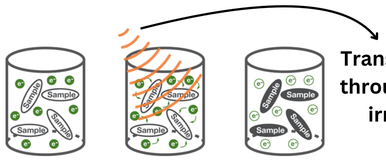
Functionalized Materials as Polarizing Agents for Dynamic Nuclear Polarization in Liquids

Daphne Broerman,[1] Kiera Powers,[1,2] Tomas Orlando[1]

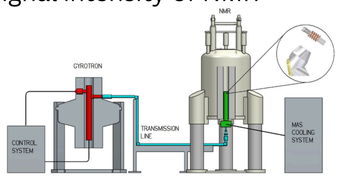
1. National High Magnetic Field Laboratory and Florida State University, Tallahassee, Florida, USA
2. Department of Chemistry and Biochemistry, Florida State University, Tallahassee, Florida, USA

Introduction

- Nuclear Magnetic Resonance (NMR) spectroscopy is used to determine the molecular structure, purity, and dynamics of chemical compounds; it has a low sensitivity and low signal intensity
- Dynamic Nuclear Polarization (DNP) describes a method of transferring the spin polarization of unpaired electrons on organic radicals to neighboring nuclear spins through the usage of microwave irradiation
- DNP methods have been developed to help boost the signal intensity of NMR



Transfer of spin polarization through usage of microwave irradiation during DNP

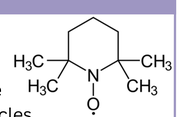


- Our work aims to develop hyperpolarized NMR of mixed-phase materials using functionalized silica materials containing a radical covalantly bonded to the surface that is able to locally hyperpolarize the liquid in the proximity of the surface of the material

Materials

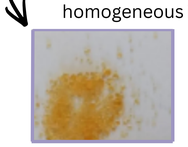
Materials:

- TEMPO Radical
- Commerical Silica Target Molecule
  - SiO_2 Beads and SiO_2 Nanoparticles
- Chloroform ($CHCl_3$) Solvent
- Toluene ($C_6H_5CH_3$) Solvent
- Carbon Tetrachloride (CCl_4) Solvent
- Methanol (CH_3OH) Solvent

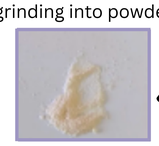


TEMPO Radical

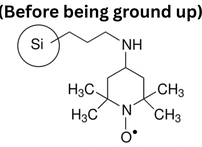
- SiTM has impurities due to the presence of free TEMPO in the molecule that we can get rid of by washing
  - Before washing we can make the beads homogeneous in size by grinding into powder



SiTM Beads (Before being ground up)



SiTM Powder (After being ground up)



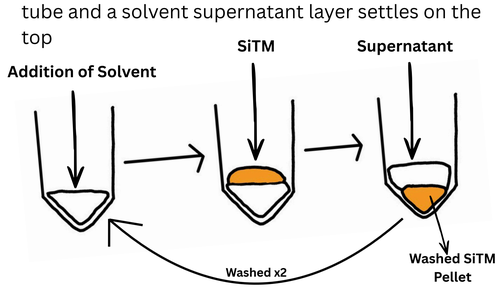
TEMPO Radical Bound to Commerical Silica Target Molecule

TEMPO (Soluble in Organic Solvents)

Sample Washing Steps

Steps:

1. An empty microcentrifuge tube is selected and solvent is added
2. SiTM bead is ground up into a fine powder using a mortar and pestle to release the radical from the surface of the silica molecule and added to the microcentrifuge tube on top of solvent layer creating a distinct non-homogeneous distribution of SiTM in solvent
3. The microcentrifuge tube is added to a balanced centrifuge
4. The sample is spun in the centrifuge for five minutes
5. After removal from the centrifuge, a distinct layer of washed SiTM pellet remains on the bottom of the tube and a solvent supernatant layer settles on the top



Why Choose EPR?

