

Triplet Dynamic Nuclear Polarization in Metal-Organic Frameworks

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(多孔性金属錯体を用いた三重項動的核偏極)

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論 文 内 容 の 要 約

Since the first observation in 1946, nuclear magnetic resonance (NMR) has evolved to versatile applications for investigating matter and utilized in diverse areas as spectroscopy and magnetic resonance imaging (MRI). However, despite such significant advancements, NMR/MRI have suffered from an intrinsically low sensitivity compared with other analytical methods. The limited sensitivity originates from the low spin polarization of nuclear spins (10^{-5} or less) at ambient conditions.

To overcome this situation, over the past few decades, various technologies have been developed to produce hyperpolarized state of nuclear spins. In particular, dynamic nuclear polarization (DNP) has become one of the most general methods that is currently applicable to a variety of investigations, such as molecular imaging with MRI. While application of DNP-enhanced NMR/MRI have opened up new possibilities, however, the use of equilibrium electron spins as the polarizing source at cryogenic temperatures (~ 1 K) leads to considerable costs of instruments and preventing from widespread use of this method.

To hyperpolarize nuclear spins at room temperature, DNP employing non-equilibrium electron polarization in photoexcited triplet state (triplet-DNP) can be a promising approach. Whereas triplet-DNP systems have been gradually explored with the aim to utilize in such NMR/MRI applications, hyperpolarization of target molecules at room temperature remains a significant challenge due to the drawbacks of the current materials, such as organic crystal and glass matrix. In this thesis, the introduction of metal-organic frameworks (MOFs) as a new host material is considered to address the issues remained in the conventional triplet-DNP systems.

Chapter 1 overviews the basic history and theory behind the NMR spectroscopy and MRI to visualize how we can or should manipulate the spins in triplet-DNP and enhance NMR/MRI sensitivity. Several hyperpolarization techniques for enhancement of NMR/MRI sensitivity are reviewed, such as spin-exchange optical pumping (SEOP), parahydrogen-induced polarization (PHIP), and DNP. Then, after the advantage and mechanism of triplet-DNP are described in detail, conventional triplet-DNP systems are summarized to get started.

Chapter 2 shows the first example of employing MOFs as host materials for triplet-DNP. MOFs offer not only rigid crystalline structures but also nanopores for guest accommodation. For the proof-of-concept, high dispersibility of polarizing agent in MOFs and long ^1H spin lattice relaxation time of MOFs are satisfied. The typical polarizing agent pentacene was modified with metal-coordinating carboxylate moieties for its introduction into MOFs. A partially deuteration of ligands effectively suppress the nuclear spin relaxation. Polarization transfer from photoexcited triplet electrons to ^1H nuclei in the MOF resulted in a clear enhancement of ^1H -NMR signals room temperature over thermal equilibrium.

In chapter 3, the spin-lattice relaxation property of MOFs is discussed by selecting a model set of isostructural sodalite topology zeolitic imidazolate frameworks (ZIFs). The spin-lattice relaxation time of ^1H nuclei exhibited a clear variation depending on the different 2-substituted imidazolate linkers. The dynamics of the each imidazolate linkers in the ZIFs is investigated by deuterium NMR measurement to gain insight into the effect of the linker substituent and dynamics on the relaxation for nuclear spin polarization in MOFs

Chapter 4 shows the first example of the hyperpolarization of guest molecules in a porous host material was achieved for the first time at around room temperature. The crystalline yet flexible MOF incorporated the guest target molecules with changing its pore structure to adjust the host-guest interactions. The unique phenomenon was observed in which the ^1H spin-lattice relaxation time T_1 was rather by the guest incorporation. In addition, the strong host-guest interaction suppresses the mobility of the guest target molecules sufficiently to realize the polarization transfer to guest molecules through triplet-DNP and CP even at around room temperature.

Chapter 5 provides a summary of this thesis and concluding remarks.