Erratum: Long-lived state in a four-spin system hyperpolarized at room temperature (2020 Quantum Sci. Technol. 5 025004)

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During the production process, the following error was introduced. The descriptions of ‘ligand’ and ‘receptor’ in figure 4 and the first sentence in section 4 in the paper are incorrect. Here we show the corrected figure 1. The sentence should read ‘As an application of this room temperature hyperpolarized long-lived state, we performed bCD/PCBA (receptor/ligand) binding experiments.’

![Figure 1](image_url)

Figure 1. (a) The circles show the relaxation curve of the singlet pair state after dissolution triplet-DNP with 2.7 mM bCD. The squares show the recovery curve of the polarization after dissolution triplet-DNP with 2.7 mM bCD. These curves were normalized as in figure. (b) The image of the ligand–receptor binding. The protons in the ligand are entangled. The dashed lines represent the interaction between the proton in ligand and the protons in receptor.
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PAPER

Long-lived state in a four-spin system hyperpolarized at room temperature

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Abstract

A solution with hyperpolarized nuclear spins encoded into a long-lived state has been utilized for sensing chemical phenomena. In a conventional way, nuclear spins are hyperpolarized at very low temperatures. In this work, we demonstrate the encoding of a four-nuclear-spin system hyperpolarized at room temperature into a long-lived state in a solution. We apply the solution with the long-lived state as a sensor in ligand-receptor binding experiments.

1. Introduction

Nuclear magnetic resonance (NMR) spectroscopy and magnetic resonance imaging are powerful methods for noninvasive analysis in a variety of fields such as chemistry, biology, and medical science. However, their sensitivities, which are proportional to the spin polarization, are very low. Dynamic nuclear polarization (DNP) [1], a technique to transfer spin polarization from electrons to nuclei that dramatically increases their sensitivity, has been extensively studied. Conventional DNP uses unpaired electrons in thermal equilibrium as a polarizing source, and requires apparatus capable of applying a high magnetic field at low temperature to achieve high electron polarization, on the order of 10%. In 2003, Ardenkjær-Larsen et al developed dissolution DNP [2], which is a method whereby solid samples that have been polarized with DNP are dissolved in hot aqueous solutions. These solutions with hyperpolarized nuclear spins are then utilized for sensing chemical phenomena in vitro [3–5] and in vivo [6, 7]. There are several applications for investigation of metabolic processes that take a long time. These applications are limited by the lifetime of the nuclear spin polarization, that is, the spin-lattice relaxation time $T_1$.

In the field of quantum information, it is known that a quantum state can be made decoherence-free when encoded in a density operator commutable with the Hamiltonian associated with relaxation [8, 9]. In some two-nuclear-spin systems, the lifetime of the polarization can be extended by encoding the spins into the singlet state [10–17]. Furthermore, it has been reported that the lifetime of the $^{13}$C spin singlet in the naphthalene derivative is more than one hour [18]. Experiments combining dissolution DNP and encoding into a long-lived singlet state have been demonstrated [19–21]. These experiments have opened the door to investigation of metabolic processes that take a long time. Encoding a many-spin system into a long-lived state, which is called a decoherence-free state in [22], was also studied [12, 13, 22–24]. Pileio et al proved that the lifetime of a four-spin system can be extended in an experiment using thermally polarized spins [23, 25]. To utilize quantum correlated state of many spins for sensing is one of the most important missions in the field of quantum sensing [26]. The usage of quantum error correcting code to quantum sensing is actively studied as important challenge [27–29].

Other polarizing methods such as para-hydrogen induced polarization and photochemically induced dynamic nuclear polarization (photo-CIDNP) combined with the singlet state have also been demonstrated [30, 31]. Another method of polarizing nuclear spins at room temperature in low magnetic fields was developed, called ‘triplet-DNP’ [32–35]. In this method, non-thermally polarized state in ‘triplet’ electron spin is used as
polarizing source instead of thermally polarized state in unpaired electron spins. It was originally demonstrated using pentacene, which also played key roles in other quantum technologies such as single spin detection [36, 37] and room temperature maser [38]. This method can reduce the cost and size of the instrument required, since photoexcited triplet state of pentacene is spontaneously polarized near unity via a quantum process independent of magnetic field strength and temperature. A proton polarization of 34% was achieved with triplet-DNP [35]. Room temperature hyperpolarization with nitrogen-vacancy centers has also been actively studied [39–41]. Room temperature hyperpolarization is one of important applications of quantum technology [42]. Furthermore, dissolution DNP at room temperature using pentacene [43] and some methods to polarize various molecules have also been demonstrated [44–46].

In this work, we have demonstrated the encoding of a four-spin system hyperpolarized at room temperature into a long-lived state, and its application. The polarization of the aromatic protons in p-chlorobenzoic acid (PCBA) was increased by using dissolution triplet-DNP at room temperature, and the protons were encoded into a long-lived state. As an application of the hyperpolarized long-lived state, we performed β-cyclodextrin(bCD)/PCBA binding experiments and assessed the performance of hyperpolarized PCBA as a sensor for the binding.

