PhD Research Proposal Form
China Scholarship Council (CSC)
2022

FIELD: Physical Chemistry

Thesis subject title:

Methods and Instrumentation (Rf/Microwave) Development for DNP NMR Applications on Metal-Organic Frameworks (MOFs)

Name of the French doctoral school/Ecole doctorale: L'école doctorale de Chimie Physique et Chimie Analytique de Paris Centre - ED 388

Name of the Research team/Equipe de recherche: Laboratoire des Biomolecules (LBM, UMR 7203)
Website: **https://www.ens.fr/en/laboratoire/laboratoire-des-biomolecules-umr-7203**

Name of the Supervisor/Directeur de thèse: Dr. Philippe Pelupessy
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PhD co-director: Prof. Kong Ooi Tan
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Lab Language/ Langue de travail: English

Research Proposal Abstract/Présentation du sujet:

Abstract

NMR spectroscopy is a non-invasive technique that can provide atomic-resolution structures of inorganic materials, e.g., metal-organic frameworks (MOFs). However, the technique is hampered by poor sensitivity. We present pioneering approaches that will overcome this drawback by exploiting dynamic nuclear polarization (DNP), a powerful sensitivity enhancement method that significantly reduces the measurement time and cost. For instance, a moderate **enhancement factor of 100** will enable a **year-long** nuclear magnetic resonance (NMR) experiment to be completed in **less than an hour** with DNP for the same quality spectra. This PhD work will focus on developing the methods in applying DNP to shed light on structures of functional MOF targeted for industrial applications, thereby generating an immense economic impact and benefits to the society.

Full Proposal

DNP is a sensitivity enhancement technique used to boost NMR signals by transferring polarization from the polarizing agents, usually organic radicals with unpaired electrons, to nuclei of interest via microwave irradiation.[1] The advantage of NMR over other spectroscopic methods is that it provides atomic-resolution structural details and is non-invasive. However, NMR spectroscopy has, in general, an intrinsic poor sensitivity due to the low polarization of the nuclear spins under ambient conditions. This issue can be circumvented by DNP, which allows a significant reduction in experimental time and cost. For instance, **Figure 1** shows a ^{13}C spectrum of urea with a DNP signal enhancement of ε ~400.[2] This means that the DNP-enhanced experiment performed in an hour would have taken an unrealistic measurement time of ~ 18 years without DNP to obtain a similar spectrum. Due to the recognition of the vast potential of DNP, more than 50 commercial and home-built DNP-NMR spectrometers have been installed worldwide to explore various NMR applications. Some successful DNP applications in solid-state NMR (ssNMR) include ribosomes, amyloid fibrils, membrane proteins, pharmaceutical products, and porous materials. DNP has become the method of choice to study natural abundance samples without expensive isotope labelling of NMR-active nuclei such as ^{13}C or ^{17}O. This is the case for MOFs, and hence we have chosen DNP as an indispensable tool to study MOFs.

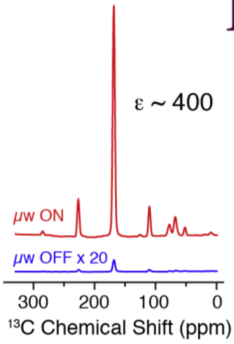

Figure 1. The ^{13}C spectrum of urea in 'DNP juice' doped with AMUPOL, a commonly used DNP biradical, shows an enhancement of ~ 400 at 380 MHz/ 250 GHz and 75 K.[2]

Zirconium-based MOFs (Zr-MOF) are materials that possess favorable features such as excellent thermal, chemical, and mechanical stability, making them well-suited for many applications, including CO_2 gas capture/separation and catalytic degradation of toxic agents. By modifying the length of the organic linker or doping with other metal ions, the Zr-MOF family can be expanded for broader applications and industrial uses. Their functionalities heavily depend on how the MOFs are structurally constructed from the metal ions and the organic linkers. Interestingly, the presence of defects in MOFs can compromise their performances or present new opportunities. There is, therefore, immense interest in obtaining the structural information about Zr-MOF so that their performances can be optimized by suppressing or promoting the defects, i.e., defect engineering. Specifically, Prof. Xueqian Kong (Zhejiang University) and our laboratory (LBM, UMR 7203) are interested in probing the missing ligand defects in Zr-MOFs.[3] Besides that, Dr. Georges Mouchaham from the Porous Materials Institute of Paris (IMAP, UMR 8004) is interested in characterizing the Zr-MOFs grafted with active metal centers (e.g. Cu), which was shown to yield efficient hydrogenation of CO_2 to alcohol groups.[4,5] Nevertheless, ^{91}Zr and ^{65}Cu are low-gamma nuclei with **inferior NMR sensitivity** due to low gyromagnetic ratio, low natural abundance, and broad linewidths. Although DNP can partially mitigate the sensitivity issue, the current DNP methodology was developed/optimized primarily for hyperpolarizing common nuclei such as ^{1}H under magic-angle spinning (MAS) conditions, which is less suited for directly polarizing low-gamma nuclei at static. This was demonstrated in literature where the DNP enhancement factor is < 1 % of the theoretical maximum.[6] Thus, this PhD proposal aims to push the current limit by developing new DNP methods and tools for directly polarizing low-gamma nuclei.

