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Electronic states of M-DNA incorporated with divalent metal ions

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ABSTRACT

DNA has attracted much interest as a material for nano science and technology. To unveil the intrinsic nature of DNA both in natural form and modified forms of M-DNA with a variety of divalent metal ions. From the magnetic and optical properties, it is concluded that the electronic states of natural salmon DNA is of semiconducting. Thus, only the hopping transport via excited states or impurity site like oxygens is expected. One of the efforts to introduce charge carriers into DNA, insertion of divalent metal ions, has been studied from magnetic, optical and structural aspects. It was concluded that the divalent metal ions are inserted in between the bases of a base pair, in place of hydrogen bonds, and the charge transfer from the metal ions to DNA occurs only in the case of Fe-DNA.

Keywords: DNA, charge transfer, divalent metal ion, magnetic susceptibility, ESR, optical absorption, STM

1. INTRODUCTION

As a container of genes, a vast number of researches on deoxyribonucleic acid (DNA) have been reported, so far, since the double helical structure was found in 1953 by Watson, Click, Wilkins and Franklin.[1–4] On the other hand, the physical properties, such as electrical and magnetic properties of pristine DNA (abbreviated as B-DNA) has also attracted our attention as one of the prospective materials for the nanotechnologies,[5–16] because of excellent ability of DNA in self-organization and designing, based on the complementation of the base pairing. The diverse conclusions, however, were reported in the electrical properties; metallic,[5] semiconducting,[6,8] vicinity effect of the Cooper pair in superconductor,[10] insulating.[11] The possible origins of these discrepancies with direct measurements of DNA double helix or DNA bundles would be due to salt residue, effective doping, for example, caused by electron bombardment of TEM, interaction with substrates and so on. At least in B-DNA a consensus has been reached on this issue that B-DNA is of semiconducting with the energy gap around 4.7 eV on the basis of transport, optical, magnetic and theoretical investigations.[7–9,11,17–19]

Thus, it is interesting for us to introduce the charge carriers into DNA from the viewpoint of nanotechnological application of DNA. Lee and coworkers reported a cooperative conformational change of DNA with divalent metal ions in 1993.[20] They proposed that the metal ions locate in between the bases of a base pair, from disappearance of the ^{1}H-NMR peaks corresponding to the hydrogen bondings connecting the bases.[20] This model is widely supported by NMR,[20] ESR[18,21–24] and IR analysis.[25] In 2001, Rakitin and coworkers suggested that DNA incorporated with Zn^{2+} could show a metallic transport nature.[15,26] Alexandre and coworkers[27] theoretically suggested the electronic states with the reduced energy gaps strongly dependent on the metal ion species for Zn^{2+}, Co^{2+} and Fe^{2+}. The magnetic studies on M-DNA with divalent metal ions, M=Ca, Mg, Mn, Co, Ni, Zn reported absence of the charge transfer from M to DNA bases, which suggests the energy gap keeps alive.[18,21–24] Very recently, on the contrary, Omerzu and coworkers have reported that Pauli-like magnetic susceptibility was observed in the specially prepared sample of dry, fluffy material as a mixture of Tris-HCl, $ZnCl_2$ and Zn^{2+}-DNA.[28] The conclusion is extremely interesting, but it is required to reexamine to resolve what is the spin carriers in Zn-DNA, where the valence of Zn has been confirmed to be Zn^{2+}, demonstrating the absence of charge transfer from Zn to DNA.[28] Another interesting fact is that Fe^{2+} ion incorporated into DNA transforms to Fe^{3+}, as evidenced by the ESR g-shift around the free electron g-value, the magnetization curves and the color change from weak greenish to light ocher, suggesting the electron transfer from Fe to bases.[21]

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In this report, a magnetic study with mainly ESR and SQUID techniques and a optical absorption study will be reviewed on pristine salmon DNA (B-DNA) and DNA incorporated with divalent metal ions (M-DNA), to unveil the intrinsic nature of B-DNA and M-DNA based on the reported works in Refs.[18,21–24]

