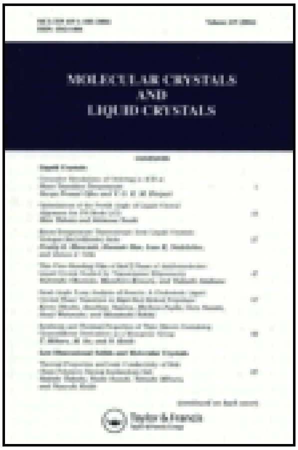

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Photomagnetism of A-DNAs Intercalated with Photoresponsive Molecules

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We have reported that the natural DNA and DNAs intercalated with organic radicals were able to show the noble magnetic properties in dry state. Extending our study on the Magnetic properties of DNAs, we intercalated the photoresponsive proflavine (PF) molecules into DNAs when the intercalated DNA complexes were illuminated by a laser beam of 488 nm. Electron magnetic resonance (EMR) new signals appeared. We succeeded in measurement of photomagnetic properties of modified DNAs through electron magnetic resonance (EMR) spectroscopy and SQUID measurement. A significant increase in magnetization was observed for the photo-illuminated DNA/proflavine samples.

Keywords: DNA; magnetism; photomagnetism; photoresponsive molecules; proflavine

1. INTRODUCTION

Recently, we reported [1,2] the intrinsic magnetism of natural DNA in dry state and significantly enhanced magnetic properties of DNAs

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FIGURE 1 The chemical structure of proflavine

intercalated with organic free radicals. The DNAs intercalated with organic free radicals at very low levels showed the surprising attraction by commercial magnets at room temperature. And we proposed that a strong induced internal magnetic field can be generated in the ordered region when A-DNAs are placed in a magnetic field and that DNA chain mediates magnetic interactions between the intercalated or newly introduced spins. If the photo-excited radicals and electrons can be introduced into the DNAs [3]. By single photo-excitation, DNA would be able to simultaneously access both localized and conductive spins needed for enhancing magnetic susceptibility. Here, in order to realize our ideas we introduced the proflavine molecules [3–5] (Fig. 1) into the DNAs and they are illuminated with a laser beam (488 nm). We will discuss the photomagnetic properties of the DNA-proflavine complex. The chemical structure of proflavine is shown below in Figure 1.

2. EXPERIMENTALS

2.1. Preparation of DNA-Proflavine Complexes

Salmon sperm DNA, sodium acetate and acetic acid were purchased from Sigma Aldrich (U.S.A.). Proflavine hemisulfate was purchased from TCI (Japan). The DNA-proflavine complex at 1:3.2 molar ratio (feed ratio) was prepared as follow. DNA (0.13 g) was dissolved in 100 ml of acetate buffer solution under protection by an aluminum foil. Separately, 1.2×10^{-6}M proflavine stock solution was prepared in 100 ml anhydrous ethanol using a volumetric flask. The proflavine solution (540 ul) was poured into 20 ml DNA of buffer solution and kept at room temperature for 24 h. The DNA-proflavine complex was precipitated by addition of enough ethanol and washed thoroughly with ethanol followed by drying in a vacuum oven (10^{-2} Torr) at 40°C for 24 h.

2.2. EMR Measurement

The sample for EMR measurement was sealed in 3 mm (diameter) quartz tube under high vacuum ($\sim 5 \times 10^{-4}$ Torr). The EMR signal was obtained for the DNA-proflavine complex before the laser beam illumination. And the 10 mW (488 nm) laser (Ar ion Laser, LEXEL 95, U.S.A.) beam was illuminated on the sample for 5 min and then EMR signal was directly measured. And the signal was measured again three weeks later. Electron magnetic resonance (EMR) measurements were performed with a Jeol FSA-200 X-band spectrometer (9.2 GHz, Japan) at the microwave power of 1 mW, and the modulation magnetic field and frequency of 5 G and 100 KHz, respectively. The swept field was from 0 to 10000 G and the receiver gain 5×10^2 for the wide scan.

2.3. SQUID Measurement

The temperature dependence of magnetization of the DNA-proflavine complex was measured at 1000 G and 10000 G before illumination and also obtained at 1000 G after illumination. And its magnetic field dependence was obtained before and after illumination. The magnetic susceptibility was measured using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design, MPMS 7.5, U.S.A.) over the temperature range of 4.5–300 K. All the measurements for this sample were performed under the helium gas atmosphere. DNA-proflavine complex was loaded in polystyrene straws and, after being cooled down to 5 K in the absence of magnetic field, 5 mW (488 nm) laser (Ar ion Laser 3500, U.S.A.) beam was illuminated for 5 min. Magnetization data at 1000 G were collected as the temperature was increased followed by decreasing and increasing again.

3. RESULTS AND DISCUSSION

Figure 2 shows the EMR signals for DNA-proflavine complex before and after illumination. After illumination, a new sharp EMR signal appeared in the region of the g-value of 2 and the generated spins are one spin per 6400 DNA duplexes. This can be explained that photo-excitation of proflavine molecules in DNA base stacks [6–10] makes localized radicals. And also one-electron donation or electron transfer into the DNA can be expected. A more detail conductivity measurement is needed to prove the carrier doping.

