

## Study on materials for photo-driven spin hyperpolarization in liquids

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## 論 文 内 容 の 要 旨

Although magnetic resonance technology has become an essential analytical technique in today's chemistry and medicine, its inherently low sensitivity is a major drawback. This is due to the extremely low nuclear spin polarization, which is related to detection sensitivity. In recent years, in order to improve the sensitivity of magnetic resonance, "dynamic nuclear polarization (DNP)," in which the nuclear spin polarization is artificially increased through various spin manipulations, have been actively studied. However, maximizing the polarization of electron spins, the source of polarization, requires special conditions such as cryogenic temperatures and strong magnetic fields, and nuclear spins must be hyperpolarized in vitro and quickly injected and measured before losing their polarization. Thus, what is truly needed is a technique to achieve hyperpolarization in situ and even in vivo. This thesis described materials that can be hyperpolarized in a mild environment, unlike conventional DNP, by utilizing light-induced transient hyperpolarization and spin-selective reactions.

Chapter 1 outlines the basic mechanism and recent developments in the hyperpolarization technology discussed in this thesis. In triplet DNP, nuclear hyperpolarization is achieved by utilizing the transient electron spin polarization of the triplet state itself and transferring it to the nuclear spin. In optically generated DNP, nuclear hyperpolarization is achieved by utilizing the electron spin polarization induced by the reaction of the triplet and radicals and transferring it to the nuclear spin. Chemically induced dynamic nuclear polarization (CIDNP) directly generates nuclear spin polarization by utilizing the specific nuclear spin-selective ISC of radical pairs produced by the reaction of electron-donor molecules. Based on the principles of these technologies, guidelines for material design are discussed and summarized.

Chapter 2 presented the first example of highly polarized nanomaterials in water by triplet-DNP. Triplet-DNP takes advantage of the fact that the excited triplet state immediately after formation becomes highly polarized by spin-selective ISC even at room temperature. On the other hand, the target for polarization has been limited to bulk organic crystals or glasses due to the insolubility of pentacene, which has been known as the optimal polarization source, and the limited choice of host materials that can accumulate polarization for a long time at room temperature. Therefore, we developed nanocrystals of pentacene as a polarization source and *para*-tarphenyl as a host material, while maintaining the composition of conventional organic crystals, and developed a nanomaterial that has both dispersion stability in water and

a long polarization lifetime. The nanomaterials have a high surface area and are protected by a dense host material with oxygen-blocking ability, which protects the triplet state. As a result, triplet DNPs have been demonstrated in water and an enhancement factor of more than 200 times was successfully obtained.

Chapter 3 focus on the fact that the efficiency of optically generated DNP strongly depends on the efficiency of electron spin polarization generation, and new molecules that achieve highly efficient electron polarization generation by intramolecular radical triplet pair mechanism (RTPM) were developed. In conventional systems, the efficiency of RTPM is low because the dye and radical are separated, and polarization generation is diffusion-limited. Based on the RTPM principle, polarization can be generated by fluctuating the distance between the dye and radicals and changing the strength of the exchange interaction. Based on this principle, new molecules consisting of a porphyrin, a stable triplet sensitizing dye, and a nitroxyl radical, a stable radical, linked by a flexible spacer were synthesized and evaluated. The novel compounds showed enhanced time-resolved ESR signal by intramolecular RTPM compared to the molecularly dispersed system. Furthermore, the sufficient distance between the dye and the radical suppressed the rapid deactivation of the triplet due to paramagnetic relaxation, and a unique time-resolved ESR signal lasting more than 10  $\mu$ s was successfully observed. This demonstrates that the strategy of linking with flexible spacers is a useful option to improve polarization generation efficiency.

Chapter 4 proposed and demonstrated a turn-on type CIDNP probe that switches the efficiency of CIDNP triggered by a reaction. Focusing on the fact that phenol derivatives form radical pairs by proton-coupled charge transfer, CIDNP of phenol derivatives were inactivated by protecting the hydroxyl group. By adding lipase, the enzyme of the hydrolysis reaction, the progress of the reaction could be monitored from the enhancement factor of CIDNP. Thus, the demonstration of the proposed turn-on type CIDNP probe is succeeded, and it shows that this new methodology actually useful as a probe for enzymatic reactions.

Chapter 5 provided a summary of this thesis and future perspectives.