2. EXPERIMENTAL

Salmon-sperm DNA in a form of fiber was purchased from Wako Pure Chemical Industries, Ltd., and oligo-DNA from Hokkaido System Science. M-DNA was prepared from the 1 mmol/L aqueous solution of DNA, mixed with the 5 to 10 mmol/L aqueous solution of MCl_2 (M = Mg, Ca, Mn, Fe, Co, Ni, Zn). Here, note that MCl_3 with M^{3+} did not form M-DNA composite. After stirring for 10 - 30 min, excess cold ethanol at -20 °C is poured into the transparent DNA-MCl_2 solution resulting in transparent precipitate for M-DNA, except for light pink/purple for Co-DNA, greenish for Ni-DNA and light ocher color for Fe-DNA. The residual MCl_2 is washed out thoroughly from the obtained precipitate in pure ethanol where DNA and M-DNA is insoluble. Thus obtained M-DNA were dried to form a film in the atmosphere. As a better way to obtain a homogeneous film, MCl_2 was removed from the mixed solution of M-DNA and MCl_2 with a dialyzer. The samples in the "wet" condition were saturated with water molecules at room temperature (RT) and sealed in a quartz tube for SQUID and ESR measurements. The "dry" samples were evacuated for one hour or more before sealed in a quartz sample tube. It was confirmed with ^{1}H NMR that the wet DNA contains about 12 H_2O molecules per each base pair in the double helix of DNA. In the dry state, it contains still about four water molecules. Circular dichroism (CD) spectra are examined to confirm the B-form of the double helix structure of B-DNA and M-DNA solutions. X-ray fluorescence analysis indicated that the molar ratio of phosphorous and metal ion was approximately two to one as expected for the metal ion located in the center of a base pair substituted for two sodium ions compensating two phosphoric anions in DNA backbone. UV/VIS absorption spectra are measured with UV-1700 (SHIMADZU).

3. NATURAL DNA

It has been controversial if natural DNA possesses intrinsic magnetic spins or not. The conclusion of this report is that the probable reason of this issue might be due to impurities contaminated or remained in the extraction processes of DNA and/or sample tube, adsorbed oxygen molecules, defects caused by irradiation, *etc.*

3.1 Electron Spin Resonance

In FIg. 1, ESR spectra is shown as an example of natural DNA, purchased from Wako Pure Chemicals, where Fe-DNA might be the contaminant to DNA. In Figs. 2 and 3, the other examples of salmon DNA purchased from

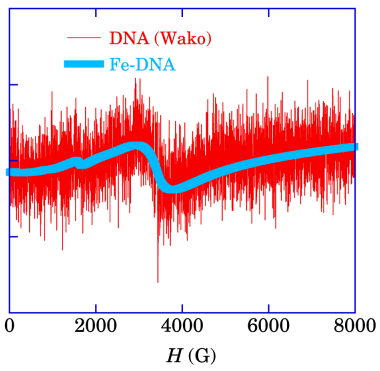


Figure 1. ESR spectrum of the salmon-sperm DNA under the dry condition purchased from Wako Pure Chemicals, taken with a Jeol FE-30 spectrometer: Microwave Power=1 mW, Frequency=9.447 GHz, Modulation Amplitude=0.5 mT, Gain=500, Time Constant=0.01 s, Average No=25 times. The signal of DNA around g=2 could be compared with that of Fe-DNA, suggesting Fe contamination in the extraction processes from salmon-sperm, resulting in a formation of Fe-DNA in part. The estimated number of spin S=5/2 is around 100 ppm/bp = 0.01 %/bp, which is enough low to consider that the origin would be contamination.

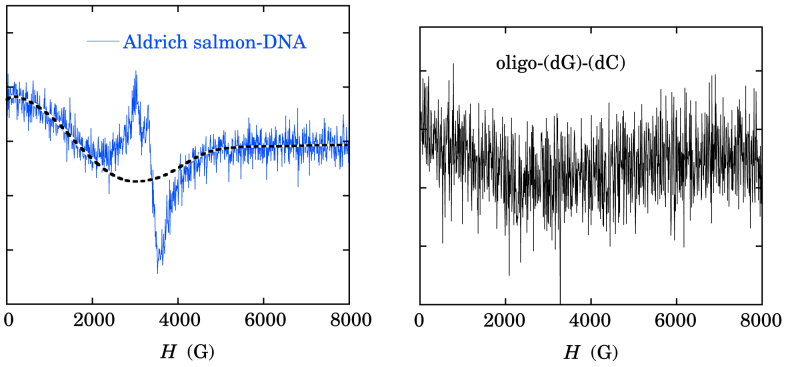


Figure 2. (Left) ESR spectra of the salmon DNA purchased from Aldrich with approximately the same sample quantity as in Fig. 1. All the measurement conditions are the same as Fig. 1, except for the Average No=10 times, suggesting several times larger signal intensity than the Wako case. In addition, more complicated features than that of the Wako case is found; Stronger signal around g=2, 340 mT, the other small, but sharp signal around 300 mT, and large baseline upturn to H=0 mT, which might be another signal around H=150 mT. This feature suggests that multiple sources of magnetic impurities are contained in this DNA.

