Magnetic Properties of Modified DNAs

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INTRODUCTION

Since the first suggestion by Eley and Spivey[1] in 1962, charge transfer/transport in DNA has attracted a considerable attention because of its important role in recognition and repair of damaged-DNA lesions[2] as well as potential applications in nanotechnology[3]. For the latter case, DNAs having appropriate sequences are able to be synthesized and, after being self-assembled, they can be utilized as molecular building blocks for nanodevices. Due to these unique advantages and possibilities a great deal of efforts have been devoted to study the charge transport in DNA by various research groups[4,5], but the conductivities reported[6] until now show incredibly diverse results covering the range of insulator, semiconductor, conductor, and proximity-induced superconductor. Nonetheless, Barton et al.[7] showed that DNA is able to mediate the transport of charge carriers generated by light illumination, and they[2] successfully applied the mechanism to explain the repair of the damaged-DNA lesions by enzymes. In their works, they utilized DNAs intercalated with separated charge donor and acceptor. Such a chemical modification is not difficult but is a very powerful method in the study of charge transport in DNAs. In order to achieve ultimate device performance of practicality, it is required to have proper electric, optical, and magnetic components available. While the DNA devices toward the electric or optical components have been proposed by various research groups during the last decade, very little is known for research where DNAs are envisaged as magnetic components. In this work, therefore, we explore and present a report on the magnetic properties of the modified DNAs together with a natural DNA[8].

RESULTS and DISCUSSION

Figure 1 shows the typical EPR lineshapes for DNAs intercalated with various contents of PTMI radicals. Although the signal intensities are different from each other depending on the amount of intercalated radicals, similar signal patterns are observed: the signal can be resolved into two different components, doublet and triplet. Another point to be noted is the face that the relative intensity of the triplet signal steadily decrease as the doping level of the free radical increases. This is a very surprising result because the average separations between the intercalated radicals are too far for the triplet spin state to be resulted, when the dopant level is very low.

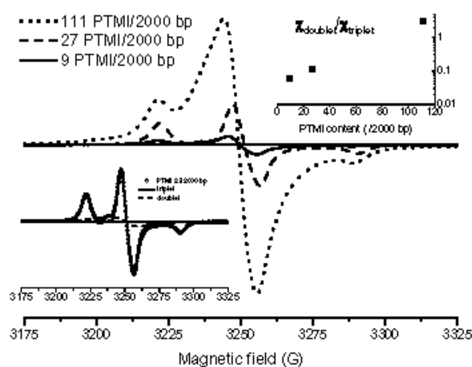

Figure 1. The typical EPR signals obtained at 200 K for the A-DNAs intercalated with various contents of PTMI. Note that the experimental EPR spectrum can be deconvoluted to the triplet and doublet signals as is seen in the left-below inset figure. The ratio of $\chi_{doublet}/\chi_{triplet}$ (the right-above inset) obtained from the deconvolution increases as the PTMI contents increases.

In order to find an EPR signal originated from such a spin carrier, we performed EPR measurements for the natural A-DNA[8] and the modified DNAs over the magnetic field range of 0~8000 G. A representative EPR spectrum observed at room temperature is displayed in Figure 2. Remarkably, the natural A-DNA shows two broad EPR signals: one at g>10 and the other at g~2. More surprising is the fact that the EPR spectra for the modified DNAs have not only the EPR signals similar to those of the natural A-DNA as a background but also additional sharper and strong EPR signals from the radicals as already shown in Figure 1, especially when the content of the dopant radical is very low. The less the radical content intercalated, the more manifest this type of EPR spectrum. If we heavily intercalate the radicals into DNA, the background EPR signal from the natural A-DNA disappears and only the EPR signals from radical species are observed as shown in Figure 2. As a consequence, total susceptibility decreases with increasing radical intercalation.

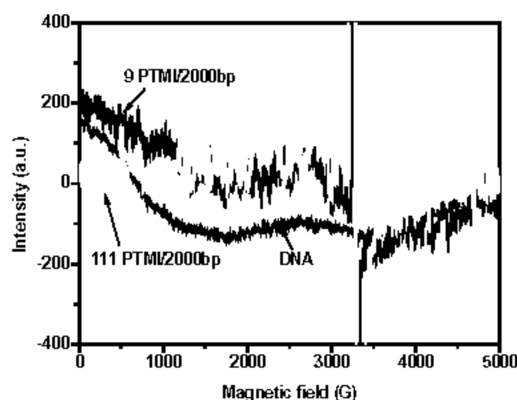

Figure 2. Comparison the EPR spectra observed for the natural A-DNA with for the modified DNAs with various PTMI contents.

Figure 3 compares the EPR spectrum of DNA with those of DNA-Au(III) complexes. Although Au(III) is spinless, complexation results in an appearance of new EPR signal at g ~2.0. The identity of the signal requires a further study. Moreover, the DNA-Au complex containing 0.025Au per nucleotide is attracted to a commercial magnet at room temperature, whereas that containing 0.82 Au per nucleotide does not. This observation parallels what was described above for the DNAs doped with organic radicals.

