved in olefin metathesis. Remarkable differences were observed from one complex to another with order parameters ranging from 0.5, for the more mobile Re and Ta complexes, to 0.9 for the more rigid Mo complexes. These different dynamic behaviors were tentatively related to the presence of bulky ligands and/or to the 4d or 5d nature of the valence electrons of the metals.

More recently we have shown that Mo-alkylidene catalysts display poor performance in ring-closing metathesis.[32] This can be most likely be explained by the rigidity of the active site, as evidenced by the SSNMR investigations, which therefore slows the rate of the metathesis reaction. However, accuracy of these studies was limited by low sensitivity, especially since it was not feasible to acquire low temperature CP/MAS ^{13}C SSNMR spectra of these complexes, due to increases in the optimal ^{1}H recycle delays. Such ^{13}C or ^{2}H variable temperature spectra are usually the centerpiece of any dynamics dynamics study. DNP SSNMR experiments will enable the low temperature spectra to be inviestigated, allowing a more precise determination of the dynamics investigated. (Note that the dynamics measurements here will be done over the whole temperature range using the wetted samples, and compared to the dynamics observed at room temperature with dry samples, in order to assess any possible changes in dynamics caused by the addition of the solvent). The dynamics obtained from all of these measurements will then be correlated to the observed reactivity of the complexes in order to form dynamics-reactivity relationships, and guide the design of more efficient new generations of catalytic species.

In addition to heterogeneous catalysts the DNP SSNMR experiments outlined in this proposal will be applicable to many other materials; many other classes of materials feature molecules/monolayers immobilized on nano- or micro-scale supports. Probing the structure of these materials at their surface interfaces is often necessary in order to understand the physical and chemical behavior of these systems. These materials have applications in diverse fields such as energy conversion and bio-interfaces.[33,34] Given the similarities between the structural motifs of these materials and that of the heterogeneous catalysts discussed herein, it is anticipated that the DNP SSNMR methodologies outlined above will be broadly applicable to these materials as well. In this way the SSNMR experiments discussed herein may also contribute to the development of many other fields that will enhance scientific excellence and competitiveness in different areas. Many of the letters of interest in the annex are from scientists working in these areas, and they will have access to the equipment through the CRMN facility.

2.2.2 STRUCTURE ET COMPOSITION DE L'EQUIPEMENT /STRUCTURE AND BUILDING OF THE EQUIPMENT

(2 pages maximum).

The CRMN Lyon is a unique, multi-disciplinary NMR platform, hosting four NMR spectrometers, with frequencies ranging from 500 to 1000 MHz. A 600 MHz standard bore (SB) spectrometer (end of 2010) and an 800 MHz WB spectrometer dedicated to methodological developments and advanced applications in solid-state NMR spectroscopy (mid-2011) will further increase the capacity of the center. The 800 MHz WB spectrometer will be fully compatible with the DNP system proposed here. So far only 400 MHz DNP spectrometers are commercially, with only two systems installed so far worldwide, but it is expected that 600 and 800 MHz DNP systems will become available for delivery next year (2011) as mentioned in the letter of support from Bruker.

The CRMN will be one of the very first laboratories worldwide to be equipped with a DNP accessories at 800 MHz, which will combine both the sensitivity enhancement of DNP with the high-resolution required for complex systems from the high magnetic field. Indeed, for many applications, it is essential to maintain the high-resolution of high-field NMR with the sensitivity gains of DNP. 400 MHz systems notably do not provide sufficient resolution for many of today's key applications in materials or in biology. Clearly, in structural biology applications, the crowded spectra arising from thousands of nuclei cannot be resolved at 400 MHz (800 MHz is today's "standard" for state-of-the-art solid state NMR investigations of proteins). There is currently much research being carried out in sample preparation strategies to preserve high resolution at cryogenic temperatures, with many encouraging early results in this area. The 800 MHz system will be a key tool in validating and developing such strategies. Further, the Lausanne group has recently published[35] a lovely demonstration of how ^{14}N NMR spectra can be enhaced by DNP at 400 MHz, but figure 1 in that paper dramatically highlights how the 400 MHz spectra of this quadrupolar nucleus are much less well resolved than "ordinary" 800 MHz spectra.

It should also be noted that, while several French laboratories have projects for installing commercial systems at 400 and 600 MHz, they have not yet been achieved, *and there are no high-field DNP systems currently in France*.

The DNP equipment will include a 527 GHz continuous-wave gyrotron, a transmission line, a cooling cabinet and two low temperature (100 K) magic angle spinning (MAS) probes: a triple resonance 3.2 mm probe, and a double resonance 1.3 mm probe.

As indicated in the letter of support from Bruker, the 1.3 mm probe system represents a completely new development, that does not exists so far, and which is expected to lead to a completely new prospective market in the area of surface enhanced NMR for new materials.

2.2.3 ENVIRONNEMENT TECHNIQUE / TECHNICAL ENVIRONNEMENT

(3 pages maximum)

The CRMN building has a spectrometer hall of 380 m^2 that will host in 2011 six high-field NMR spectrometers. The DNP equipment (including the 9.7 T superconducting magnet and the control system of the gyrotron) was envisioned as a possibility at the design stage of the building, and it will be located next to the 800 MHz WB spectrometer, where a suitable space of about 30 m^2 is reserved. Only minor building work (mainly electrical work) will be necessary prior to the installation of the DNP instrument. Note that a liquid nitrogen line, connected to an external tank, already serves the spectrometer hall, and will be used to continuously fill the cooling cabinet. This will greatly simplify the day to day handling of the DNP equipment. The chillers that should be isolated from the work area will be installed in the basement (under the floor).

We note that this project has the double advantage that we already have the significant technical infrastructure and space required for the installation at the CRMN, and we have already acquired the 800 MHz WB NMR system (itself one of only a handful in the world) to be delivered in 2011 that is obviously a prerequisite for DNP. ***This greatly simplifies this project, at both the technical and financial level***. (The 800 WB system itself cost over 3 million euros, which would more than double the cost of a DNP project “from scratch”!). The CRMN thus appears a natural choice for the installation of a high field DNP system at low cost and high efficiency. The highly skilled personnel required to operate the system is also already in place, with previous DNP experience.

3. STRATEGIE DE VALORISATION DES RESULTATS/ DISSEMINATION AND EXPLOITATION OF RESULTS

(2 à 3 pages maximum)

DNP is an emerging technology in the field of solid-state NMR spectroscopy. Therefore, we anticipate that the results of this project will make significant impact in the areas of catalysis and NMR spectroscopy. Currently, NMR spectroscopy is limited to samples which contain a high concentration of nuclear spins due to the intrinsic insensitivity of the technique. As a result of this, the development of methods which can enhance the signal of NMR experiments, and broaden the applications of NMR spectroscopy are of great importance. In particular, given the difficulties in probing the structure of heterogeneous catalysts at the molecular level, the development of new methods capable of examining these systems is invaluable for the further design, and improvement of more efficient and environmentally friendly catalysts, in the context of sustainable development.

The results that will be obtained in this project will be published in high impact journals and are of interest to a wide community of scientists. They will be continuously presented, as the work progresses at international conferences and as publications.

Solid-sate DNP NMR spectroscopy should be applicable to a wide range of materials, with applications in environmental science, biology, or medicine, further widening the applicability of this method. The technical advances in analytical capacity that are the direct result of this project will ***directly*** enable other scientists to attack new materials systems that were previously impossible.

The project will have a clear impact on the competitivity of industrial research (see the letter of support from Rhodia for instance). As mentioned in the letter of support from Bruker, the potential market for this type of equipment is expected to be large. The demonstration experiments that will be done in the context of the current project will therefore considerably stimulate the research teams in industry all around the world. The collaboration with Bruker on the development of a DNP 1.3 mm probe will result in the creation of highly skilled jobs within the company over an enduring period, of at least 10 years, as well as in the academic and industrial laboratories that will acquire such systems.

This scientific project deals with quite fundamental science and the main fallout will be to enhance the state of the art in the field, enabling other scientists to make faster progress towards the structural characterization of challenging solid materials. However, any result, intermediate or final, that are identified as having potential added value will be systematically patented by our institutions.

4. MANAGEMENT DU PROJET / PROJECT MANAGEMENT

4.1. ASPECTS ORGANISATIONNELS / MANAGEMENT

4.1.1 QUALIFICATION DU COORDINATEUR DE PROJET /RELEVANT EXPERIENCE OF THE PROJECT COORDINATOR

(1 page maximum)

The project will be coordinated and managed by Professor Lyndon Emsley (Scientific Director of the CRMN Lyon), assisted by Anne Lesage (IR1 CNRS, technical director of the CRMN Lyon), and Audrey Marchetti (Gestionnaire du CRMN). Emsley has extensive managerial experience that includes managing other ANR or large European grants, as well as managing the activity of the CRMN as a National and European Large Scale User Facility. The CRMN currently provides around 300 days of spectrometer time per year to external users on our high-field machines. He has extensive experience with managing the funding and installation of complex high-field NMR equipment. The CNRS will provide the required infrastructure for accounting and auditing.

The Emsley group have established themselves as one of the premier research groups in the field of solid-state NMR of heterogeneous catalysts, evidenced by a large number of high impact publications concerning the characterization of heterogeneous catalysts since 2001. The group has established international collaborations in the areas of SSNMR and catalysis, leading to publications with collaborators including:

Nobel Laureate Prof. Richard R. Schrock (MIT, USA)
Prof. Christophe Copéret (ETH Zurich, Switzerland)
Prof. Geoffrey Bodenhausen (EPFL, Switzerland)
Prof. Robert L. Vold (William and Mary, USA)
Prof. Eric Oldfield (University of Illinois, USA)
Prof. Adriano Zecchina (University of Turin, Italy)

In addition to collaborations with international research groups, much work is done with other French research groups such as Prof. Odile Eisenstein (Montpellier) and French Academy of Science member J.M. Basset (CNRS Lyon). The work resulting from these collaborations has been published in prestigious journals such as the *Journal of the American Chemical Society*, *Angewandte Chemie*, *Proceedings of the National Academy of Sciences*, and *Science*.

The research group also has access to some of the best facilities and equipment in the world for SSNMR studies of heterogeneous catalysts.

4.1.2 MODALITES DE COORDINATION/ COORDINATION MODALITIES

(1 page maximum)

Since there is only one funded partner, project coordination of finances and reporting should be straightforward, and no major problems are foreseen. Scientific coordination with the international collaborating Laboratories in academia and industry, as well as provision of access to third party users, builds on extensive previous experience a number of well-established collaborations, and coordination should again not be an issue.

The DNP equipment will be shared between in-house research and external users.

Since 2008, the CRMN is a founding member and driving force of the national “Très Grand Infrastructure de Recherche” for NMR (TGIR-RMN), and provides 30% of access to national users on its high-field NMR spectrometers. The 800 MHz WB spectrometer will be part of this national facility and in this context up to 100 days per year could be provided to national users.

The DNP equipment **is neither funded by the TGIR-RMN Federation nor is it part of the TGIR programming**. The equipment therefore qualifies for funding through EQUIPEX. We do propose however that operationally this DNP capacity will benefit from the experience and infrastructure of the Laboratory for providing access to external users. Since the 800 MHz WB spectrometer to which it will be connected is included in the access scheme of the TGIR-RMN, the DNP accessory will naturally be made available to external French users through this national federation, with projects reviewed and selected by national experts. The DNP instrument will be a unique platform optimized for the development of high-level DNP experiments, and is expected to attract many national users (see the letters of support from the French community). Similarly the equipment will be available to European Users through the Integrated Infrastructure Initiative, Bio-NMR (the successor program to EU-NMR).

The DNP equipment will increase the capacity of the center both for its activity as a Large Scale Facility at the National and European levels, as well for in-house research activity and for the strong network of local, regional, national and international collaborations in a range of interdisciplinary areas ranging from catalysis and sustainable development, to structural biology.

The TGIR and EU platforms will clearly guarantee the accessibility of the equipment to the broadest possible user community. Notably the access protocols and review procedures meet the highest standards of transparence, and the results of the access programs are critically reviewed annually (for the national TGIR structure) and bis annually for the EU facility.

Specifically, access to the 800 MHz wide bore NMR system will be governed by the rules typical for most TGIR type infrastructures (Synchrotron sources, Neutron sources, High-Field NMR…) (details can be found at www.ralf-nmr.fr, www.tgir-rmn.org, and www.eu-nmr.eu), with a continuous call for proposals, which are submitted through a website. The proposals are sent for critical evaluation to an external review panel, and if the review is positive spectrometer time is assigned, and the costs of the spectrometer time, and travel and lodging of the visiting scientists, are covered by the CRMN through dedicated CNRS

TGIR or EU funds. The CRMN has several years of experience successfully operating this kind of open access procedure.

4.2. ORGANISATION DU PARTENARIAT / COLLABORATION ORGANIZATION

4.2.1 DESCRIPTION, ADEQUATION ET COMPLEMENTARITE DES PARTENAIRES/PARTNERS DESCRIPTION , RELEVANCE AND COMPLEMENTARITY

The Centre for High Field NMR (CRMN) in Lyon is part of the Université de Lyon, and is operated by the CNRS and the Ecole Normale Supérieure de Lyon (one of France's foremost teaching and research institutions). The centre is led by Prof. L. Emsley and there is an internationally recognized group of over 20 scientists employed in the group. The center is devoted to developing novel applications of very high-field multi-nuclear NMR spectroscopy, in all areas of science ranging from physics and chemistry to medicine. The CRMN thus provides high-level expertise in NMR techniques for the investigation of molecular structure, dynamics, and function. The Emsley research group now has accumulated more than 150 publications in international journals, with papers appearing in prestigious peer-reviewed journals such as Science, Proceedings of the National Academy of Sciences (USA), the Journal of the American Chemical Society and Angewandte Chemie.

The Center houses a 500, a 700 and a 800 MHz spectrometers, all equipped with solid-state NMR hardware. The world's first 1 GHz NMR system was installed in July 2009 and, is now fully operative for solution and solid-state NMR spectroscopy. In addition to these pre-existing capabilities, the delivery of an 800 MHz WB solid-state NMR spectrometer will take place in 2011. The DNP equipment will be installed on this instrument and will add another unique capability to the CRMN. Lyon is recognized as one of only four national centers of excellence in Chemical Sciences.

The centre operates a national and international user facility, providing access to its unique infrastructure. This activity has been recognized by the European Commission, through the award of two I3 grants to support trans-national access (see www.ralf-nmr.fr). In conclusion, the CRMN Lyon provides a unique, high-level, multi-disciplinary research environment for NMR spectroscopy, perfect for developing new experimental methods capable of probing the structure of materials and heterogeneous catalysts.

In relation to the current project, as described in section 4.1.1. above, the Emsley group has extensive experience in applying advanced high resolution solid-state NMR techniques to characterize a variety of heterogeneous catalysts, with many international collaborations. The CRMN thus provides the perfect environment to develop the project proposed here, both in terms of an internationally recognized scientific surrounding, and in terms of a world-class infrastructure.