Figure 3. (Right) ESR spectra of the oligo-(dG)-(dC) evacuated for 50 hours at 40 °C, taken with the same parameters as Fig. 2, purchased from Hokkaido System Science. The spectrum is similar to the broad signal centered at 150 mT in Fig. 2, but no signal around g=2, H=340 mT.

Aldrich and the oligo DNA, poly(dG)-poly(dC) purchased from Hokkaido System Science are demonstrated. The clear differences in these spectra for DNA with the different sources might be a hint to interpret the magnetic properties of the natural DNAs. It is known that the salmon-sperm DNA might contain Fe impurity in the extraction process, consistent with the Fe-DNA contaminant in the salmon-DNA (Wako). It is difficult to assign definitely the sources of the signals for the salmon-DNA (Aldrich), but the signals around H=340 mT would be concerned with Fe-DNA or other 3d transition metal impurities. It is noteworthy that the divalent metal ions could be inserted in between the bases of a base pair, which is highly stable and difficult to purify it.

The broad signals around H=150 mT in Figs. 2 and 3 might be caused by the magnetic impurity like Ni-DNA or Co-DNA, which gives a similar ESR spectrum. It is reasonable that the oligo-DNA contains only one magnetic species, since it was prepared by synthesis, although the details are not released. The difference in two salmon-DNAs in Figs. 1 and 2 could also be understood as the difference of the extraction procedure from the salmon-sperm. Important point is that the magnetic behavior as small as possible might reflect the intrinsic magnetic property of the natural DNAs if the base sequences have not critical role in magnetism of DNA. As a conclusion, the magnetic property of DNA would be nonmagnetic with some paramagnetic impurities in between the bases of a base pair, such as Fe, Co, Ni, *etc.*

Lee and coworkers reported that A-form DNA extracted from Salmon sperm shows the broad signal around 500 G together with the relatively narrow signals around 3000 G.[29] And long-term evacuation induced an enhancement of the ESR signal intensity. We reexamined a similar procedure, evacuation for 50 hours at 40 °C in the oligo-(dG)-(dC) and found negligible change of the spectrum as shown in Fig. 3.

3.2 UV/VIS absorption

Based on the diamagnetic nature of natural DNA, salmon DNA is concluded to be semiconducting. The optical absorption spectrum of the salmon DNA (Wako) in Fig. 4 also supports this conclusion. The definite energy gap of 4.7 to 4.8 eV corresponds to the π-π^* absorption band. It is noteworthy that the Hückel estimation of the HOMO-LUMO gap for the four bases reasonably agrees with the π-π^* band of DNA. This finding suggests that the interaction energy between the bases should be much less than the π-π^* band width of 0.5 eV. Since usually we measure the magnetic properties in a film form, the UV/VIS spectrum in the film has also been studied. The observed changes are 1) the tiny red shift of π-π^* band of 0.03 eV, and 2) the absorption tail into the energy gap. The red shift might be caused by some change of the base stacking interaction in a crystalline form, for

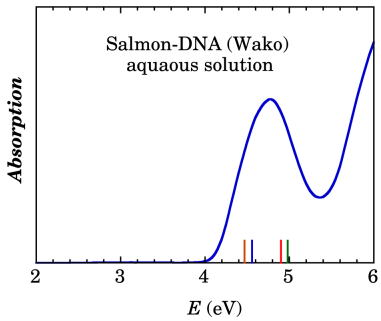


Figure 4. UV/VIS absorption spectrum of the salmon-DNA (Wako) in aqueous solution. The small bars indicate the position of HOMO-LUMO gaps for Guanine (blue), Cytosine (brown), Adenine (red) and Thymine (green) base molecules, estimated by Iguchi with a Hückel calculation.[9]

example, due to inter-helixs interaction. The origin of the absorption tail in the energy gap is not clear, right now. It is known that a film of single walled carbon nanotubes shows a similar effect to the present result.