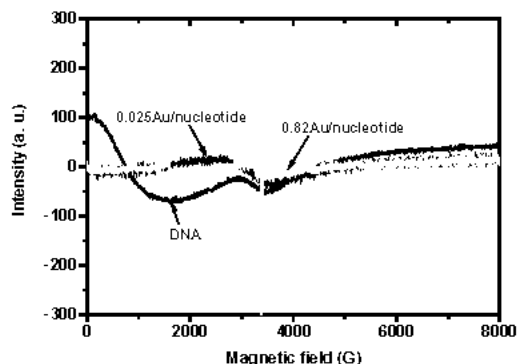

Figure 3. Comparison the EPR spectrum observed for the natural A-DNA with that for the DNA-Au(III) complexes.

For the purpose of confirming this surprising phenomenon, we performed a DC magnetic measurement of DNA samples using a

SQUID magnetometer (Quantum Design mpms 7.7, USA). Figure 4 shows the temperature dependence of the DC susceptibility including the natural A-DNA and the modified DNAs. Interestingly, the PTMI radical content dependence of the absolute value of DC susceptibilities supports the above suggestion. In other words, the absolute value of DC susceptibility decreases as the content of radical increases. This phenomenon is reconfirmed by the fact that the modified DNAs containing a low concentration of the intercalators (e.g., 9 PTMI or 27 PTMI/2000bp) are well attracted at room temperature to the commercial magnet, while those containing high concentrations are not attracted at all. The exact same trend is observed for Au(III) complexes.

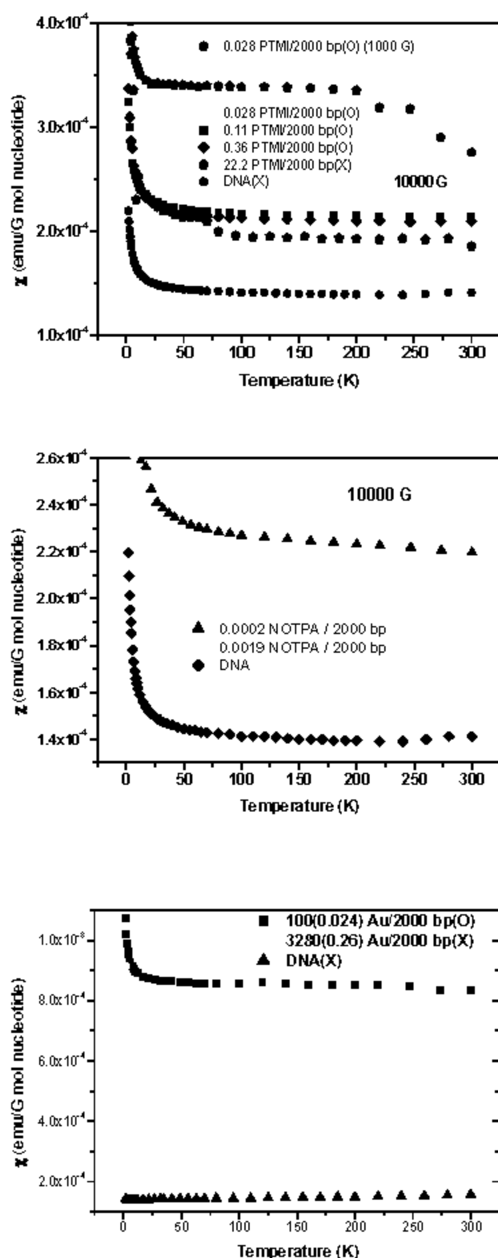

Figure 4. The intercalator type (Figure a, b, and c) and content dependence of the absolute susceptibilities (χ) vs. temperature (T) obtained from DC SQUID measurements. One can immediately notice that the less the intercalator level, the higher susceptibility becomes regardless of the type of intercalators.

CONCLUSION

This investigation clearly demonstrates that the π-stacked electronic structure of dry DNA or A-DNA facilitates magnetic interactions between intercalated spins. This conclusion is supported by the EPR studies and SQUID measurement of magnetization of A-DNAs intercalated with stable organic free radicals and also complexed with Au(III). The EPR study of modified A-DNAs strongly supports the heterogeneous nature of their morphology: they consist of the ordered and disordered regions. The magnetic interactions are stronger in the ordered region, where the triplet spin state is readily formed resulting in stronger magnetization. This physical picture endorses the observation that only A-DNAs doped with low levels of free radical compounds or complexed with low levels of Au(III) are attracted at room temperature to the commercial magnets. Most probably, a strong induced internal magnetic field is generated in the ordered region when A-DNAs are placed in a magnetic field[9]. High level doping or complexation will increase the number and size of disordered domains reducing the possibility for an overlapping in the π-stacked system. This, in turn, will reduce the ability for the DNA chain to mediate magnetic interactions between the intercalated or newly introduced spins.

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