4.2.2 QUALIFICATION, ROLE ET IMPLICATION DES PARTENAIRES / QUALIFICATION, ROLE AND INVOLVEMENT OF INDIVIDUAL PARTNERS

Pr. Lyndon Emsley is a professor at the Ecole Normale Supérieure de Lyon and the scientific director of the CRMN Lyon. He has been pioneered novel experimental approaches for significant advances in solid-sate NMR over the last 20 years. His research was consequently been internationally honored and has resulted in over 150 publications in international journals, stimulating major impact in areas ranging from catalysis to systems biology. Prof. Emsley has extensive previous experience successfully leading and managing dozens of previous contract based mono- or multi-partner research projects funded by the EU, France, or industry, ranging from 100 k€ to over 15 million €.
(http://perso.ens-lyon.fr/lyndon.emsley/)

Dr. Anne Lesage, IR1 at the CNRS, is an outstanding spectroscopist behind many pulse sequences developed in the Center. The quality and originality of her recent research are proved by more than 80 papers published in excellent high-profile international journals. She is coordinating and pursuing an extremely productive and innovative research line on the demanding structural characterization of surface catalysts by NMR. At the same time, she is responsible for the technical infrastructure of the CRMN and, was notably in charge of planning, realizing and organizing the setup of the new High-Field centre of NMR in Lyon

Dr. Moreno Lelli recently joined the European Centre for High-Field NMR in Lyon as Ingénieur de Recherche (IR 2). His expertise in the field of solid-state NMR spectroscopy started in the group of Prof. Bertini (University of Florence) and is recognized as documented by high-impact publications (among which 6 JACS papers, 1 PNAS…). Moreno Lelli is notably in charge of the external national and international users at the CRMN and of the maintenance of the NMR spectrometers.

Partner	Surname	First name	Position	Domain	Organization or company	Contribution in the project (4 lines max)
CRMN	EMSLEY	Lyndon	Professor	NMR spectroscopy	ENS-Lyon	Coordination du projet, suivi de la mise en place de l'appareillage, orientations stratégiques, développements méthodologiques.
CRMN	LESAGE	Anne	IR 1 CNRS	NMR spectroscopy	CNRS	Coordination de la mise en place de l'équipement, maintenance de l'appareillage, développements de nouvelles methodologies, acquisition des spectres.
CRMN	LELLI	Moreno	IR 2 CNR	NMR spectroscopy	CNRS	Maintenance de l'appareillage., acquisition des spectres, développements de nouvelles methodologies, assistance aux utilisateurs.

In summary the CRMN is a world-class (**AERES A+**) research laboratory in NMR spectroscopy, and the project leaders are internationally recognized, prize-wining scientists.

Lyndon Emsley:

1991. Fellow of the Miller Institute for Basic Research in Science, Berkeley, CA

1994. Foreign Member of the Institut Universitaire de France.

2002. Member of the Institut Universitaire de France.

2004. Gallileo Lecturer in Chemistry, Università di Pisa, Italy

2005. CNRS Silver Medal in Chemistry

2009. EAS Award for Outstanding Achievement in Magnetic Resonance

2010. Luigi Sacconi Medal of the Italian Chemical Society.

Anne Lesage:

2010. Cristal du CNRS

5. EVALUATION FINANCIERE DU PROJET/ FINANCIAL ASSESSMENT

1. La justification scientifique et financière des montants demandés au titre du coût d'investissement

Bruker BioSpin developed and introduced in 2009 the world's first commercially available 263 GHz Solid-State DNP-NMR spectrometer (400 MHz NMR frequency) that takes advantage of the inherent dramatic sensitivity enhancements enabled by the Dynamic Nuclear Polarization technique. As mentioned in the letter of support from Bruker, this technological, scientific and industrial success leads them to now develop and commercialize the first 527 GHz DNP system that will be compatible with 800 MHz WB NMR spectrometers, and available for delivery in 2011. (Bruker is currently the only company in the world offering this type of equipment).

Notably, the 1.3 mm probe system represents a completely new development, which would not be possible without this order. This probe will open outstanding new perspectives in the study of surface materials.

In order to further reinforce the partnership between the company and the CRMN, Bruker proposes a special discount of 350 k€ for the 800 MHz DNP equipment.

Gyrotron DNP system : (includes the electronic tube, the superconducting magnet, and the control system)	1 190 000 €
Low temperature (100 K) triple resonance 3.2 mm MAS probe at 800 MHz	240 500 €
Low temperature (100 K) double resonance 1.3 mm MAS probe at 800 MHz	360 000 €
Cooling Unit	190 000 €
Total of the DNP NMR equipment: (according to the quotation provided by Bruker and given in the annex)	**1 980 500 €**
Co-funding by Bruker Biospin (Special discount):	***- 350 000 €***
Building work and miscellaneous equipments (liquid nitrogen line fitting, liquid nitrogen dewars, electrical works)	40 000 €
Total of the investment costs:	**1 670 500 € HT**
	1 996 248 € TTC

Note that this investment is not supported or programmed by the TGIR-RMN, and is therefore eligible for EQUIPEX.

2. La justification scientifique et financière des montants demandés au titre du coût de fonctionnement hors masse salariale.

Running costs are estimated at: **57 000 € HT**
(per year, corresponding to 3 full months of experiments):

They include :

The cost of the liquid nitrogen	14 k€
The cost of the dry nitrogen gas	8 k€
The costs for the maintenance of the equipment	12 k€
The fluids for the gyrotron	7 k€
The DNP rotors (four 3.2 mm and four 1.3 mm rotors per year)	16 k€

The running costs calculated for a period of 8 years are: **456 000 € HT**

545 376 € TTC

Note that these costs correspond only to the additional running cost associated directly with the DNP accessory, and will not be funded by the TGIR programming. They are therefore eligible for EQUIPEX. Note that these costs do not include the ordinary running costs of the 800 WB spectrometer and magnet itself, nor do they include costs for user travel and lodging, as these costs are already included in the 800 MHz WB TGIR activity.

3- La justification scientifique et financière des autres frais engendrés par l'acquisition et le fonctionnement de l'équipement, qui ne seront pas financés (hors assiette de l'aide), mais qui seront pris en compte pour le calcul du coût complet de l'opération.

NOM	%temps passé pour la phase de fonctionnement	Grade/échelon
Lyndon Emsley	8 hommes.mois*	Professeur
Anne Lesage	16 hommes.mois*	IR 1
Moreno Lelli	16 hommes.mois*	IR 2
xx	16 hommes.mois*	Doctorant 1
xx	16 hommes.mois*	Doctorant 2
xx	16 hommes.mois*	Post-Doctorant 1
xx	16 hommes.mois*	Post-Doctorant 2

* pour une durée de fonctionnement de l'équipement de 8 ans.

6. ANNEXES / APPENDICES

6.1. REFERENCES BIBLIOGRAPHIQUES DE L'ETAT DE L'ART/STATE OF ART REFERENCES

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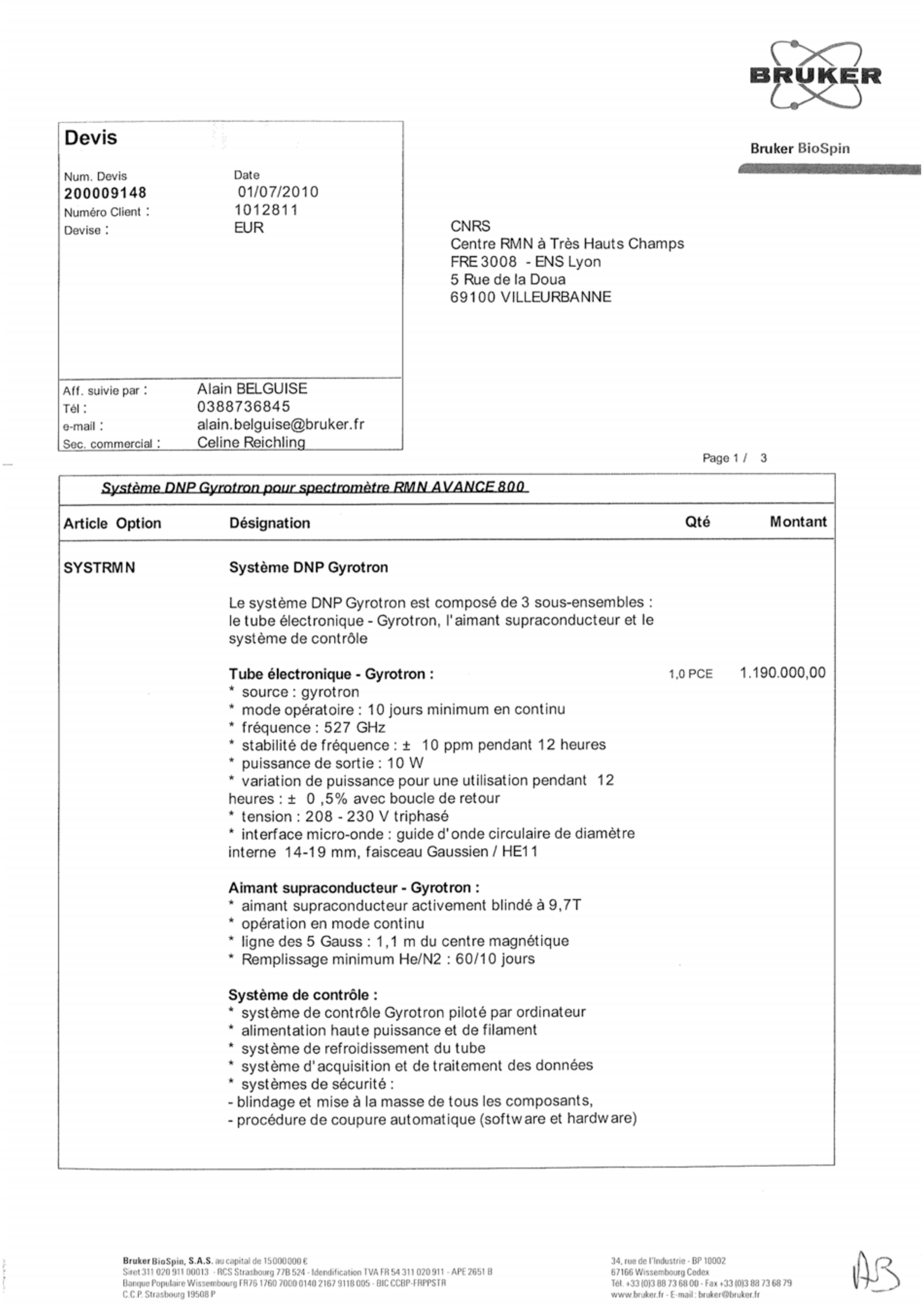
6.3. DEVIS POUR L'EQUIPEMENT/ESTIMATE FOR THE EQUIPEMENT



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Devis

Num. Devis **200009148**	Date 01/07/2010
Numéro Client :	1012811
Devise :	EUR
Aff. suivie par :	Alain BELGUISE
Tél :	0388736845
e-mail :	alain.belguise@bruker.fr
Sec. commercial :	Celine Reichling

CNRS
Centre RMN à Très Hauts Champs
FRE 3008 - ENS Lyon
5 Rue de la Doua
69100 VILLEURBANNE

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Système DNP Gyrotron pour spectromètre RMN AVANCE 800

Article Option	Désignation	Qté	Montant
SYSTRMN	**Système DNP Gyrotron**		
	Le système DNP Gyrotron est composé de 3 sous-ensembles : le tube électronique - Gyrotron, l'aimant supraconducteur et le système de contrôle		
	Tube électronique - Gyrotron : * source : gyrotron * mode opératoire : 10 jours minimum en continu * fréquence : 527 GHz * stabilité de fréquence : ± 10 ppm pendant 12 heures * puissance de sortie : 10 W * variation de puissance pour une utilisation pendant 12 heures : ± 0 ,5% avec boucle de retour * tension : 208 - 230 V triphasé * interface micro-onde : guide d'onde circulaire de diamètre interne 14-19 mm, faisceau Gaussien / HE11	1,0 PCE	1.190.000,00
	Aimant supraconducteur - Gyrotron : * aimant supraconducteur activement blindé à 9,7T * opération en mode continu * ligne des 5 Gauss : 1,1 m du centre magnétique * Remplissage minimum He/N2 : 60/10 jours		
	Système de contrôle : * système de contrôle Gyrotron piloté par ordinateur * alimentation haute puissance et de filament * système de refroidissement du tube * système d'acquisition et de traitement des données * systèmes de sécurité : - blindage et mise à la masse de tous les composants, - procédure de coupure automatique (software et hardware)		

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AB

BRUKER

Bruker BioSpin

Devis

Num. Devis
200009148 Du 01/07/2010

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Article	Option	Désignation	Qté	Montant
		Accessoires complémentaires : * Ligne de transmission des micro-ondes incluant des détecteurs pour liaison entre la tête de mesure et le système DNP Gyrotron * Calorimètre pour mesures de puissance * Unité d'affichage vecteur		
		Têtes de mesures et unité de refroidissement.		
		Tête de mesure LTMAS 800 MHz basse température, diamètre 3.2 mm. Comprenant une ligne de transmission des micro-ondes vers la sonde et un système de transfert du gaz froid pour une utilisation avec azote pour des mesures à 100K. Cette sonde est équipée d'un système MAS 3.2 mm et optimisée pour l'observation 13C et/ou 15N, découplage 1H.	1,0 PCE	240.500,00
		Tête de mesure LTMAS 800 MHz basse température, diamètre 1.3 mm. Comprenant une ligne de transmission des micro-ondes vers la sonde et un système de transfert du gaz froid pour une utilisation avec azote pour des mesures à 100K. Cette sonde est équipée d'un système MAS 1.3 mm et optimisée pour l'observation 13C et/ou 15N, découplage 1H.	1,0 PCE	360.000,00
		Unité de refroidissement MAS avec échangeur de chaleur, dewar azote liquide et système de transfert.	1,0 PCE	190.000,00

Montant brut HT		1.980.500,00
Remise exceptionnelle		-350.000,00
Montant net HT		1.630.500,00
Total T.V.A	19,60 %	319.578,00
Montant TTC		**1.950.078,00**

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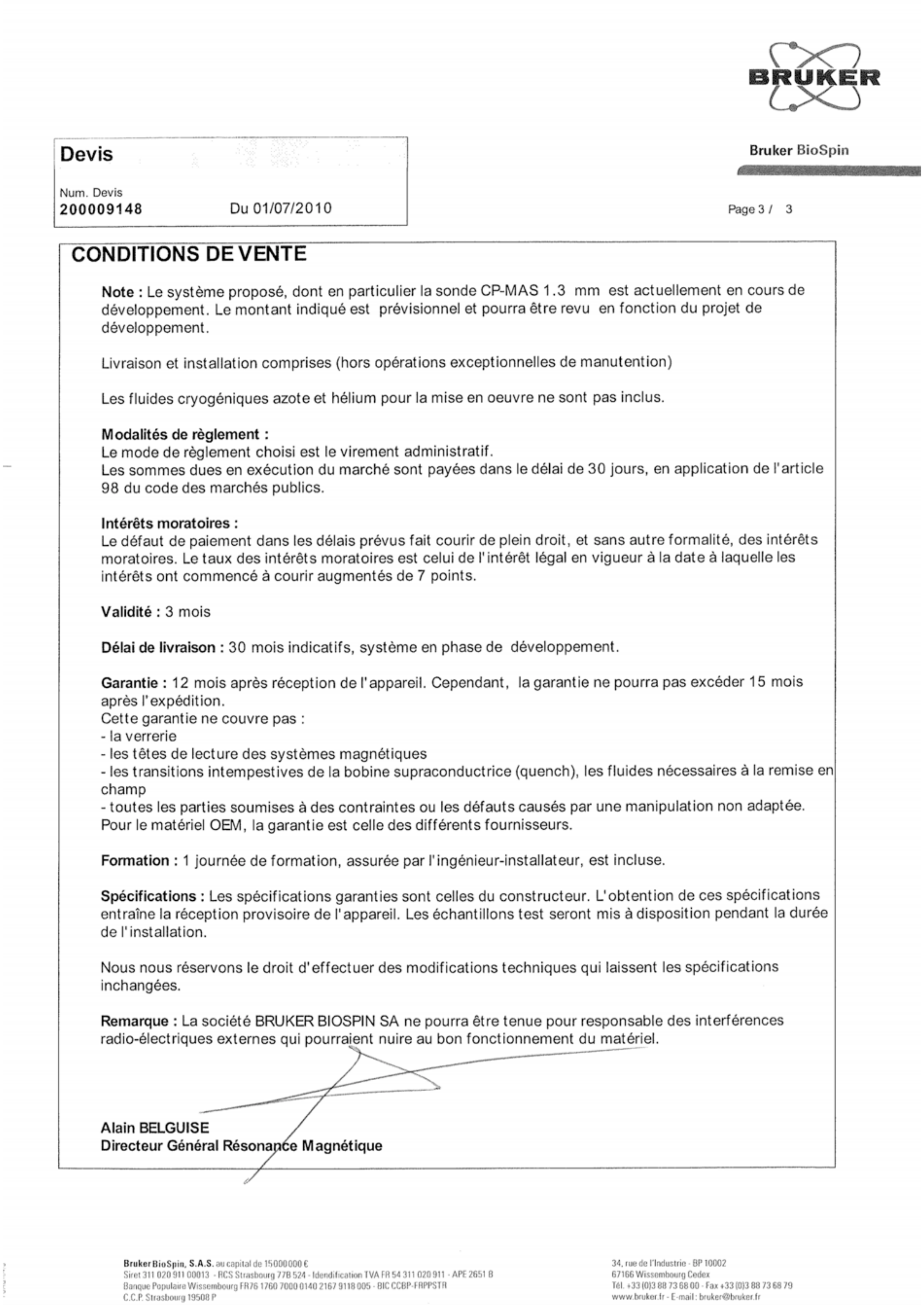

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Num. Devis
200009148 Du 01/07/2010

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CONDITIONS DE VENTE

Note : Le système proposé, dont en particulier la sonde CP-MAS 1.3 mm est actuellement en cours de développement. Le montant indiqué est prévisionnel et pourra être revu en fonction du projet de développement.