This DNA-proflavine complex may find utilization in the photomagnetic devices, for example, ROM and RAM. After three weeks, we again obtained the exactly same EMR signals for the illuminated DNA-proflavine complex. The new radical peaks did not disappear and also the intensity did not change in the vacuum sealed state.

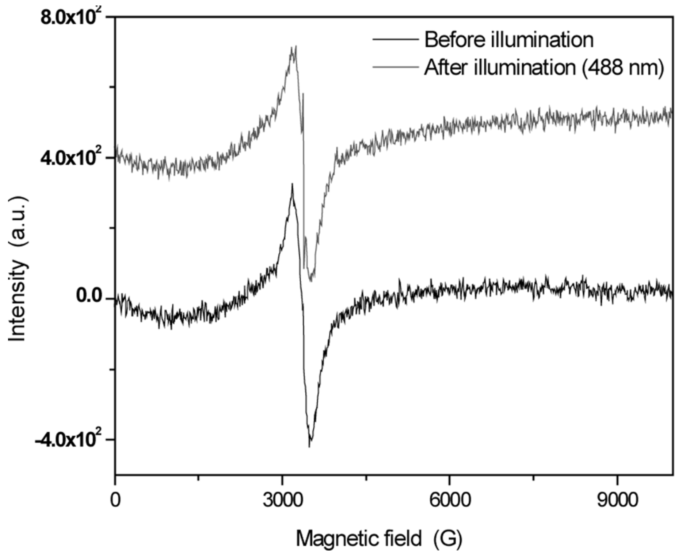

FIGURE 2 Electron magnetic resonance spectra of DNA-proflavine complexes before and after illumination with 488 nm laser beam.

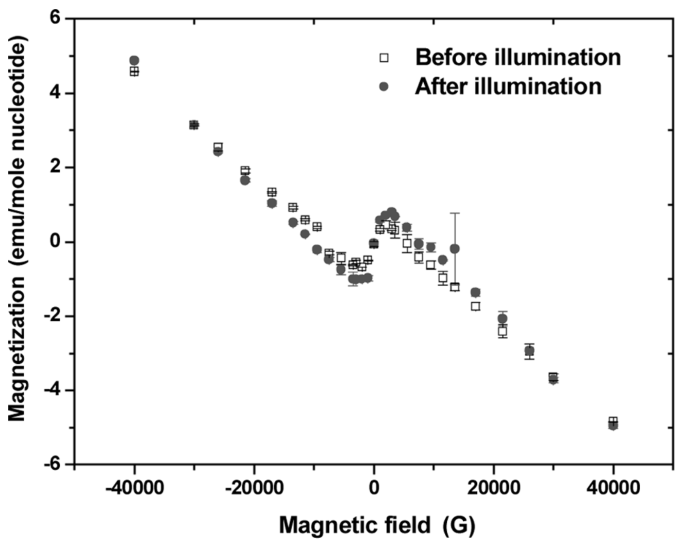

FIGURE 3 Magnetic field dependence of the DNA-proflavine complex before and after 488 nm laser beam illumination.

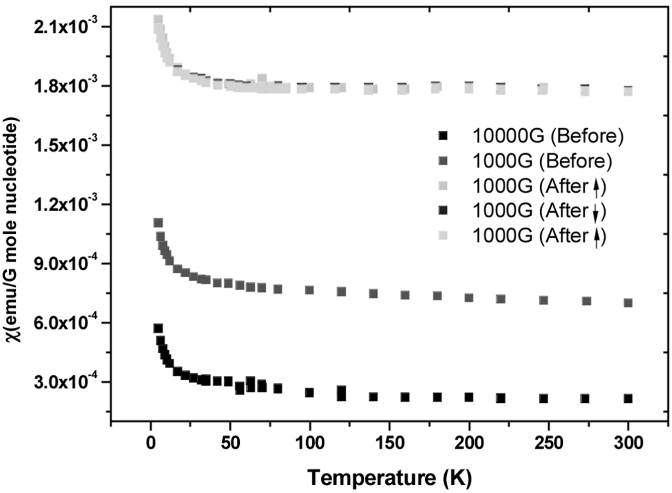

FIGURE 4 Temperature dependence of magnetic susceptibility of DNA-proflavine complex before and after 488 nm laser illumination (↑ stands for heating and ↓ cooling).

Figure 3 shows the magnetic field dependence of the DNA-proflavine complex before and after 5 mW (488 nm, 5 min) laser beam illumination. The DNA-proflavine complex shows the S-shaped magnetization behavior and the S-shape was enhanced by illumination. And Figure 4 shows that the magnetic susceptibility of the DNA-proflavine complex at 1000 G is increased significantly by illumination. Figure 4 also compares magnetic susceptibility of the illuminated sample at 1000 G after a heating, cooling and heating cycle. As we can see from the figure, no relaxation is observed. This study shows that a strong magnetic property is obtained by photo-excitation of the DNA-proflavine complex. And it is also observed that the magnetic susceptibility is independent of temperature.

4. CONCLUSION

The EMR result of the DNA-proflavine complex shows that the localized spins can be newly generated by laser illumination and be kept unchanged for several weeks in vacuum. And magnetic susceptibility of the DNA-proflavine complex is significantly increased by illumination and it remains the same over the temperature range from 4.5 K to 300 K. This study demonstrates the feasibility of the photomagnetic device applications by using the DNA-photoresponsive molecule system.

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