2. Dissolution triplet-DNP

Powder samples of PCBA doped with 0.04 mol% pentacene were used in all experiments. The procedure and experimental setup of triplet-DNP used in this work are similar to those in [43]. A dye laser with a wavelength of 594 nm and a repetition frequency of 100 Hz was used as a light source. A static magnetic field of 0.39 T was generated by an electromagnet. All DNP experiments were carried out at room temperature.

A buildup curve of proton polarization for 0.37 mg of the sample is shown in figure 1(a). We obtained a proton polarization of 0.25% for \( \tau > 300 \) s, which is 1740 times higher than the thermal polarization at the same temperature and magnetic field. The finally attainable polarization 0.25% in the solid state may be improved by partial deuteration of the carboxyl group or increasing the laser repetition frequency [35, 47].

After 3 mg of the sample was polarized by triplet-DNP for 5 min, we dissolved it in 0.35 ml of hot sodium carbonate solution (Na2CO3:D2O = 1:10 (mass ratio)), and then transferred it into a superconducting magnet with a magnetic field of 11.7 T. This process of dissolution and transfer took around 10 s. The enhanced NMR spectrum of the aromatic protons is shown in figure 1(b). The intensity of the spectrum is 17 times larger than that at thermal equilibrium in a field of 11.7 T.

The thermal polarization of the protons at room temperature in 11.7 T is \( 4.0 \times 10^{-3}\% \). Thus, the polarization after dissolution was estimated to be \( 6.8 \times 10^{-2}\% \). This enhancement factor was smaller than expected when compared to the proton polarization at room temperature in 11.7 T. The main reasons for this result is that the sample tube for the dissolution experiments is larger than that for the measurement of \(^1\text{H}\) polarization and our light source could not penetrate the whole sample for the dissolution experiments. By comparing the enhanced NMR spectrum, we estimated that only about half of the sample was exposed to laser irradiation in our triplet-DNP system. Another reason is that the polarization of the aromatic protons decreased during the transfer and dissolution process. The enhanced \(^1\text{H}\) polarization decreases about 6% during the transfer process and the polarization decreases due to its short relaxation time \( T_1 \) during the dissolution process. The former can be improved by using a more powerful light source and the latter can be mitigated by using a rapid transfer system.

3. Lifetime measurements

We measured the lifetimes of the aromatic protons of the sample dissolved in 0.35 ml of sodium carbonate solution at room temperature in a field of 11.7 T. \( T_1 \) was measured as 5.3 ± 0.1 s with an inversion recovery pulse sequence. The recovery curve is shown by the squares and the dotted line in figure 2(a).

In the case of a four-spin system \( \text{A}'\text{X}'\text{X}'\text{X}' \) such as the aromatic protons in PCBA (figure 1(b)), the relaxation is predominantly caused by the dipolar interaction between \( \text{A} \) and \( \text{X} \), \( H_{\text{DD},\text{AX}} \), and that between \( \text{A}' \) and \( \text{X}' \), \( H_{\text{DD},\text{AX}'} \). It was recently demonstrated that the singlet pair states \( \rho_{\text{SP}} \)

\[
\rho_{\text{SP}} = \frac{1}{2} \left( |S\rangle \langle S| I_{\text{AX}} \otimes I_{\text{AX}'} + I_{\text{AX}} \otimes |S\rangle \langle S| I_{\text{AX}'} \right) + \frac{I_{\text{AX}} \otimes I_{\text{AX}'} - 1}{4},
\]

are decoherence-free against the dipolar relaxation and the lifetime is longer than \( T_1 \) [23, 25]. Here, \( |S\rangle = (|00\rangle - |10\rangle)/\sqrt{2} \), \( \epsilon \) is the polarization and \( I \) is the identity operator. This is because the density operators of the singlet states commute with the dipolar interaction Hamiltonian. Although the singlet does not commute
with the out-of-pair (AX', A'X, AA' and XX') J-couplings, it is shown that the strong intra-pair (AX and A'X') J-coupling protects the singlet state against the weak out-of-pair J-couplings [25].

The lifetime $T_S$ of the singlet pair state at room temperature was measured with the singlet-locking pulse sequence [48, 49] shown in figure 2(b). The thermally polarized state at room temperature was encoded into the pair of the singlet state by the preparation pulse. The relaxation curve is shown by the circles and the solid line in figure 2(a). The $T_S$ value for protons was $15 \pm 1$ s. This is 2.8 times longer than the $T_1$ value. Some of the residual relaxation mechanisms are (i) intramolecular dipolar interactions with out-of-pair protons and chloride [16], (ii) the chemical shift anisotropy [16], (iii) out-of-pair J coupling [25], (iv) spin-rotation interaction [15] and (v) intermolecular dipolar interactions with spins of solvent [50].