Livraison et installation comprises (hors opérations exceptionnelles de manutention)

Les fluides cryogéniques azote et hélium pour la mise en oeuvre ne sont pas inclus.

Modalités de règlement :
Le mode de règlement choisi est le virement administratif.
Les sommes dues en exécution du marché sont payées dans le délai de 30 jours, en application de l'article 98 du code des marchés publics.

Intérêts moratoires :
Le défaut de paiement dans les délais prévus fait courir de plein droit, et sans autre formalité, des intérêts moratoires. Le taux des intérêts moratoires est celui de l'intérêt légal en vigueur à la date à laquelle les intérêts ont commencé à courir augmentés de 7 points.

Validité : 3 mois

Délai de livraison : 30 mois indicatifs, système en phase de développement.

Garantie : 12 mois après réception de l'appareil. Cependant, la garantie ne pourra pas excéder 15 mois après l'expédition.
Cette garantie ne couvre pas :
- la verrerie
- les têtes de lecture des systèmes magnétiques
- les transitions intempestives de la bobine supraconductrice (quench), les fluides nécessaires à la remise en champ
- toutes les parties soumises à des contraintes ou les défauts causés par une manipulation non adaptée.

Pour le matériel OEM, la garantie est celle des différents fournisseurs.

Formation : 1 journée de formation, assurée par l'ingénieur-installateur, est incluse.

Spécifications : Les spécifications garanties sont celles du constructeur. L'obtention de ces spécifications entraîne la réception provisoire de l'appareil. Les échantillons test seront mis à disposition pendant la durée de l'installation.

Nous nous réservons le droit d'effectuer des modifications techniques qui laissent les spécifications inchangées.

Remarque : La société BRUKER BIOSPIN SA ne pourra être tenue pour responsable des interférences radio-électriques externes qui pourraient nuire au bon fonctionnement du matériel.

Alain BELGUISE
Directeur Général Résonance Magnétique

6.4. LETTERS OF SUPPORT

Mr. Philippe SAUTET
Directeur de l'Institut de Chimie de Lyon
Directeur du Laboratoire de Chimie de l'ENS Lyon

Objet : Soutien de la demande Equipex du CRMN (Grand Emprunt)

Lyon, le 14 Septembre 2010

Le Centre de Résonance Magnétique Nucléaire à très Hauts Champs de Lyon (CRMN) qui regroupe en son sein une expertise pluridisciplinaire de pointe en spectroscopie RMN et une plateforme technique unique au monde, constitue l'un des acteurs majeurs de l'Institut de Chimie de Lyon.

Le CRMN a notamment développé, en collaboration avec d'autres laboratoires lyonnais, un axe de recherche fort sur la caractérisation structurale et dynamique à l'échelle moléculaire du site actif de catalyseurs hétérogènes complexes, par RMN solide haute résolution. Il possède dans ce domaine une expertise scientifique reconnue internationalement.

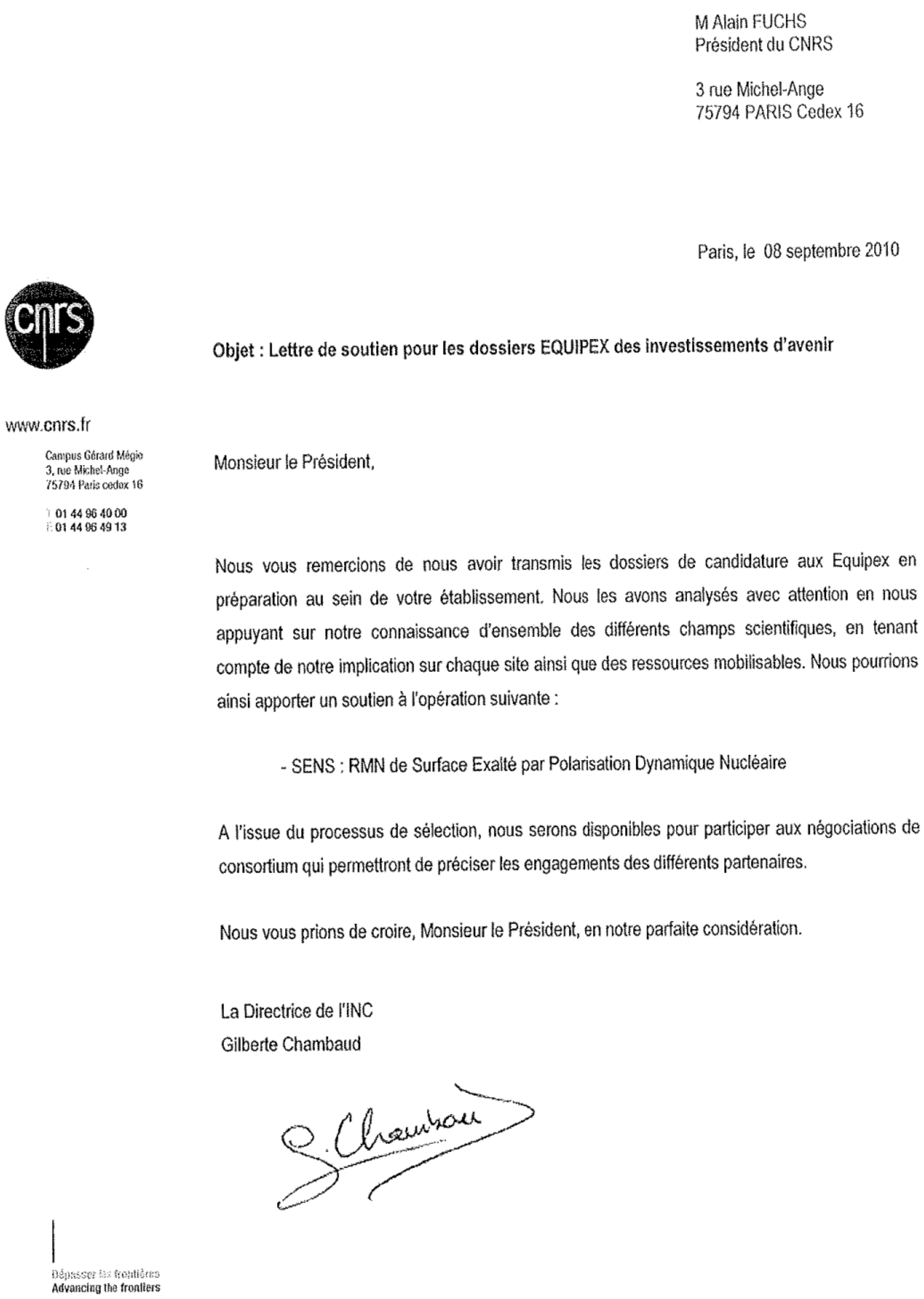
Le CRMN souhaite aujourd'hui acquérir un équipement de DNP (Dynamic Nuclear Polarization) à 800 MHz. Comme l'ont montré récemment les chercheurs du CRMN lors une étude pilote, un tel équipement devrait permettre d'accroître considérablement la sensibilité des expériences RMN réalisées à l'état solide, sur des systèmes moléculaires tels que des catalyseurs organométalliques, des silices mésoporeuses, des matériaux hybrides... L'appareillage de DNP permettra notamment l'étude structurale détaillée d'espèces de surface jusqu'alors inaccessibles et contribuera aux développements de nouveaux matériaux, notamment dans le domaine de la chimie durable.

L'acquisition de cet équipement DNP à 800 MHz permettra aux laboratoires régionaux d'avoir accès à l'état de l'art en termes de méthodologie en RMN du solide haute résolution, au sein de l'un des centres leaders dans ce domaine. Il contribuera ainsi fortement au rayonnement scientifique des laboratoires lyonnais et placera Lyon au tout premier plan mondial en RMN solide haute résolution

L'ICL soutient par conséquent sans réserve aucune et avec le plus grand enthousiasme la demande d'équipement formulée par Lyndon Emsley, directeur du CRMN, dans le cadre de l'appel d'offre Equipex.

Philippe SAUTET
Directeur de l'ICL

INSTITUT DE CHIMIE DE LYON
43 Bd du 11 novembre 1918 ● 69622 Villeurbanne Cedex ● France
tél : 04 72 43 29 95 ● fax : 04 72 44 81 14



M Alain FUCHS
Président du CNRS

3 rue Michel-Ange
75794 PARIS Cedex 16

Paris, le 08 septembre 2010

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75794 Paris cedex 16

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F 01 44 96 49 13

Objet : Lettre de soutien pour les dossiers EQUIPEX des investissements d'avenir

Monsieur le Président,

Nous vous remercions de nous avoir transmis les dossiers de candidature aux Equipex en préparation au sein de votre établissement. Nous les avons analysés avec attention en nous appuyant sur notre connaissance d'ensemble des différents champs scientifiques, en tenant compte de notre implication sur chaque site ainsi que des ressources mobilisables. Nous pourrions ainsi apporter un soutien à l'opération suivante :

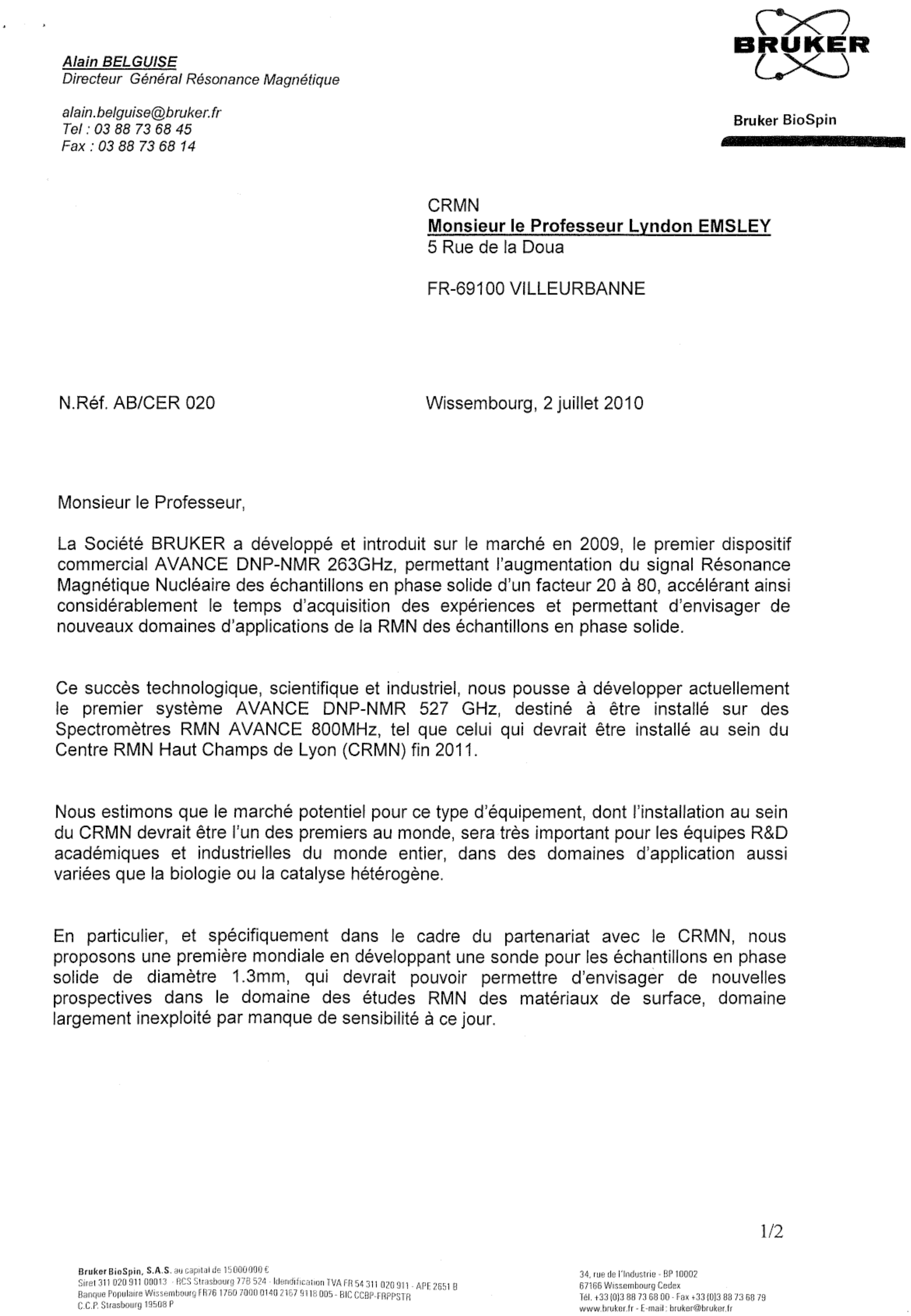
- SENS : RMN de Surface Exalté par Polarisation Dynamique Nucléaire

A l'issue du processus de sélection, nous serons disponibles pour participer aux négociations de consortium qui permettront de préciser les engagements des différents partenaires.

Nous vous prions de croire, Monsieur le Président, en notre parfaite considération.

La Directrice de l'INC
Gilberte Chambaud

Dépasser les frontières
Advancing the frontiers



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Alain BELGUISE
Directeur Général Résonance Magnétique

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CRMN
Monsieur le Professeur Lyndon EMSLEY
5 Rue de la Doua

FR-69100 VILLEURBANNE

N.Réf. AB/CER 020

Wissembourg, 2 juillet 2010

Monsieur le Professeur,

La Société BRUKER a développé et introduit sur le marché en 2009, le premier dispositif commercial AVANCE DNP-NMR 263GHz, permettant l'augmentation du signal Résonance Magnétique Nucléaire des échantillons en phase solide d'un facteur 20 à 80, accélérant ainsi considérablement le temps d'acquisition des expériences et permettant d'envisager de nouveaux domaines d'applications de la RMN des échantillons en phase solide.

