Dynamic nuclear polarization with photoexcited triplet electrons in a glassy matrix†

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In this decade, dynamic nuclear polarization (DNP) using equilibrated electron spin has attracted considerable attention in the fields of NMR spectroscopy and MRI as a method to enhance sensitivity.[1)] The intensity of a signal from nuclear spins is proportional to the spin polarization. DNP is a means of transferring spin polarization from electrons to nuclei, and the equilibrated polarization of electron spins is 660 times larger than that of ^{1}H spins. Developing special peripheral equipment, we are able to combine hyperpolarization at cryogenic temperatures around liquid helium temperature with high-resolution NMR spectroscopy or MRI. For such applications, the sample preparation method which materials of interest are codoped into a glassy matrix together with free radicals is one of the most important factors in terms of versatility.

On the other hand, by using single crystal of organic molecules, we have developed a polarized solid-state target with DNP using photoexcited triplet electron spin (triplet-DNP) of pentacene.[2)] The polarization of such non-equilibrated electron spins is more than 70% independent of temperature and magnetic field. Using this method, we can overcome the upper limit (660) of the polarization enhancement factor achieved by conventional DNP. Herein, we report the first demonstration of triplet-DNP in a glassy matrix for application in NMR spectroscopy and MRI.

We applied two types of host molecules that have higher glass transition temperature than conventionally used glasses. One is a non-polar molecule, o-terphenyl (OTP).[3)] The other is a polar molecule, benzophenone (BZP).[4)] Using partially deuterated OTP and BZP as host materials, we obtained 1.5% and 0.7% ^{1}H spin polarization under 0.4 T at 120 K, respectively (Fig. 1). The enhancement factor for OTP and BZP was 4,250 and 1,900, respectively. We have also succeeded in polarizing third molecules, 2, 3, 4-trifluorobenzoic acid and 5-fluorouracil, codoped into a glassy matrix with polarizing agent (Fig. 2). ^{19}F spin in the thrid molecules were polarized using the field cycling method.[5)]

The use of photoexcited triplet electrons is a promising method to extend the limitation of DNP to higher temperatures. If hyperpolarization can be achieved above liquid nitrogen temperature, the peripheral equipment and the experiments for spectroscopy will be simplified, and the application field will be broadened. There are many samples of interest for which a higher temperature is preferable. DNP using photoexcited triplet electrons has the potential to significantly enhance the NMR/MRI sensitivity while the sample is kept at room temperature.

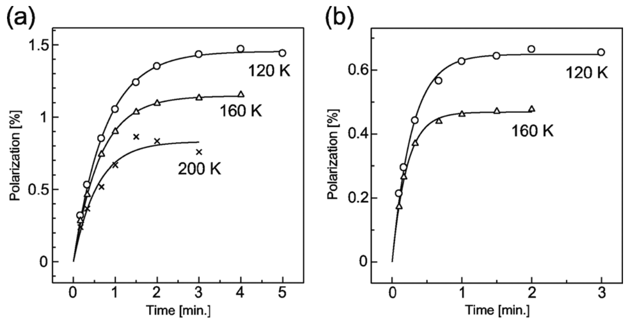

Fig. 1. ^{1}H spin polarization buildup curves for (a) partially deuterated OTP ([D14]OTP/OTP=90:10 wt%) and (b) partially deuterated BZP ([D10]BZP/BZP=90:10 wt%) doped with 0.05 mol% pentacene.

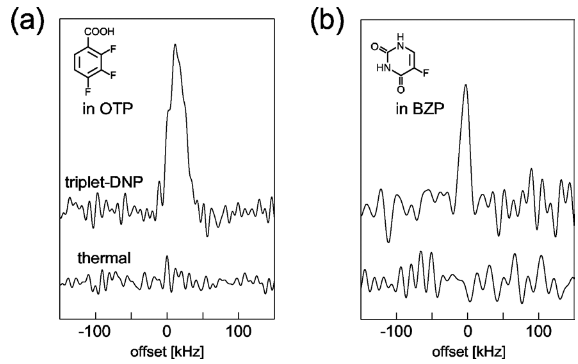

Fig. 2. Polarized ^{19}F NMR spectra of (a) 2,3,4-trifluorobenzoic acid and (b) 5-fluorouracil in glassy matrices. After DNP for 3 min and field cycling, the ^{19}F NMR signals were acquired. The NMR signals of the samples under 0.40 T at 120 K in thermal equilibrium are also shown.

References
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