

Screening DNP Agents with the EMXnano Benchtop EPR Spectrometer

Correct concentration of DNP polarizing agents is crucial to the success of a DNP experiment. Samples can be pre-screened before DNP experiments using the patented SpinCount module, even in the MAS rotor. Relaxation times are critical for DNP efficiency therefore $P_{1/2}$ measurements at low temperature to estimate the DNP efficiencies of new polarization agents are invaluable. Another characteristic of importance in DNP measurements is the electron-electron dipolar coupling that is easily measured from solution and frozen solution EPR spectra.

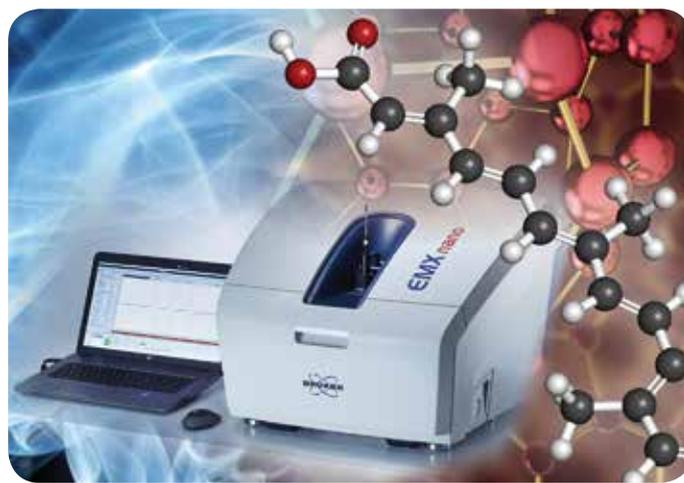
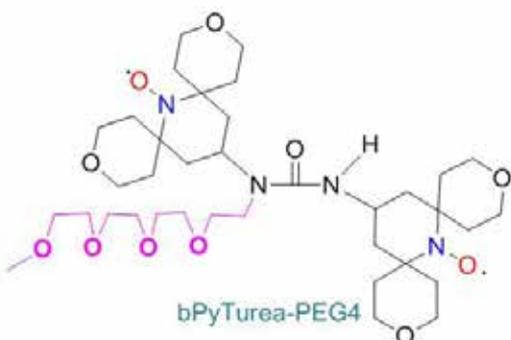
Introduction

DNP (Dynamic Nuclear Polarization) can enhance the sensitivity of solid state NMR experiments by factors of up to 80. The key to success in a DNP experiment is the paramagnetic enhancement agent. These DNP agents are typically dinitroxides. Nitroxides are stable radicals in which the unpaired electron is localized on an NO group in the molecule.

Challenge

Properties of these DNP agents that are important for DNP efficiency and need to be measured are:

- Agent concentration
- Dipolar coupling between the two nitroxides
- Exchange interaction between the nitroxides
- Electronic relaxation times of the nitroxides

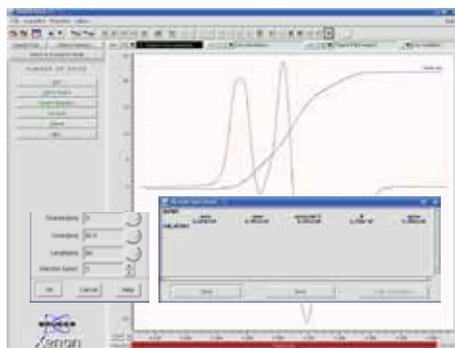


Solution

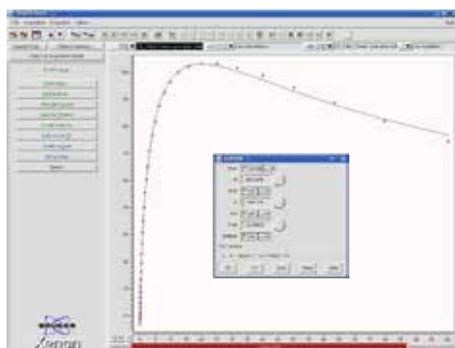
These paramagnetic agents and their properties can be measured via EPR with the EMXnano. SpinCount facilitates quick and easy screening of DNP agents, often even for samples already loaded in an NMR rotor. Exchange interactions can be screened by room temperature measurements. Dipolar couplings can be estimated from analysis of low temperature measurements. Relaxation times can be estimated and compared from microwave power saturation characterized by the $P_{1/2}$ parameter at the same temperature as the solid-state DNP experiments.

Equipment

Built with a new generation of magnet system and a highly efficient microwave resonator, the EMXnano gives consistently accurate results and superior sensitivity. The EMXnano spectrometer enables researchers and students with limited EPR experience to use the power of EPR spectroscopy to characterize the DNP agents and their characteristics that are important for DNP enhancement. A full workflow for measuring, analyzing and quantifying DNP agents guides you through the entire procedure.

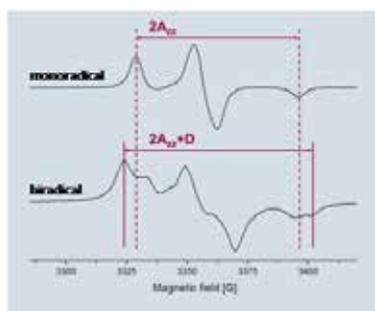
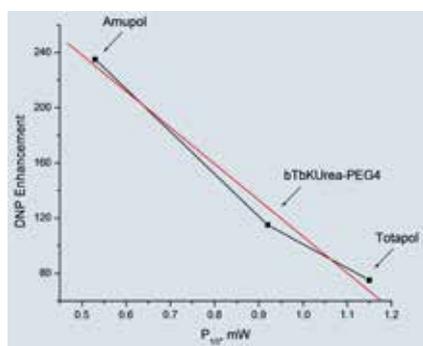


- Using SpinCount the Totapol concentration can be quickly and easily determined from the EPR spectrum.



- By fitting the microwave power saturation data the $P_{1/2}$ value can be determined providing insight into the electron relaxation times.
- For the DNP agent Amupol the 2D Power vs Field data the $P_{1/2}$ was determined to be 0.53 mW.

- The $P_{1/2}$ value determined by EPR measurements at 110K correlates well with the DNP enhancements observed.



- The low temperature EPR spectra of TEMPOL (monoradical) and bTbK (biradical). Analysis of the biradical features allows the determination of the electron-electron dipolar coupling.

Key Features include:

- Easy-to-use software
- SpinCount module to quantify the DNP agent concentration
- 2D EPR field vs. microwave power experiments to estimate and compare electron relaxation times.
- Fitting routines to obtain $P_{1/2}$ values.
- Variable temperature accessory for measurements from 100 K to 300 K.

References

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- Alexandre Zagdoun, Gilles Casano, Olivier Ouari, Giuseppe Lapadula, Aaron J. Rossini, Moreno Lelli, Mathieu Baffert, David Gajan, Laurent Veyre, Werner E. Maas, Melanie Rosay, Ralph T. Weber, Chloé Thieuleux, Christophe Coperet, Anne Lesage, Paul Tordo, and Lyndon Emsley, *J. Am. Chem. Soc.*, Volume 134 (4), 2284–2291 (2012) . A Slowly Relaxing Rigid Biradical for Efficient Dynamic Nuclear Polarization Surface Enhanced NMR Spectroscopy: Expedient Characterization of Functional Group Manipulation in Hybrid Materials