Ce succès technologique, scientifique et industriel, nous pousse à développer actuellement le premier système AVANCE DNP-NMR 527 GHz, destiné à être installé sur des Spectromètres RMN AVANCE 800MHz, tel que celui qui devrait être installé au sein du Centre RMN Haut Champs de Lyon (CRMN) fin 2011.

Nous estimons que le marché potentiel pour ce type d'équipement, dont l'installation au sein du CRMN devrait être l'un des premiers au monde, sera très important pour les équipes R&D académiques et industrielles du monde entier, dans des domaines d'application aussi variées que la biologie ou la catalyse hétérogène.

En particulier, et spécifiquement dans le cadre du partenariat avec le CRMN, nous proposons une première mondiale en développant une sonde pour les échantillons en phase solide de diamètre 1.3mm, qui devrait pouvoir permettre d'envisager de nouvelles prospectives dans le domaine des études RMN des matériaux de surface, domaine largement inexploité par manque de sensibilité à ce jour.

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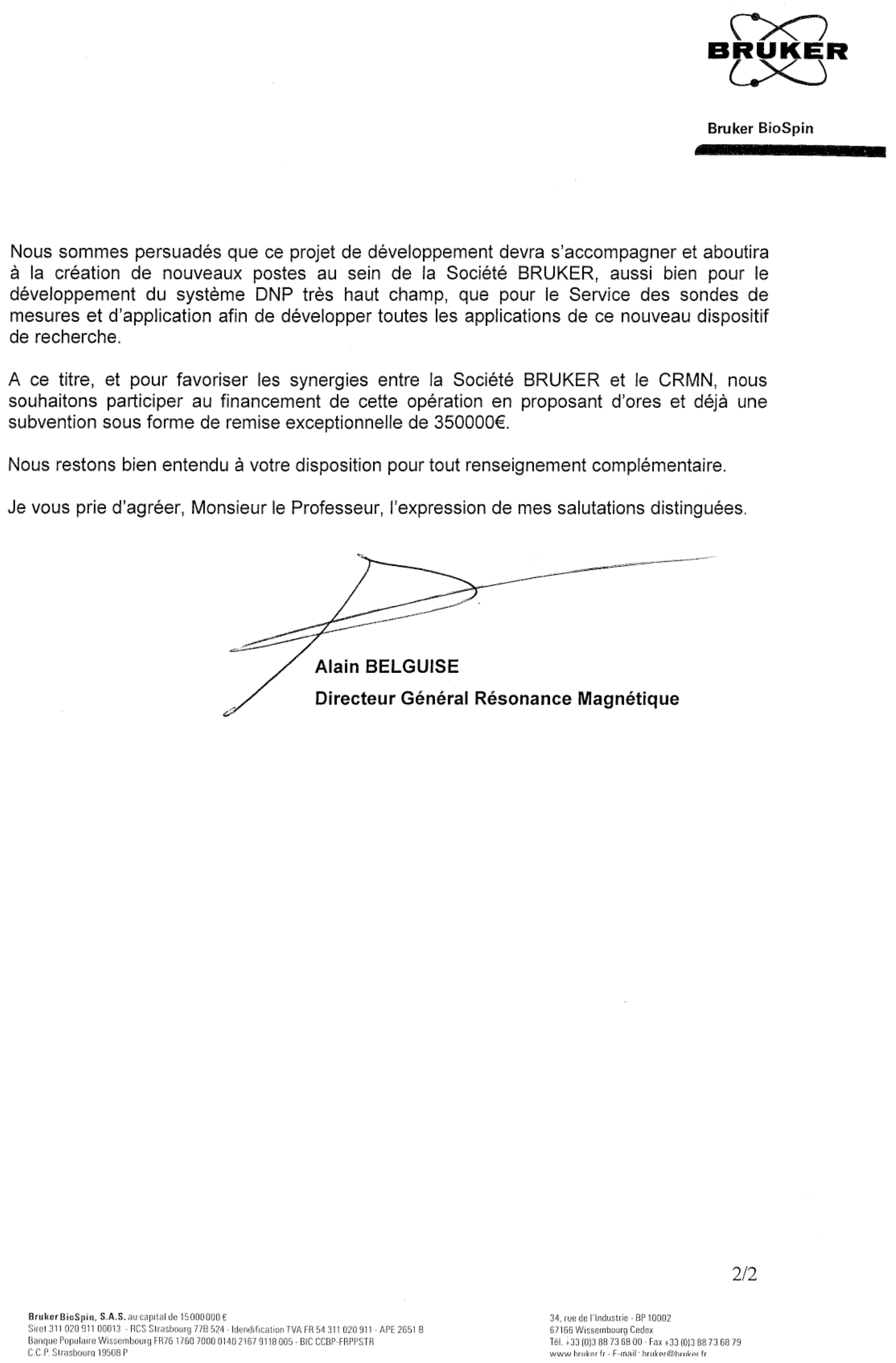

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Nous sommes persuadés que ce projet de développement devra s'accompagner et aboutira à la création de nouveaux postes au sein de la Société BRUKER, aussi bien pour le développement du système DNP très haut champ, que pour le Service des sondes de mesures et d'application afin de développer toutes les applications de ce nouveau dispositif de recherche.

A ce titre, et pour favoriser les synergies entre la Société BRUKER et le CRMN, nous souhaitons participer au financement de cette opération en proposant d'ores et déjà une subvention sous forme de remise exceptionnelle de 350000€.

Nous restons bien entendu à votre disposition pour tout renseignement complémentaire.

Je vous prie d'agréer, Monsieur le Professeur, l'expression de mes salutations distinguées.

Alain BELGUISE
Directeur Général Résonance Magnétique

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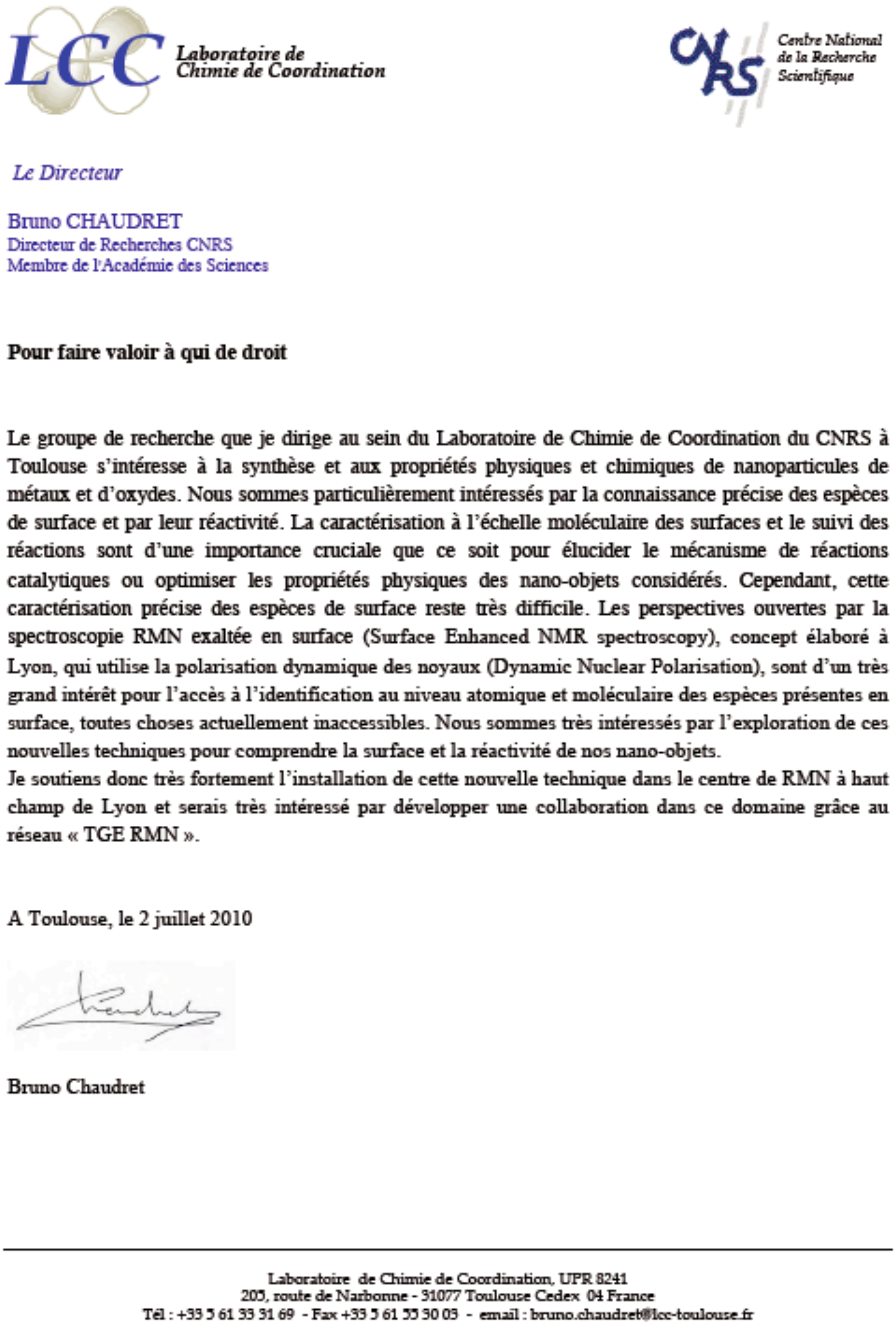

LCC Laboratoire de Chimie de Coordination

CNRS Centre National de la Recherche Scientifique

Le Directeur

Bruno CHAUDRET
Directeur de Recherches CNRS
Membre de l'Académie des Sciences

Pour faire valoir à qui de droit

Le groupe de recherche que je dirige au sein du Laboratoire de Chimie de Coordination du CNRS à Toulouse s'intéresse à la synthèse et aux propriétés physiques et chimiques de nanoparticules de métaux et d'oxydes. Nous sommes particulièrement intéressés par la connaissance précise des espèces de surface et par leur réactivité. La caractérisation à l'échelle moléculaire des surfaces et le suivi des réactions sont d'une importance cruciale que ce soit pour élucider le mécanisme de réactions catalytiques ou optimiser les propriétés physiques des nano-objets considérés. Cependant, cette caractérisation précise des espèces de surface reste très difficile. Les perspectives ouvertes par la spectroscopie RMN exaltée en surface (Surface Enhanced NMR spectroscopy), concept élaboré à Lyon, qui utilise la polarisation dynamique des noyaux (Dynamic Nuclear Polarisation), sont d'un très grand intérêt pour l'accès à l'identification au niveau atomique et moléculaire des espèces présentes en surface, toutes choses actuellement inaccessibles. Nous sommes très intéressés par l'exploration de ces nouvelles techniques pour comprendre la surface et la réactivité de nos nano-objets.
Je soutiens donc très fortement l'installation de cette nouvelle technique dans le centre de RMN à haut champ de Lyon et serais très intéressé par développer une collaboration dans ce domaine grâce au réseau « TGE RMN ».

A Toulouse, le 2 juillet 2010

Bruno Chaudret

Laboratoire de Chimie de Coordination, UPR 8241
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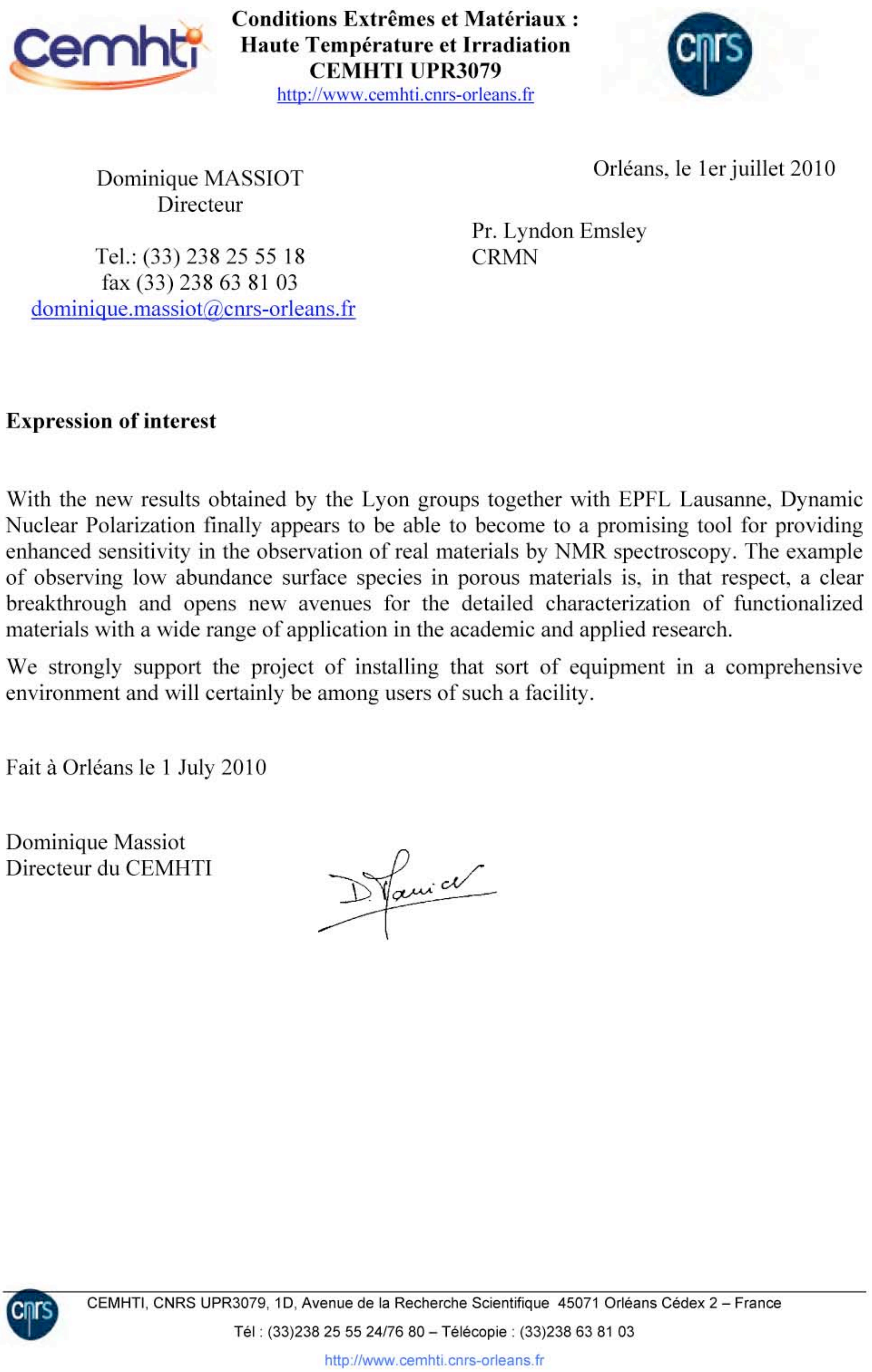
Tél : +33 5 61 33 31 69 - Fax +33 5 61 55 30 03 - email : bruno.chaudret@lcc-toulouse.fr



Conditions Extrêmes et Matériaux :
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CEMHTI UPR3079
http://www.cemhti.cnrs-orleans.fr

Dominique MASSIOT
Directeur

Tel.: (33) 238 25 55 18
fax (33) 238 63 81 03
dominique.massiot@cnrs-orleans.fr

Orléans, le 1er juillet 2010

Pr. Lyndon Emsley
CRMN

Expression of interest

With the new results obtained by the Lyon groups together with EPFL Lausanne, Dynamic Nuclear Polarization finally appears to be able to become to a promising tool for providing enhanced sensitivity in the observation of real materials by NMR spectroscopy. The example of observing low abundance surface species in porous materials is, in that respect, a clear breakthrough and opens new avenues for the detailed characterization of functionalized materials with a wide range of application in the academic and applied research.