We aim to achieve this objective by (1) building an EPR/pulsed DNP spectrometer at 9.4 T (**Fig. 2**),[7] and (2) exploring novel DNP polarizing agents with the existing 18.8 T/ 527 GHz gyrotron DNP spectrometer in our laboratory.[8] **Objective 1** can be achieved by upgrading our laboratory's 9.4 T/400 MHz dissolution DNP setup with a pulsed microwave bridge and a DNP probe. This equipment (Fig. 1) will be co-financed by a regional grant (RESPORE http://www.respore.fr) awarded for a collaborative project between LBM and IMAP. As the awarded grant (50 k€) was designated for purchasing new equipment, this PhD proposal will supplement the personnel needed for these projects. The PhD

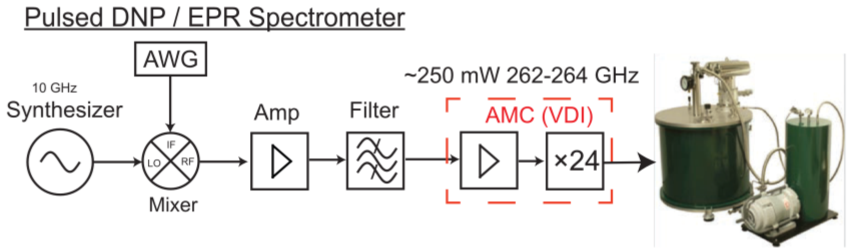

Figure 2. Schematic diagram of a pulsed DNP spectrometer that will be assembled in this proposal.

candidate is expected to build a broadband and efficient double-channel DNP probe equipped with improved microwave waveguides and a resonator.[9] Following that, the 263 GHz pulsed microwave device will generate chirped microwave pulses for adiabatic solid effect (ASE) DNP—a promising pulsed DNP sequence demonstrated to yield ε ~388.[10] Besides, it was reported in the literature that some radicals and solvents might react with the surfaces of MOFs and present misleading results.[11,12] Hence, the PhD student is expected to perform electron paramagnetic resonance (EPR) experiments to ensure chemical compatibility between the radicals and the custom-made Zr-MOFs from IMAP and Zhejiang University.

Despite a lower DNP performance, it is favorable to study the quadrupolar nuclei at higher magnetic fields ($\geq$ 18.8 T) due to higher resolutions of the NMR central transitions. To improve DNP efficiency, we will collaborate with Prof. Yangping Liu at Tianjin Medical University to explore and develop better polarizing agents for direct polarization of low-gamma nuclei. The PhD candidate will characterize these radicals and optimize the DNP conditions (**Objective 2**) using our lab's 18.8 T / 527 GHz DNP spectrometer.[8]

We emphasize that our proposed pulsed DNP instrument and the hyperpolarization technique are <u>general setups that are well suited to study *any* nuclei that suffer sensitivity issues at static conditions.</u> For instance, ^{195}Pt, $^{47/49}$Ti, ^{207}Pb, ^{35}Cl, ^{119}Sn, etc., are nuclei that have both ultrawide NMR linewidths and poor sensitivities. We foresee that this novel equipment will improve the design of MOFs not only for catalytic conversion of CO_2 but also for other industrial applications, including drug delivery, heterogeneous catalysis, CO_2 gas capture, etc.

<u>Strategic collaboration between the French and Chinese research laboratories</u>

The PhD project spans 48 months, and it involves a strategic collaboration between two French and two Chinese laboratories:

- Laboratoire des Biomolecules (LBM, UMR 7203) at ENS Ulm. Expertise: DNP hyperpolarization, instrumentation development, and solid-state NMR.
- The Porous Materials Institute of Paris (IMAP, UMR 8004) at ENS Ulm (https://www.chimie.ens.fr/recherche/laboratoire-imap/imap/). Expertise: synthesis and characterization of MOFs.
- Prof. Xueqian Kong's lab in Zhejiang University, China (http://www.supermagnetic.cn). Expertise: solid-state NMR spectroscopy in MOFs.
- Prof. Yangping Liu's lab in Tianjin Medical University, China. Expertise: Synthesis of DNP polarizing agents.

These four laboratories have complementary expertise and knowledge essential for completing this PhD project, which is highly cross-disciplinary and potentially novel. Moreover, this synergic collaboration will promote international collaborations between French and Chinese institutions.

<u>Previous/ongoing collaborations with the Chinese laboratories</u>

The co-director of this PhD proposal, Prof. Kong Ooi Tan, has been working closely with the other three laboratories (on various projects) since his appointment at ENS last year. In particular, the LBM team has been using the new DNP radicals developed by Prof. Yangping Liu for NMR applications on proteins, which resulted in a world-record DNP performance (unpublished results). Besides, LBM has been developing a new theoretical description of DNP mechanisms with Prof. Xueqian Kong. The manuscripts for both works are in preparation.

<u>Other cofounding/supports</u>

A regional grant (50 k€ from RESPORE, convention Régionale:20002707) was awarded to purchase the new equipment needed for this PhD project. Additionally, the consumables required in this project can be co-financed by the ANR grant (acronym: HFPulsedDNP) awarded to Prof. Kong Ooi Tan.

References:

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Type of PhD :

1.Full PhD

- Joint PhD/cotutelle (leading to a double diploma) : NO
- Regular PhD (leading to a single French diploma) : YES

2. Visiting PhD (students enrolled at a Chinese institution who come to ENS for mobility period) : NO

3. Provisional duration and timetable of the PhD student
The PhD student will spend a total of 48 months (Sept 2022- Aug 2026) at ENS Ulm, France.

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