Room-temperature hyperpolarization of nuclear spins in bulk[†]

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Dynamic Nuclear Polarization (DNP) is a means of transferring spin polarization from electrons to nuclei. As a method for enhancing bulk nuclear spin polarization, DNP has been successfully applied to areas ranging from fundamental physics to materials science, biology, and medical science. However, as long as electron spins in thermal equilibrium are used as polarizing agents, the upper limit of the polarization enhancement will be 660 for ^{1}H spin and cryogenic temperatures of around 4.2 K will be required for hyperpolarization in the order of 10% even under the strong magnetic fields used for NMR.[1] One approach for overcoming the upper limit of the enhancement factor is to use non-thermalized electron spins. DNP with electron spins in the photo-excited triplet state (triplet-DNP) can achieve hyperpolarization independent of the magnetic field strength and temperature.[2] We report 34% ^{1}H spin polarization in 0.40 T at room temperature.

We employed pentacene as a polarizing agent in which the excited electron spins polarize 73%, and p-terphenyl as a host material because of its stability at room temperature and large pentacene capacity. The curve obtained using ThPh in Fig. 1 is the buildup curve of ^{1}H spin polarization by triplet-DNP in a single crystal of p-terphenyl-h_{14} doped with pentacene-h_{14} 0.05 mol%. We attained a ^{1}H spin polarization of 14%.

The key breakthrough in the present work for attaining higher polarization at room temperature is the suppression of the spin-lattice relaxation by stable-isotope labeling of the constituent molecules. The ^{1}H spin-lattice relaxation in p-terphenyl-h_{14} was mainly due to the pendulum motion of the central benzene ring, which modulates the local dipolar field of the ^{1}H spins in and near the central ring.[3] To suppress the spin-lattice relaxation, we synthesized p-terphenyl-2',3',5',6'-d_4, with which the ^{1}H spin-lattice relaxation time was increased from 11 min to 37 min. The attainable polarization was increased to 16% in the regioselectively-deuterated host doped with pentacene-h_{14} (TdPh in Fig. 1).

There is another source of ^{1}H spin-lattice relaxation that affects DNP. The triplet electrons play the role of a polarizing agent as well as contribute to ^{1}H spin-lattice relaxation through a perturbation of the local field of the ^{1}H spins in the vicinities. To suppress the spin-lattice relaxation, we used pentacene-d_{14} as the polarizing agent. The attainable polarization was
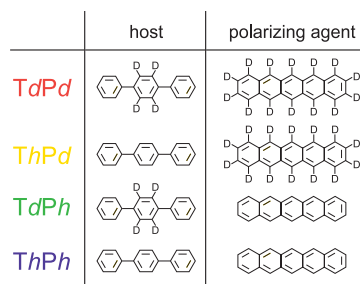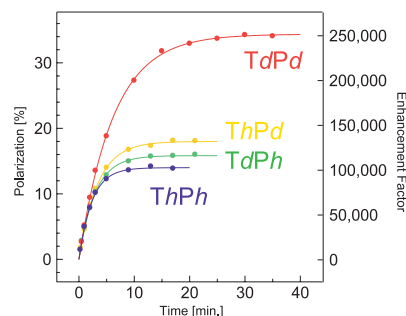

Fig. 1. Polarization buildup curves. The blue, green, yellow, and red curves denote the polarization buildup curves using ThPh, TdPh, ThPd, and TdPd, respectively. The polarizations and enhancement factors were estimated by comparing the intensities of the hyperpolarized signals and the thermal ones in 0.40 T at room temperature.

increased to 18% in the p-terphenyl-h_{14} doped with pentacene-d_{14} (ThPd in Fig. 1).

Suppressing either of the two relaxation sources was not sufficient. By using p-terphenyl-2',3',5',6'-d_4 doped with pentacene-d_{14} (TdPd in Fig. 1), we achieved a bulk ^{1}H spin polarization of 34% at room temperature in 0.40 T, which results in an enhancement factor of 250,000.

Room-temperature hyperpolarization techniques using photoexcited triplet electrons simplify DNP experiments. The NMR sensitivity of samples that prefer ambient temperatures can be boosted significantly. Bulk nuclear hyperpolarization in such low magnetic fields is also desirable for the polarized target for RI beams[4] and the polarized filter for neutron beams.[5]

References
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