We strongly support the project of installing that sort of equipment in a comprehensive environment and will certainly be among users of such a facility.

Fait à Orléans le 1 July 2010

Dominique Massiot
Directeur du CEMHTI

CEMHTI, CNRS UPR3079, 1D, Avenue de la Recherche Scientifique 45071 Orléans Cédex 2 – France
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ECOLE NORMALE SUPERIEURE
DEPARTEMENT DE CHIMIE

24 RUE LHOMOND; 75231 PARIS CEDEX 05; FRANCE

Dr. Geoffrey Bodenhausen
Professeur

Tel: 0033 1 44 32 34 89
Fax: 0033 1 44 32 33 97

Prof Lyndon Emsley
CRMN
Lyon

29 juin 2010

Cher Lyndon,

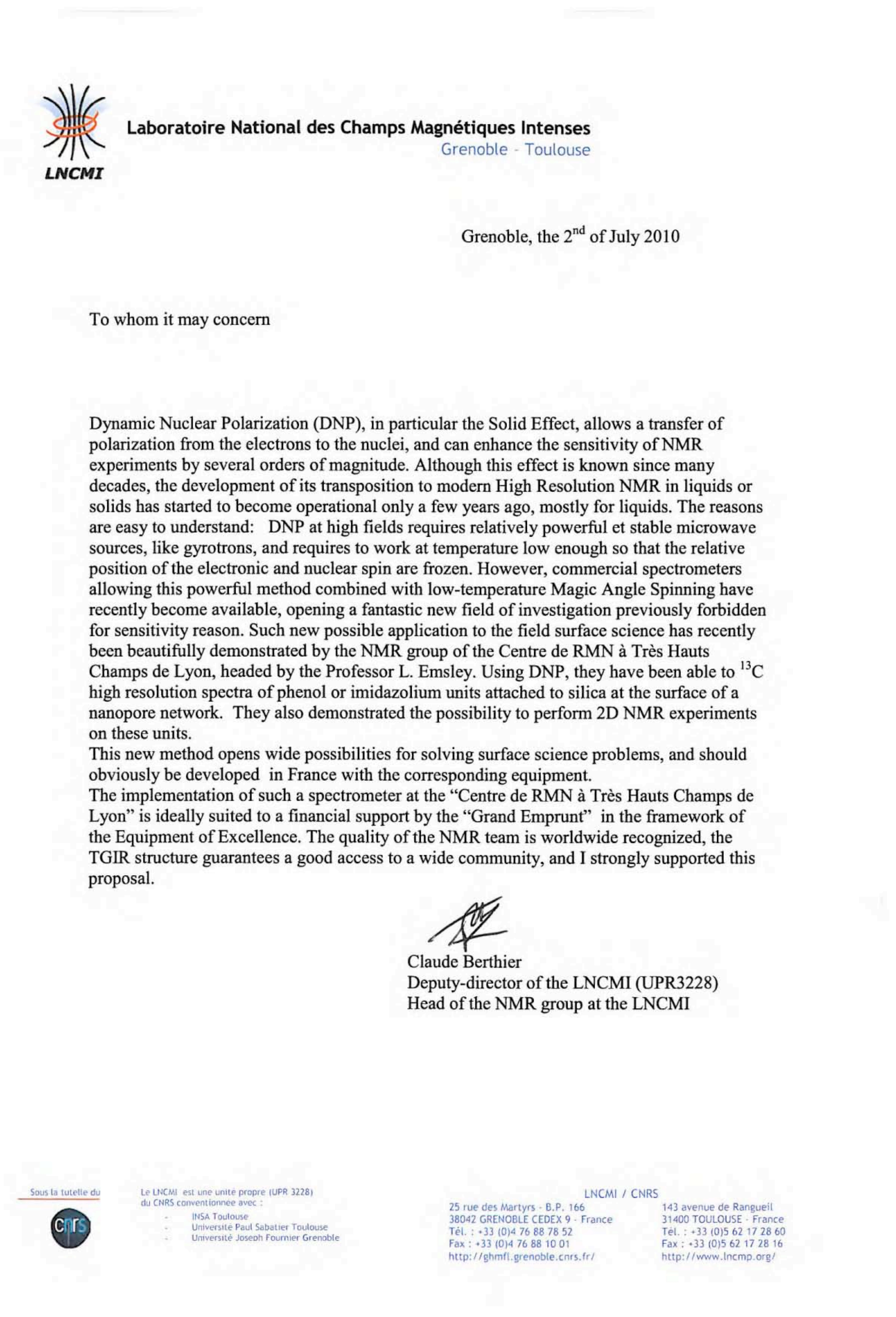
C'est avec plaisir que je voudrais apporter mon soutien au projet du CNMR d'acquérir un équipement pour la *dynamic nuclear polarization* (DNP) afin d'amplifier les signaux de RMN. L'installation d'un gyrotron capable de générer une puisssance d'environ 5 W de micro-ondes à 526 GHz à proximité de l'appareil RMN 800 MHz wide-bore, en combinaison avec une sonde à rotation à l'angle magique (MAS) refroidie à environ 100 K, permettrait d'amplifier les signaux d'un facteur entre 100 et 300, soit de gagner du temps par un facteur qui varierait entre 10 000 et 100 000.

Etant moi-même responsable d'une telle machine combinée avec une RMN 400 MHz wide-bore installée à l'EPFL en Suisse, je puis exprimer ma conviction que cela serait une fort bonne chose pour la communauté française (à travers le réseau TGI/TGE RMN THC) que de disposer d'un tel instrument au CNMR à Lyon.

Meilleurs sentiments

G B.

Geoffrey Bodenhausen



LNCMI
Laboratoire National des Champs Magnétiques Intenses
Grenoble - Toulouse

Grenoble, the 2nd of July 2010

To whom it may concern

Dynamic Nuclear Polarization (DNP), in particular the Solid Effect, allows a transfer of polarization from the electrons to the nuclei, and can enhance the sensitivity of NMR experiments by several orders of magnitude. Although this effect is known since many decades, the development of its transposition to modern High Resolution NMR in liquids or solids has started to become operational only a few years ago, mostly for liquids. The reasons are easy to understand: DNP at high fields requires relatively powerful et stable microwave sources, like gyrotrons, and requires to work at temperature low enough so that the relative position of the electronic and nuclear spin are frozen. However, commercial spectrometers allowing this powerful method combined with low-temperature Magic Angle Spinning have recently become available, opening a fantastic new field of investigation previously forbidden for sensitivity reason. Such new possible application to the field surface science has recently been beautifully demonstrated by the NMR group of the Centre de RMN à Très Hauts Champs de Lyon, headed by the Professor L. Emsley. Using DNP, they have been able to ^{13}C high resolution spectra of phenol or imidazolium units attached to silica at the surface of a nanopore network. They also demonstrated the possibility to perform 2D NMR experiments on these units.
This new method opens wide possibilities for solving surface science problems, and should obviously be developed in France with the corresponding equipment.
The implementation of such a spectrometer at the "Centre de RMN à Très Hauts Champs de Lyon" is ideally suited to a financial support by the "Grand Emprunt" in the framework of the Equipment of Excellence. The quality of the NMR team is worldwide recognized, the TGIR structure guarantees a good access to a wide community, and I strongly supported this proposal.

Claude Berthier
Deputy-director of the LNCMI (UPR3228)
Head of the NMR group at the LNCMI

Sous la tutelle du
cnrs

Le LNCMI est une unité propre (UPR 3228)
du CNRS conventionnée avec :
- INSA Toulouse
- Université Paul Sabatier Toulouse
- Université Joseph Fournier Grenoble

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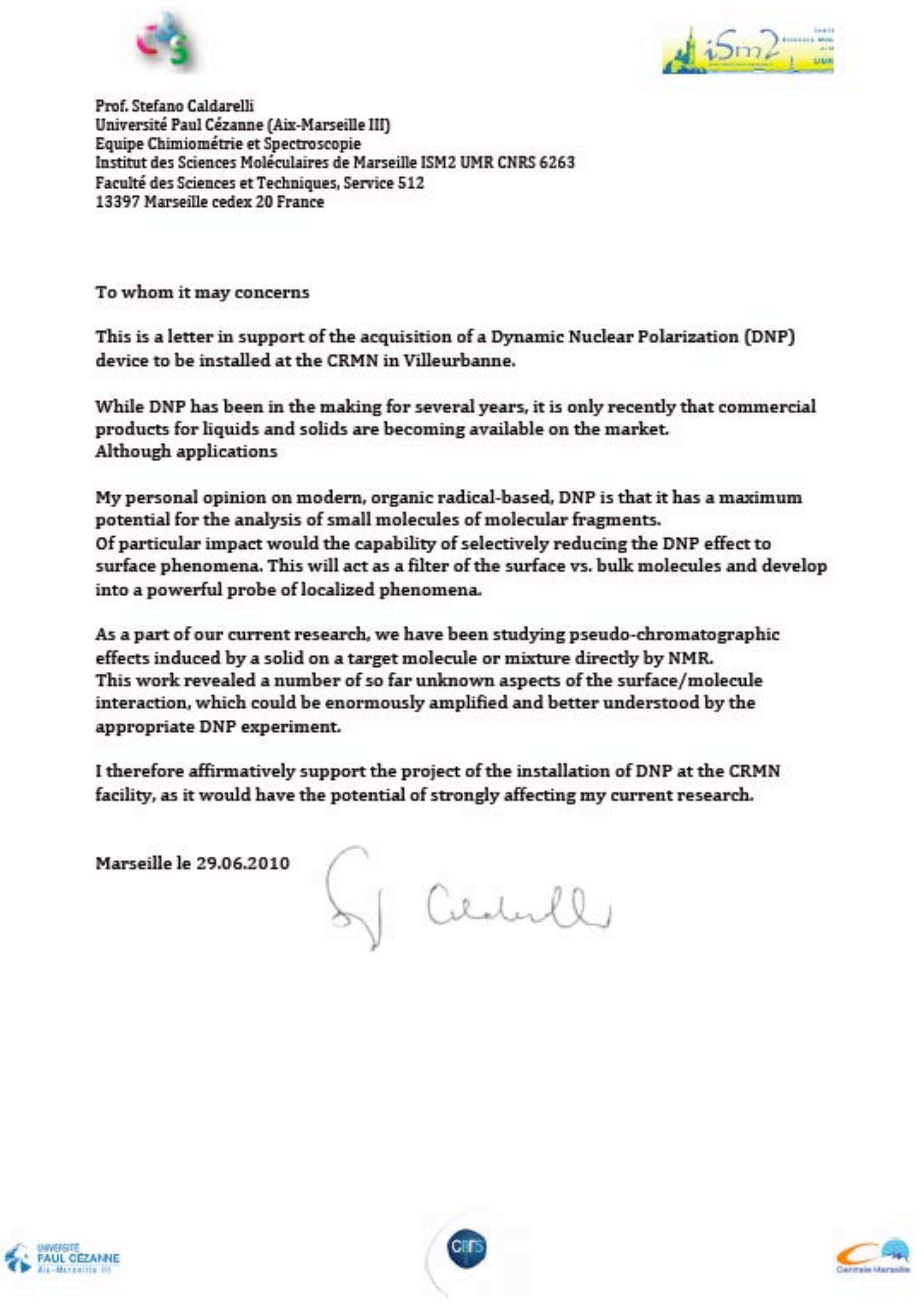


Prof. Stefano Caldarelli
Université Paul Cézanne (Aix-Marseille III)
Equipe Chimiométrie et Spectroscopie
Institut des Sciences Moléculaires de Marseille ISM2 UMR CNRS 6263
Faculté des Sciences et Techniques, Service 512
13397 Marseille cedex 20 France

To whom it may concerns

This is a letter in support of the acquisition of a Dynamic Nuclear Polarization (DNP) device to be installed at the CRMN in Villeurbanne.

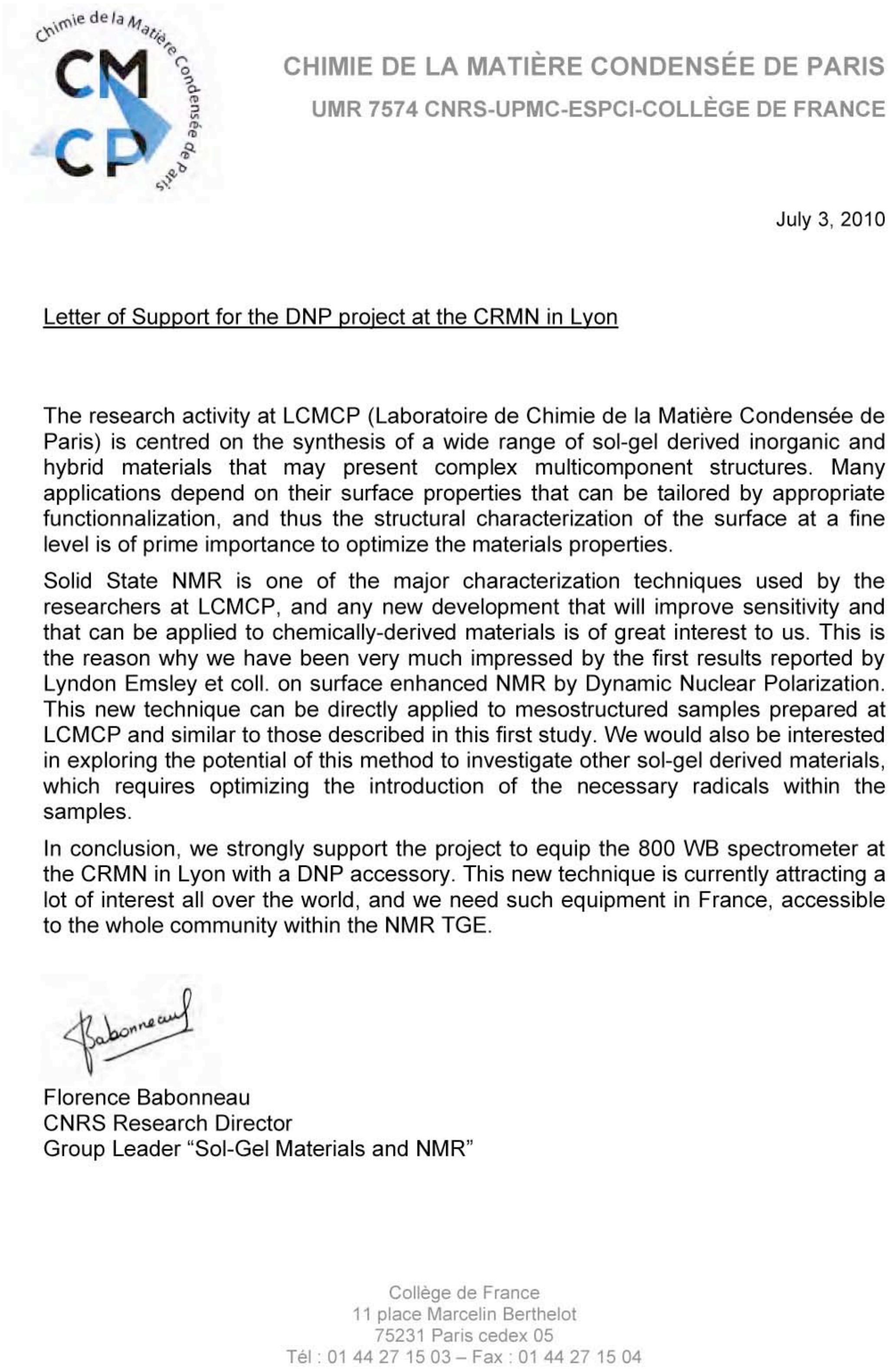
While DNP has been in the making for several years, it is only recently that commercial products for liquids and solids are becoming available on the market.
Although applications

My personal opinion on modern, organic radical-based, DNP is that it has a maximum potential for the analysis of small molecules of molecular fragments.
Of particular impact would the capability of selectively reducing the DNP effect to surface phenomena. This will act as a filter of the surface vs. bulk molecules and develop into a powerful probe of localized phenomena.