- Electron Paramagnetic Resonance (EPR) is a spectroscopic technique that can be used to detect unpaired electrons (radicals) by putting a sample inside a magnetic field and applying microwave radiation, inducing transition states between energy states of the radicals
- Focuses on electron spin rather than nuclear spin, which enables the detection of much lower concentrations of paramagnetic species
- EPR is the only technique that is able to directly detect radicals
- EPR can determine the concentration of radical in a sample

EPR Characterization

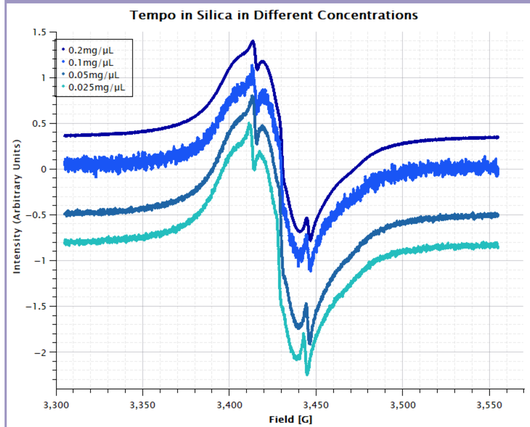


Fig. 1 Normalized EPR spectra of SiTM powder (washed twice) in chloroform with concentrations of 0.2, 0.1, 0.05, and 0.025mg/µL

- Sharp components of EPR spectra indicates high mobility molecules.
  - This is ascribed to free TEMPO in solution not covalantly bound to the silica
  - Solubility of the compound depends on the polarity of the solvent
- Broad components of EPR spectra indicate low mobility molecules
  - these are TEMPO radicals covalently bound to the silica
- The shape of EPR spectra is not affected by concentration of TEMPO
  - Fundamental magnetic environment of each individual radical is identical

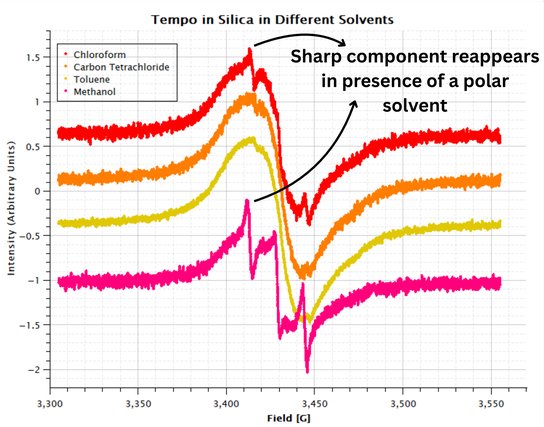
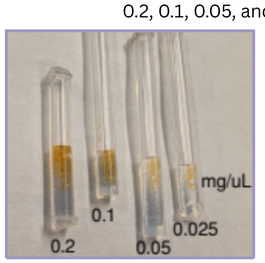
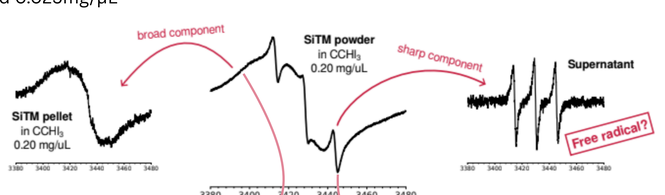


Fig. 2 Normalized EPR spectra of SiTM powder (washed twice) dispersed in different solvents (chloroform, carbon tetrachloride, toluene, methanol), with concentration 0.1mg/µL.



Non-homogeneous distribution of SiTM in chloroform



Occurs when radical is restricted in motion; can occur when radical is in high concentrations; indicates heterogeneous conditions

Occurs when radical moves freely within a solution with a polar solvent such as chloroform, water, or methanol

Results and Outlook

- These experiments have given us an effective preparation protocol that we can utilize in future DNP/microwave experiments
- Silica is a promising substrate for DNP in heterogeneous systems that can be further explored in future experiments

References

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Acknowledgements

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