We measured the $T_S$ and $T_1$ after the polarization of the sample was enhanced by triplet-DNP. The hyperpolarized sample was dissolved into a sodium carbonate solution, which was transferred to an 11.7 T superconducting magnet. The sample temperature just after dissolution was ca. 343 K. After the 30° tip pulse measurements, the $T_S$ was measured with the singlet-locking pulse sequence and the $T_1$ was measured with the inversion recovery pulse sequence. In these measurement results, the $T_1$ value for the aromatic protons hyperpolarized by triplet-DNP was $7.4 \pm 0.7$ s and the $T_S$ value was $18 \pm 2$ s as shown in figure 3.

This result shows that the lifetime of the polarization made by dissolution triplet-DNP can also be extended by using the singlet pair state. Both the $T_S$ and $T_1$ after dissolution triplet-DNP are longer than those in the thermally polarized state at room temperature. This is because the temperature after the dissolution 343 K is higher than the room temperature and the correlation time, which depends on the temperature and the viscosity of the solvent, becomes smaller than that at 300 K.
4. Binding experiments

As an application of this room temperature hyperpolarized long-lived state, we performed bCD/PCBA (ligand/receptor) binding experiments. In [3], the sensing of bCD/benzoic acid binding was demonstrated by measuring the decrease in the $T_1$ of the $\alpha$-13C of benzoic acid due to the change of the rotational correlation time by binding...
and additional relaxation caused by the intermolecular dipolar interaction with the protons in bCD. In the experiment, hyperpolarized $\alpha$-$^{13}$C was used.

The $\alpha$-$^{13}$C of benzoic acid was hyperpolarized with conventional DNP. It is known that proton singlet states can be used as a highly sensitive probe for binding experiments due to the dipolar interactions between the nuclear spins of the ligand and receptor [5, 51]. The singlet state is sensitive to the environment in the presence of the receptor, while it is insensitive to the environment without the receptor. The hyperpolarized singlet state has been applied to NMR drug screening and in vivo imaging [21, 52, 53].

In our experiment, we dissolved the hyperpolarized sample into a sodium carbonate solution with 2.7 mM bCD. The results were $T_1 = 4.7 \pm 0.7$ s and $T_S = 9.6 \pm 0.8$ s, as shown in figure 4. Each lifetime was shorter than that without bCD.

To prove the advantage of the decoherence-free state, we employed the contrast $C(T_i)$ between these lifetimes, defined as [5]

$$C(T_i) = \left| \frac{T_i^{\text{free}} - T_i^{\text{obs}}}{T_i^{\text{free}} + T_i^{\text{obs}}} \right|,$$

where $T_i$ is $T_1$ or $T_S$, $T_i^{\text{free}}$ is the lifetime for the free ligand, and $T_i^{\text{obs}}$ is the lifetime when some ligands are bound to receptors. The contrast $C(T_1)$ was 22% and $C(T_S)$ was 30%. This shows that the encoded state is more sensitive than the non-encoded state. The singlet state, which is decoherence-free against the interaction between the spin pair, is generally more sensitive to binding events than non-encoded state. In the binding event as shown in figure 4(b), only one of the spins in the ligand is exposed by strong intermolecular interactions. In the case of non-encoded state, the intermolecular interaction between the spins in the ligand and receptor causes strong decoherence on the closer spin. However, in the case of the encoded state, the interaction causes decoherence on all the entangled spins simultaneously. The more spins are entangled inseparably, the stronger the effect with the interaction becomes, that is, the more sensitive the sensor becomes.

The difference of the measurement times for encoded state and non-encoded state is the duration for encoding. The duration is the order of ten milliseconds which is much smaller than the total measurement time of the order of ten seconds. Therefore, the difference can be ignored regarding the contrast. Given a certain total measurement time for both measurements, the contrast for encoded state should be still higher.

Figure 4. (a) The circles show the relaxation curve of the singlet pair state after dissolution triplet-DNP with 2.7 mM bCD. The squares show the recovery curve of the polarization after dissolution triplet-DNP with 2.7 mM bCD. These curves were normalized as in figure 3. (b) The image of the ligand-receptor binding. The protons in the receptor are entangled. The dashed lines represent the interaction between the proton in ligand and the protons in receptor.
5. Conclusions

We have demonstrated that the lifetime of proton polarization enhanced by dissolution triplet-DNP can be prolonged by quantum encoding of a four-proton-spin system. We have also demonstrated that the quantum encoded state has an advantage in sensing chemical phenomena. Except for PCBA, aromatic protons in the benzene ring modified at the para positions can be encoded into the singlet pair state. In [23], the other type of the aromatic molecules has been encoded into the singlet pair state. As for the biological application, aromatic protons in tyrosine, which is an endogenous substance, is one of the candidates. In [54], 4-((trifluoromethyl) benzene-1-carboximidamide has been used as a sensor but the aromatic protons in the molecule have not been encoded. If these aromatic molecules are encoded, the binding event can be more sensitive. Furthermore, room-temperature hyperpolarization using triplet-DNP has been applied to various aromatic carboxylic acids such as benzoic acid, salicylic acid, and 2-naphthoic acid [44], and a number of methods to polarize various molecules have been developed [45, 46]. Our result represents the first step for NMR drug screening and in vivo metabolic imaging using room-temperature hyperpolarization and quantum encoding of multispin systems of various molecules.

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