As a part of our current research, we have been studying pseudo-chromatographic effects induced by a solid on a target molecule or mixture directly by NMR.
This work revealed a number of so far unknown aspects of the surface/molecule interaction, which could be enormously amplified and better understood by the appropriate DNP experiment.

I therefore affirmatively support the project of the installation of DNP at the CRMN facility, as it would have the potential of strongly affecting my current research.

Marseille le 29.06.2010



Chimie de la Matière Condensée de Paris
CMCP

CHIMIE DE LA MATIÈRE CONDENSÉE DE PARIS
UMR 7574 CNRS-UPMC-ESPCI-COLLÈGE DE FRANCE

July 3, 2010

Letter of Support for the DNP project at the CRMN in Lyon

The research activity at LCMCP (Laboratoire de Chimie de la Matière Condensée de Paris) is centred on the synthesis of a wide range of sol-gel derived inorganic and hybrid materials that may present complex multicomponent structures. Many applications depend on their surface properties that can be tailored by appropriate functionnalization, and thus the structural characterization of the surface at a fine level is of prime importance to optimize the materials properties.

Solid State NMR is one of the major characterization techniques used by the researchers at LCMCP, and any new development that will improve sensitivity and that can be applied to chemically-derived materials is of great interest to us. This is the reason why we have been very much impressed by the first results reported by Lyndon Emsley et coll. on surface enhanced NMR by Dynamic Nuclear Polarization. This new technique can be directly applied to mesostructured samples prepared at LCMCP and similar to those described in this first study. We would also be interested in exploring the potential of this method to investigate other sol-gel derived materials, which requires optimizing the introduction of the necessary radicals within the samples.

In conclusion, we strongly support the project to equip the 800 WB spectrometer at the CRMN in Lyon with a DNP accessory. This new technique is currently attracting a lot of interest all over the world, and we need such equipment in France, accessible to the whole community within the NMR TGE.

Babonneau

Florence Babonneau
CNRS Research Director
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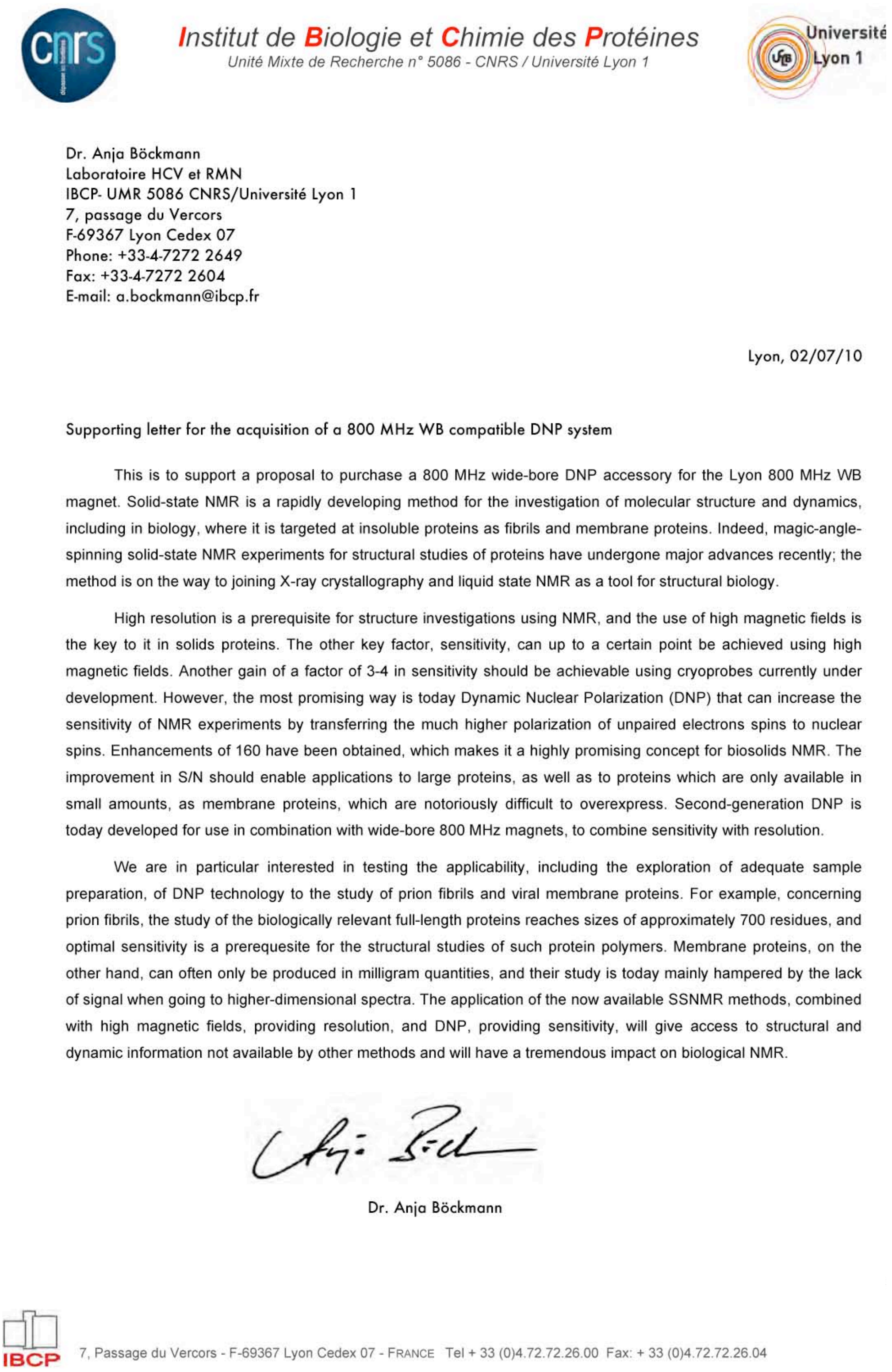

Institut de Biologie et Chimie des Protéines
Unité Mixte de Recherche n° 5086 - CNRS / Université Lyon 1

Université Lyon 1

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Lyon, 02/07/10

Supporting letter for the acquisition of a 800 MHz WB compatible DNP system

This is to support a proposal to purchase a 800 MHz wide-bore DNP accessory for the Lyon 800 MHz WB magnet. Solid-state NMR is a rapidly developing method for the investigation of molecular structure and dynamics, including in biology, where it is targeted at insoluble proteins as fibrils and membrane proteins. Indeed, magic-angle-spinning solid-state NMR experiments for structural studies of proteins have undergone major advances recently; the method is on the way to joining X-ray crystallography and liquid state NMR as a tool for structural biology.

High resolution is a prerequisite for structure investigations using NMR, and the use of high magnetic fields is the key to it in solids proteins. The other key factor, sensitivity, can up to a certain point be achieved using high magnetic fields. Another gain of a factor of 3-4 in sensitivity should be achievable using cryoprobes currently under development. However, the most promising way is today Dynamic Nuclear Polarization (DNP) that can increase the sensitivity of NMR experiments by transferring the much higher polarization of unpaired electrons spins to nuclear spins. Enhancements of 160 have been obtained, which makes it a highly promising concept for biosolids NMR. The improvement in S/N should enable applications to large proteins, as well as to proteins which are only available in small amounts, as membrane proteins, which are notoriously difficult to overexpress. Second-generation DNP is today developed for use in combination with wide-bore 800 MHz magnets, to combine sensitivity with resolution.

We are in particular interested in testing the applicability, including the exploration of adequate sample preparation, of DNP technology to the study of prion fibrils and viral membrane proteins. For example, concerning prion fibrils, the study of the biologically relevant full-length proteins reaches sizes of approximately 700 residues, and optimal sensitivity is a prerequesite for the structural studies of such protein polymers. Membrane proteins, on the other hand, can often only be produced in milligram quantities, and their study is today mainly hampered by the lack of signal when going to higher-dimensional spectra. The application of the now available SSNMR methods, combined with high magnetic fields, providing resolution, and DNP, providing sensitivity, will give access to structural and dynamic information not available by other methods and will have a tremendous impact on biological NMR.

Dr. Anja Böckmann

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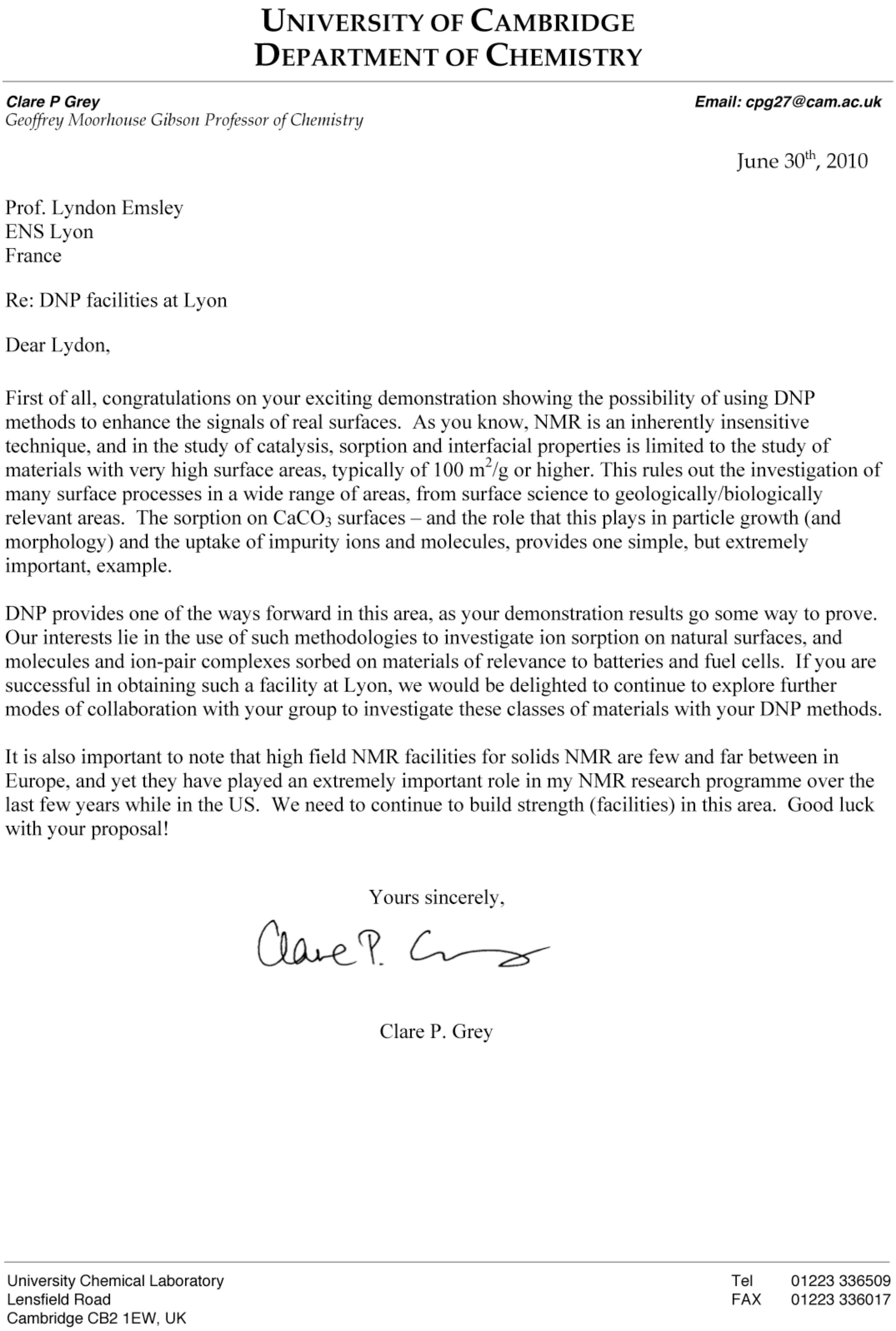

UNIVERSITY OF CAMBRIDGE
DEPARTMENT OF CHEMISTRY

Clare P Grey
Geoffrey Moorhouse Gibson Professor of Chemistry
Email: cpg27@cam.ac.uk

June 30th, 2010

Prof. Lyndon Emsley
ENS Lyon
France

Re: DNP facilities at Lyon

Dear Lydon,

First of all, congratulations on your exciting demonstration showing the possibility of using DNP methods to enhance the signals of real surfaces. As you know, NMR is an inherently insensitive technique, and in the study of catalysis, sorption and interfacial properties is limited to the study of materials with very high surface areas, typically of 100 m^2/g or higher. This rules out the investigation of many surface processes in a wide range of areas, from surface science to geologically/biologically relevant areas. The sorption on $CaCO_3$ surfaces – and the role that this plays in particle growth (and morphology) and the uptake of impurity ions and molecules, provides one simple, but extremely important, example.

DNP provides one of the ways forward in this area, as your demonstration results go some way to prove. Our interests lie in the use of such methodologies to investigate ion sorption on natural surfaces, and molecules and ion-pair complexes sorbed on materials of relevance to batteries and fuel cells. If you are successful in obtaining such a facility at Lyon, we would be delighted to continue to explore further modes of collaboration with your group to investigate these classes of materials with your DNP methods.

It is also important to note that high field NMR facilities for solids NMR are few and far between in Europe, and yet they have played an extremely important role in my NMR research programme over the last few years while in the US. We need to continue to build strength (facilities) in this area. Good luck with your proposal!

Yours sincerely,

Clare P. Grey

Clare P. Grey

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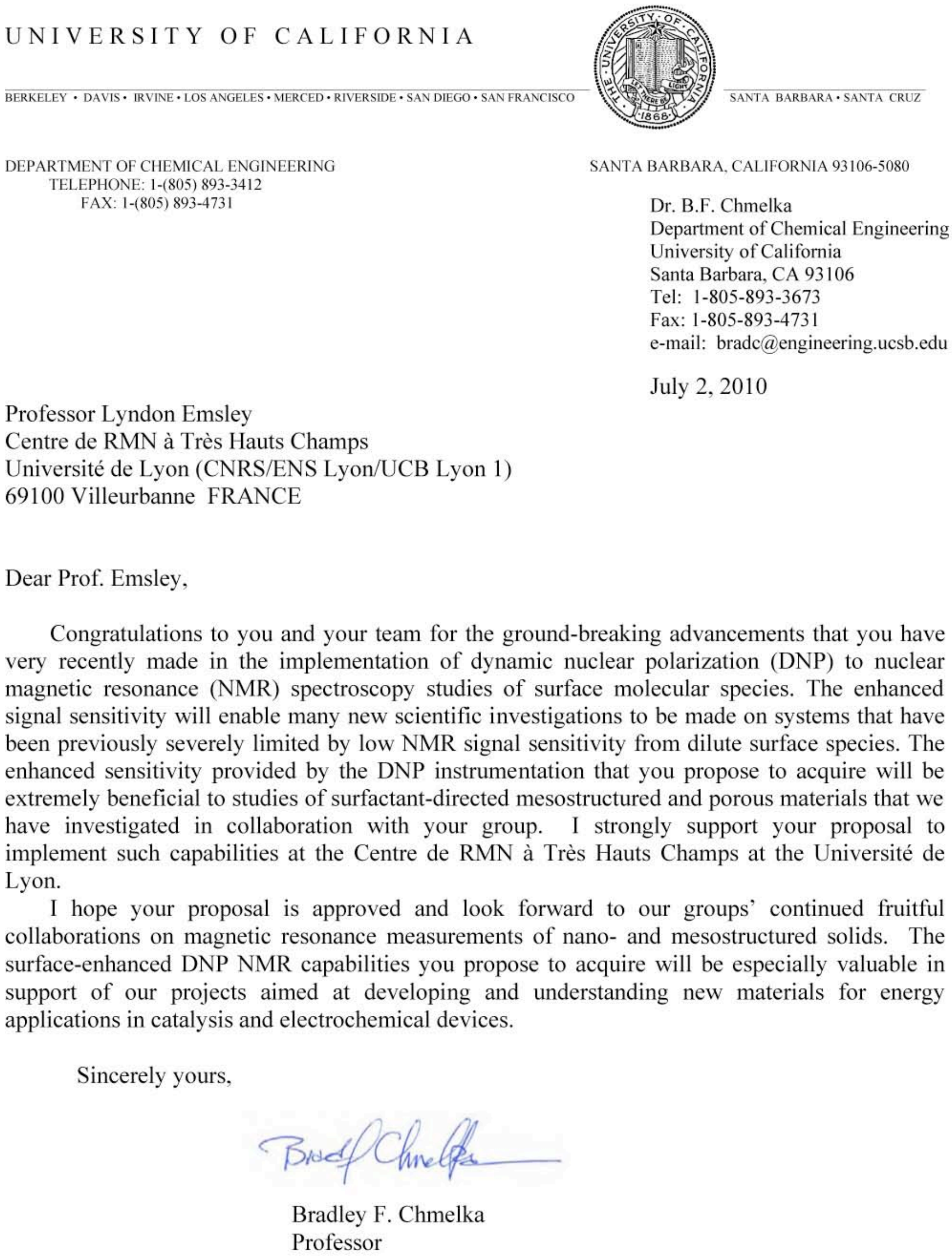

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July 2, 2010

Professor Lyndon Emsley
Centre de RMN à Très Hauts Champs
Université de Lyon (CNRS/ENS Lyon/UCB Lyon 1)
69100 Villeurbanne FRANCE

Dear Prof. Emsley,

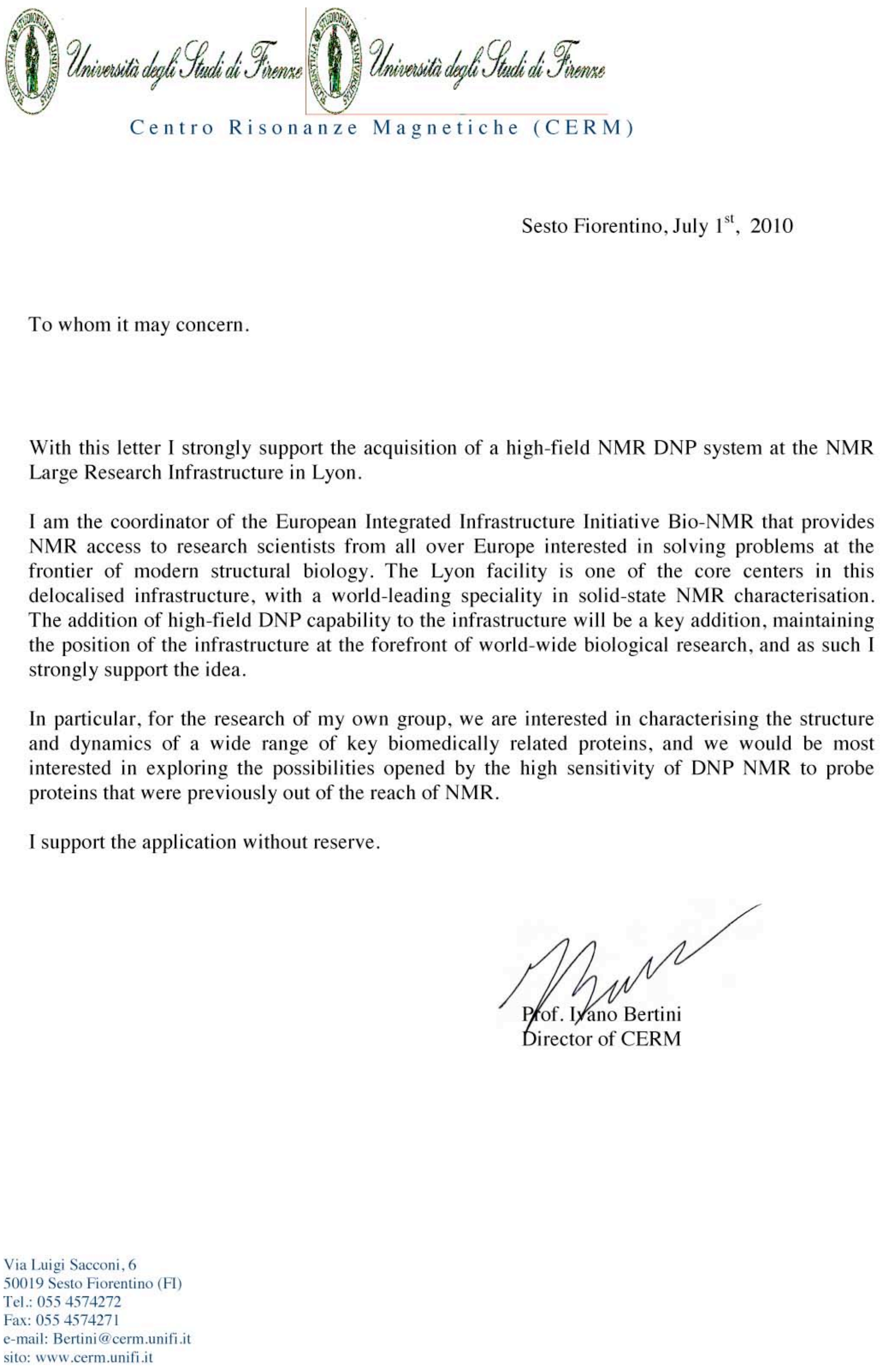
Congratulations to you and your team for the ground-breaking advancements that you have very recently made in the implementation of dynamic nuclear polarization (DNP) to nuclear magnetic resonance (NMR) spectroscopy studies of surface molecular species. The enhanced signal sensitivity will enable many new scientific investigations to be made on systems that have been previously severely limited by low NMR signal sensitivity from dilute surface species. The enhanced sensitivity provided by the DNP instrumentation that you propose to acquire will be extremely beneficial to studies of surfactant-directed mesostructured and porous materials that we have investigated in collaboration with your group. I strongly support your proposal to implement such capabilities at the Centre de RMN à Très Hauts Champs at the Université de Lyon.

I hope your proposal is approved and look forward to our groups' continued fruitful collaborations on magnetic resonance measurements of nano- and mesostructured solids. The surface-enhanced DNP NMR capabilities you propose to acquire will be especially valuable in support of our projects aimed at developing and understanding new materials for energy applications in catalysis and electrochemical devices.

Sincerely yours,

Brad Chmelka

Bradley F. Chmelka
Professor



Università degli Studi di Firenze Università degli Studi di Firenze
Centro Risonanze Magnetiche (CERM)

Sesto Fiorentino, July 1st, 2010

To whom it may concern.

With this letter I strongly support the acquisition of a high-field NMR DNP system at the NMR Large Research Infrastructure in Lyon.

I am the coordinator of the European Integrated Infrastructure Initiative Bio-NMR that provides NMR access to research scientists from all over Europe interested in solving problems at the frontier of modern structural biology. The Lyon facility is one of the core centers in this delocalised infrastructure, with a world-leading speciality in solid-state NMR characterisation. The addition of high-field DNP capability to the infrastructure will be a key addition, maintaining the position of the infrastructure at the forefront of world-wide biological research, and as such I strongly support the idea.

In particular, for the research of my own group, we are interested in characterising the structure and dynamics of a wide range of key biomedically related proteins, and we would be most interested in exploring the possibilities opened by the high sensitivity of DNP NMR to probe proteins that were previously out of the reach of NMR.

I support the application without reserve.

Prof. Ivano Bertini
Director of CERM

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Jean Marie Basset
Director, and Named Professor of Chemical Science
KAUST Catalysis Centre (KCC)
Division of Chemical and Life Sciences & Engineering

كاوست
KAUST

30th June 2010

Object :

Acquisition in Lyon of an equipment in Surface Enhanced NMR spectroscopy using Dynamic Nuclear Polarisation

Dear Professor Emsley

This is to indicate that the Catalysis Laboratory at KAUST, of which I am the director, is particularly interested in the characterization of materials and surfaces. We have a long tradition of collaboration between our Laboratory and the CRMN in Lyon which provides a driving force for new chemistry. This new technique opens up an entirely new perspective for surface characterization at the atomic and molecular level.

The perspectives opened up by the introduction of the idea of Surface Enhanced NMR spectroscopy, using Dynamic Nuclear Polarisation, as invented by the Lyon group, are particularly exciting and will allow us to provide a detailed atomic level characterisation of materials that were previously inaccessible. In particular, I would be interested in exploring the potential of this method in the area of Surface Organometallic Chemistry of early and late transition metal alkyls. It is clear that this new method will increase dramatically the sensitivity in the identification of molecular species on a surface which in turn will allow spectacular progresses in the development of new catalysts or catalytic reactions. For KAUST, the collaboration with the Lyon group will strongly benefit from such equipment.

I therefore most strongly support the proposal to acquire this unique instrumentation for the Lyon facility.

Very best regards.

Jean Marie Basset
Director, and Named Professor of Chemical Science
KAUST Catalysis Centre (KCC)
Division of Chemical and Life Sciences & Engineering

Lyon, le 1 Juillet 2010

Madame Anne Lesage

Centre de RMN à Très Hauts Champs
FRE 3008 CNRS / ENS Lyon
5 rue de la Doua
69100 Villeurbanne, France.

Madame,

Vous nous avez demandé d'appuyer votre demande d'investissement d'un équipement RMN de haute qualité pour étudier la RMN d'espèces situées à la surface de solides pulvérulents.

Cette caractérisation est au cœur de plusieurs de nos activités car Rhodia développe à la fois des solides pour la catalyse et le renfort des polymères, et des polymères qui doivent être renforcés. Dans tous ces cas les méthodes de caractérisation d'interface sont la clef de la compréhension des interactions et donc de l'amélioration des produits.

Aussi, je vous confirme que le groupe Rhodia est fortement intéressé à ce qu'une telle méthode se développe en France où nous avons nos principaux laboratoires pour polymères, charges de renforcement et catalyse hétérogène.

Meilleure salutations

Philippe JOST
Directeur R&D Silice et Catalyse
190 Av THIERS
69457 LYON Cedex 06

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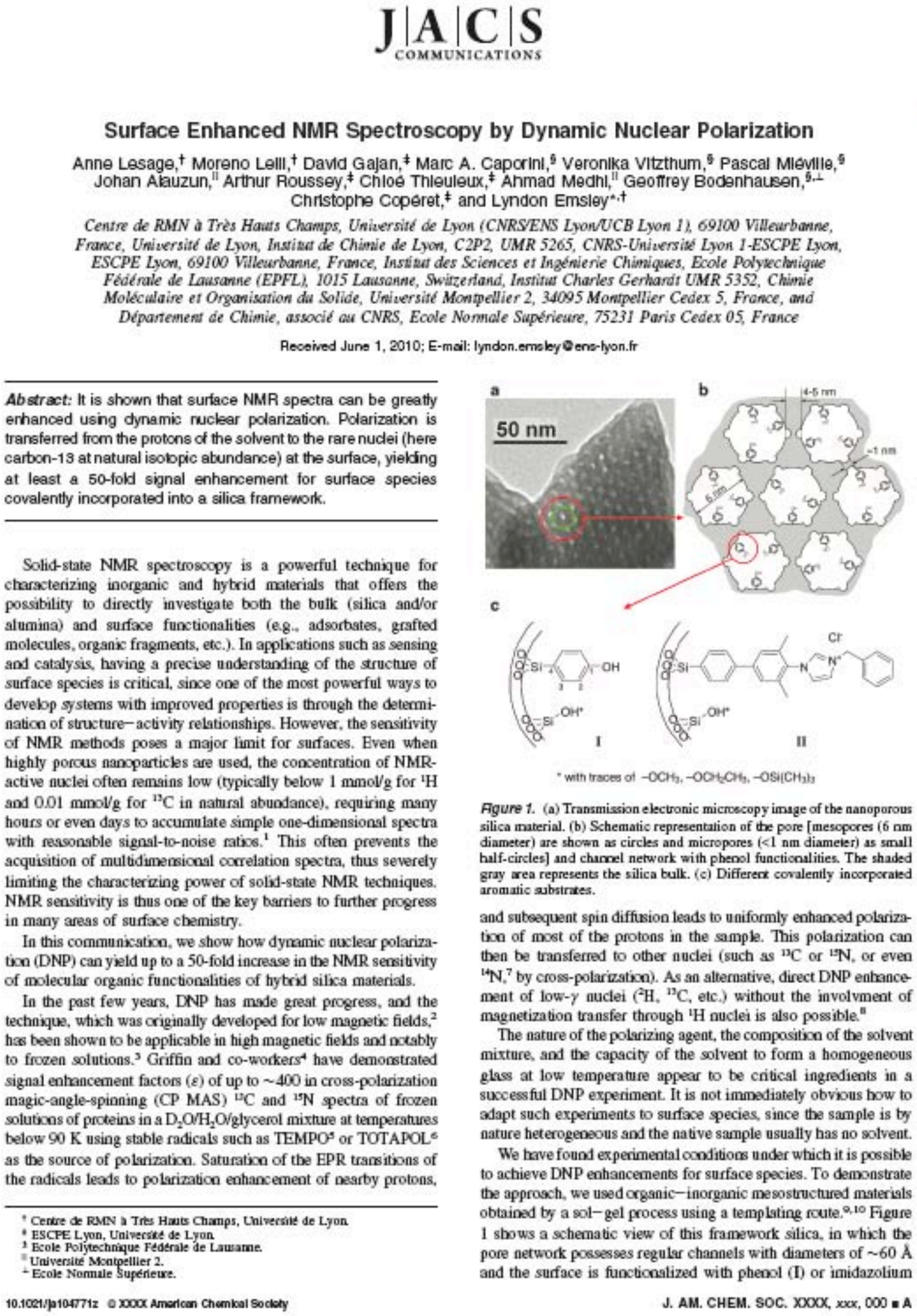

J|A|C|S
COMMUNICATIONS

Surface Enhanced NMR Spectroscopy by Dynamic Nuclear Polarization

Anne Lesage,[†] Moreno Lelli,[†] David Gajan,[‡] Marc A. Caporini,[§] Veronika Vitzthum,[§] Pascal Miéville,[§]
Johan Alauzun,[∥] Arthur Roussey,[‡] Chloé Thieuleux,[‡] Ahmad Mehdi,[∥] Geoffrey Bodenhausen,[§,⊥]
Christophe Copéret,[‡] and Lyndon Emsley[*,†]

Centre de RMN à Très Hauts Champs, Université de Lyon (CNRS/ENS Lyon/UCB Lyon 1), 69100 Villeurbanne, France, Université de Lyon, Institut de Chimie de Lyon, C2P2, UMR 5265, CNRS-Université Lyon 1-ESCPE Lyon, ESCPE Lyon, 69100 Villeurbanne, France, Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne (EPFL), 1015 Lausanne, Switzerland, Institut Charles Gerhardt UMR 5352, Chimie Moléculaire et Organisation du Solide, Université Montpellier 2, 34095 Montpellier Cedex 5, France, and Département de Chimie, associé au CNRS, Ecole Normale Supérieure, 75231 Paris Cedex 05, France

Received June 1, 2010; E-mail: lyndon.emsley@ens-lyon.fr

Abstract: It is shown that surface NMR spectra can be greatly enhanced using dynamic nuclear polarization. Polarization is transferred from the protons of the solvent to the rare nuclei (here carbon-13 at natural isotopic abundance) at the surface, yielding at least a 50-fold signal enhancement for surface species covalently incorporated into a silica framework.

Solid-state NMR spectroscopy is a powerful technique for characterizing inorganic and hybrid materials that offers the possibility to directly investigate both the bulk (silica and/or alumina) and surface functionalities (e.g., adsorbates, grafted molecules, organic fragments, etc.). In applications such as sensing and catalysis, having a precise understanding of the structure of surface species is critical, since one of the most powerful ways to develop systems with improved properties is through the determination of structure–activity relationships. However, the sensitivity of NMR methods poses a major limit for surfaces. Even when highly porous nanoparticles are used, the concentration of NMR-active nuclei often remains low (typically below 1 mmol/g for ^1H and 0.01 mmol/g for ^{13}C in natural abundance), requiring many hours or even days to accumulate simple one-dimensional spectra with reasonable signal-to-noise ratios.[1] This often prevents the acquisition of multidimensional correlation spectra, thus severely limiting the characterizing power of solid-state NMR techniques. NMR sensitivity is thus one of the key barriers to further progress in many areas of surface chemistry.

In this communication, we show how dynamic nuclear polarization (DNP) can yield up to a 50-fold increase in the NMR sensitivity of molecular organic functionalities of hybrid silica materials.

In the past few years, DNP has made great progress, and the technique, which was originally developed for low magnetic fields,[2] has been shown to be applicable in high magnetic fields and notably to frozen solutions.[3] Griffin and co-workers[4] have demonstrated signal enhancement factors (ε) of up to ~400 in cross-polarization magic-angle-spinning (CP MAS) ^{13}C and ^{15}N spectra of frozen solutions of proteins in a D_2O/H_2O/glycerol mixture at temperatures below 90 K using stable radicals such as TEMPO[5] or TOTAPOL[6] as the source of polarization. Saturation of the EPR transitions of the radicals leads to polarization enhancement of nearby protons, and subsequent spin diffusion leads to uniformly enhanced polarization of most of the protons in the sample. This polarization can then be transferred to other nuclei (such as ^{13}C or ^{15}N, or even ^{14}N,[7] by cross-polarization). As an alternative, direct DNP enhancement of low-γ nuclei (^2H, ^{13}C, etc.) without the involvment of magnetization transfer through ^1H nuclei is also possible.[8]

Figure 1. (a) Transmission electronic microscopy image of the nanoporous silica material. (b) Schematic representation of the pore [mesopores (6 nm diameter) are shown as circles and micropores (<1 nm diameter) as small half-circles] and channel network with phenol functionalities. The shaded gray area represents the silica bulk. (c) Different covalently incorporated aromatic substrates.

The nature of the polarizing agent, the composition of the solvent mixture, and the capacity of the solvent to form a homogeneous glass at low temperature appear to be critical ingredients in a successful DNP experiment. It is not immediately obvious how to adapt such experiments to surface species, since the sample is by nature heterogeneous and the native sample usually has no solvent.

We have found experimental conditions under which it is possible to achieve DNP enhancements for surface species. To demonstrate the approach, we used organic–inorganic mesostructured materials obtained by a sol–gel process using a templating route.[9,10] Figure 1 shows a schematic view of this framework silica, in which the pore network possesses regular channels with diameters of ~60 Å and the surface is functionalized with phenol (I) or imidazolium

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[⊥] Ecole Normale Supérieure.

10.1021/ja104771z

(II) units [see the Supporting Information (SI) for details of the syntheses of these two materials].

The sample preparation is key to obtaining DNP enhancements in these materials. Here we carefully wetted the dry samples by incipient wetness impregnation with a solution of the organic radical species before filling the rotor with the wet solid. Notably, the sample volume did not increase significantly in this process, and after wetting it had the aspect of a translucent slush.

Figure 2 shows the DNP enhancements obtained in this way for the surface substrate I shown in Figure 1 using the pulse sequence in Figure 2a. Figure 2b shows the carbon-13 CP MAS spectrum obtained using the TEMPO radical (dissolved in a 90:10 D_2O/H_2O solution) as the polarization agent. Notably, with this solvent combination, ~90% of the surface SiOH groups were replaced by SiOD. Spectra were obtained with and without microwave irradiation. With 30 mM TEMPO, a direct enhancement of $\varepsilon_H = 18$ was observed in the proton spectrum of the solvent (see the SI). The observed ^{13}C enhancement, $\varepsilon_C \geq 17$, demonstrates that the polarization can be efficiently transferred from the ^1H spins of the solvent to those of the surface organic functionality. The ^{13}C spectra of Figure 2b were obtained using only 2048 scans in less than 35 min. Experiments done with variable polarization-buildup times indicated that the optimal signal-to-noise ratio per unit time is obtained when the recycle delay is ~1 s. Greater polarization per scan is obtained with longer delays, but the increased polarization does not compensate for the longer delay required in determining the optimum signal-to-noise ratio per unit time. Proton T_1 measurements (with microwaves on) clearly indicated a fast-relaxing component with a T_1 value of ~900 ms that is related to the solvent protons and a second minor component with a much longer T_1 of ~8 s that is possibly related to ^1H spins in the silica pores that are not in contact with the radical and thus do not benefit from paramagnetic relaxation enhancement[11] (these could be in the micropores, which are too small for TEMPO to enter). This made it possible to combine sizable DNP enhancements with unusually short recycle delays, opening the way to viable multiscan experiments. Notably, we observed DNP enhancements without adding glycerol[4] to the water solution to form a homogeneous glass. It is possible that disordered phases are formed directly upon freezing water in mesoporous materials.[12] This important point will be the subject of further investigations.

Figure 2c shows the ^1H DNP enhancement (ε_H) and the ^{13}C CP MAS peak integral as a function of TEMPO concentration. While ε_H increased with the radical concentration for all concentrations measured here, the ^{13}C spectrum reached a maximum enhancement at ~30 mM TEMPO. Higher radical concentrations provoked increased paramagnetic relaxation of both the ^1H and ^{13}C spins,[4a,6] reducing the efficiency of CP transfer to the species on the silica surface. Higher radical concentrations also led to broadening in the ^{13}C spectrum.[4a] Broadening was minor at the optimum carbon-13 conditions found here (the 5−8 ppm linewidths observed here are typical for these kinds of materials).

Griffin and co-workers have shown that the biradical TOTAPOL can produce larger DNP enhancements than single radicals because of a more efficient transfer mechanism.[13,6] Indeed, when we used TOTAPOL as the source of polarization instead of TEMPO, we found that merely 25 mM TOTAPOL yielded $\varepsilon_H = 25$. The enhancement was even higher in the ^{13}C CP MAS spectrum, being a factor of 3.2 greater than with 30 mM TEMPO, yielding an estimated ^{13}C enhancement of $\varepsilon_C \geq 56$ (carbon-13 enhancements were estimated as described in the SI). Obtaining a carbon-13 spectrum with the same signal-to-noise ratio without DNP would take at least 70 days!

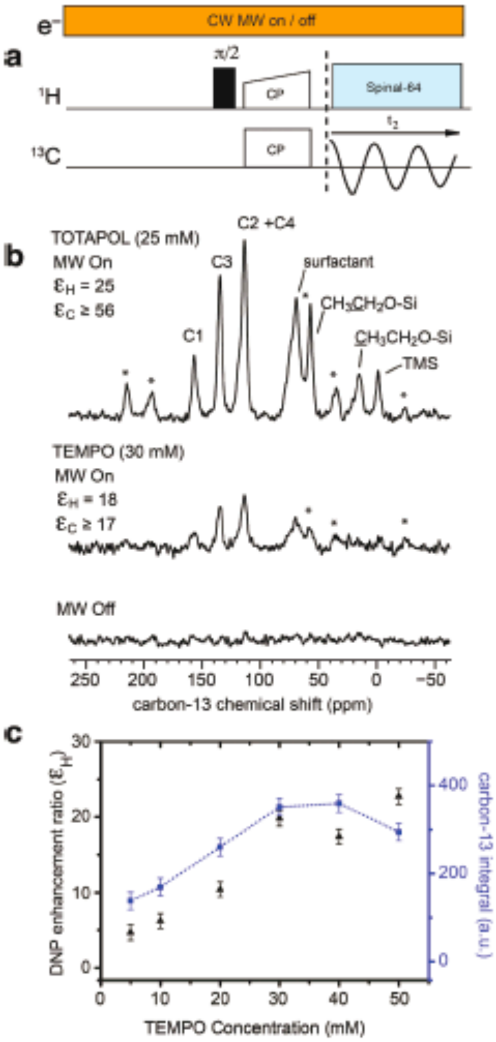

Figure 2. (a) Pulse sequence used for 1D CP MAS NMR spectroscopy. The microwave (MW) irradiation was switched on or off continuously. (b) Carbon-13 CP MAS spectra of I with (top and middle) and without (bottom) MW irradiation at 263 GHz to induce DNP. All of the spectra were recorded using 2048 scans with an interval of 1 s between scans. The figures compare the best enhancements observed using TEMPO and TOTAPOL radicals ($T \approx 105$ K, $B_0 = 9.4$ T, $\omega_H/2\pi = 400$ MHz, $\omega_C/2\pi = 100$ MHz, $\omega_{rot}/2\pi = 8.0$ kHz). It should be noted that significant DNP enhancement of the alkyl moiety of the surface ethoxy groups was also observed. (c) Experimental ^1H DNP enhancement (ε_H, black ▲) and integrals of the ^{13}C peak at 115 ppm (blue ■) as a function of the TEMPO concentration.

In order to extend the method to systems that may be sensitive to water, we investigated the use of aprotic solvents. When I wetted with a solution of 30 mM TEMPO in 90:10 toluene-d_8/toluene was used, the enhancement was lower than in water but still sizable ($\varepsilon_H \approx \varepsilon_C = 10$). Further experiments would be required to fully optimize the solvent systems, with room for improvement for both aqueous and nonaqueous solvents.

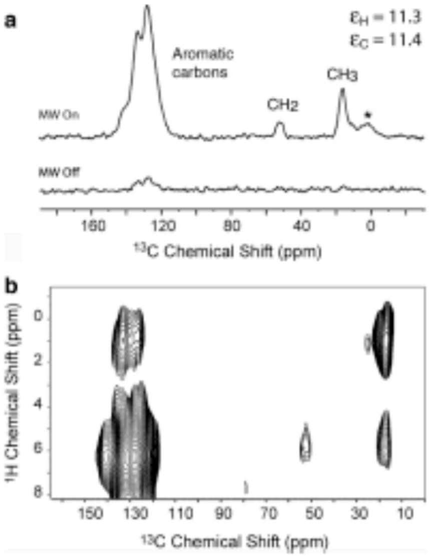

Figure 3. (a) Carbon-13 CP MAS spectra of II with (top) and without (bottom) MW irradiation at 263 GHz to induce DNP. All of the spectra were recorded using 2048 scans with an interval of 1.5 s between scans. The sample was wetted with 30 mM TEMPO in 90:10 D_2O/H_2O, $T \approx 105$ K, $B_0 = 9.4$ T, $\omega_H/2\pi = 400$ MHz, $\omega_C/2\pi = 100$ MHz, $\omega_{rot}/2\pi = 12.5$ kHz. The star indicates a spinning sideband. (b) Contour plot of a two-dimensional $^1H-^{13}C$ spectrum of II recorded with DNP using MW irradiation at 263 GHz. A total of 72 t_1 increments of 64 μs with 128 scans each were recorded. The overall acquisition times in t_1 and t_2 were 2.3 and 20 ms, respectively. The cross-polarization contact time was 1 ms, and the polarization-buildup interval was 1.5 s. The total experiment time was 3.8 h. SPINAL-64[14] heteronuclear decoupling was applied during t_2 ($\omega_1/2\pi = 80$ kHz, $\tau_c = 6$ μs). During t_1, eDUMBO-1_{22}[15] homonuclear decoupling was applied with an rf amplitude of $\omega_1^H/2\pi = 100$ kHz. Quadrature detection was achieved using the States-TPPI scheme[16] by incrementing the phase of the ^{1}H spin-lock pulse of the CP step. A scaling factor of 0.56 was applied to correct the ^{1}H chemical shift scale.[15]

The surface sensitivity enhancements obtained using DNP here open the way to the broad use of multidimensional correlation spectroscopy. Clearly, such spectra are required for detailed characterization of surface species, but they are not feasible without DNP in the systems considered here. Figure 3b shows a contour plot of the 2D $^1H-^{13}C$ correlation spectra acquired on the more complex imidazolium species II (Figure 1). The DNP enhancement was obtained here using a sample wetted with 30 mM TEMPO in 90:10 D_2O/H_2O (it should be noted that the spectrum was obtained with a sample spinning frequency of $\omega_{rot}/2\pi = 12.5$ kHz, rather than 8 kHz as used in Figure 2, which may explain the slightly lower enhancement factor). This spectrum was acquired using 128 scans for each of 72 t_1 increments, with a 1.5 s polarization-buildup delay, yielding a total experimental time of less than 4 h. It allows the detailed characterization of the material (including the assignment of the methylene resonances at 50 ppm). Acquisition of this kind of spectrum at natural isotopic abundance is inconceivable without polarization enhancement.

In conclusion, we have shown that surface enhanced NMR spectra can be obtained using DNP. Polarization is transferred from the protons of the solvent to the rare nuclei (here carbon-13 at natural isotopic abundance) at the surface, yielding at least a 50-fold signal enhancement. The implications of this new method for a broad range of surface science problems are enormous. This approach is in principle general and could be applied even to the investigation of adsorbed substrates or, by finding appropriate experimental conditions (solvent, radical concentration, etc.), to the investigation of surface catalytic processes.

Acknowledgment. We thank Mélanie Rosay, Frank Engelke, Fabien Aussenac, and Werner Maas of Bruker Biospin for providing support for the DNP systems. D.G. thanks the "Cluster de Recherche Chimie de la Région Rhône-Alpes". This work was supported in part by the Swiss National Science Foundation (to support M.A.C.), the Swiss Commission pour la Technologie et l'Innovation (to support V.V. and P.M.), and the Agence Nationale de la Recherche (ANR-08-BLAN-0151-01).

Supporting Information Available: Sample preparation, experimental methods, and proton NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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