3.3 Direct observation of DNA by STM

There is a long history to try to observe DNA directly by STM (Scanning Tunneling Microscopy) after the invention of the STM technique by Binnig and Rohrer and coworkers.[30] We have started a try to observe DNA with STM, keeping in mind its very high difficulty to realize and very low, almost zero possibility to resolve metal ions of M-DNA. As a reference, we have measured natural DNA at first with easyScan2 by Nanosurf.

The presence of DNA strands are easily confirmed with AFM, which can reflect actual dimension only in hight, but the tip width in width of images. Without dipping a HOPG substrate into a DNA solution, nothing like wires could be found with AFM. After dipping into an aqueous solution with appropriate DNA concentration, we could find a long straight wire with a height of 2 nm, consistent with DNA double helix.

Thus, we tried to apply STM to it. A lot of different images were found, like double helix like structure, bundles, and occasionally flat-ladder images with definite dimensions; 2 nm in width consistent with the diameter of double helical DNA, and 0.7 nm of periodicity along DNA backbone, as demonstrated in Fig. 5. In the center part of the flat-ladder DNA, a dark region could be recognized, which would correspond to hydrogen bonding part.

4. DIVALENT METAL ION INSERTION

Several types of investigations to introduce charge carriers into the natural DNA have been reported, so far. One is an effect of oxygen molecules. It was experimentally found that the electrical conductivity could be controlled

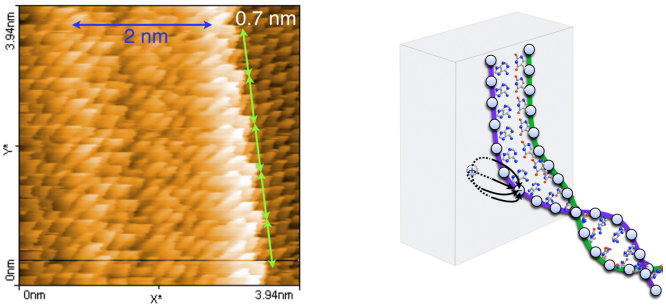


Figure 5. (Left) An example of STM images of the salmon DNA (Wako) with a novel flat-ladder form on HOPG (highly oriented pyrolytic graphite) substrate. (Right) A model for the formation of a flat-ladder DNA on a conducting substrate like HOPG when lift up the HOPG substrate from a dilute DNA aqueous solution, see text in detail. Nice images of Mn-DNA, Co-DNA have also been observed successfully and will be appear elsewhere.

by the oxygen concentration.[31] Starikov has theoretically proposed the hole carrier doping mechanism with oxygen molecules.[32,33] It was also reported that iodine molecules could supply hole carriers into the bases of DNA.[34,35] It is noteworthy that these hole injections could occur site-selectively, particularly in G-C unit. In the present report we will not discuss further on these points, but we concentrate on the divalent metal ion insertion to DNA.

Lee and coworkers have reported that the divalent metal ions, such as Zn^{2+}, Co^{2+} and Ni^{2+}, could be incorporated in between the bases of a base pair and made DNA conducting, useful for nanotechnological applications.[15,20,26] They reported that the incorporation of divalent metal ions, Zn^{2+}, Co^{2+} and Ni^{2+}, to DNA could be controlled by pH of solution and metal ion concentration. We started our study with the procedure as reported, however, it is not applicable to Mn^{2+}, particularly useful for ESR technique to study the electronic states of M-DNA. Thus, we developed the simple, but powerful new procedure to form M-DNA with a wide variety of divalent metal ions, as describe in § 2, which makes us possible to study the magnetic properties of M-DNA and the electronic states through them.[18,21–23]

4.1 Structure

Fig. 6 shows the schematic structures of DNA of B-form and M-DNA proposed by Lee et. al.[15,20,26] The divalent metal ions locate in the center of DNA double helix structure, instead of hydrogen bonds. They confirmed this model directly with the reduction and disappearance of ^{1}H NMR intensity assigned to the hydrogen bonds.[20] Furthermore, since the metal cations in M-DNA repel ethidium$^+$ cations in an ethidium bromide (EtBr) solution, the expected fluorescence enhancement for the ethidium binding DNA could not be observed with M-DNA.

We also found other facts which support this model, as follows.

1) ESR line width of Mn-DNA could be well accounted for by the electronic dipolar interaction with one-dimensional Mn chain separated by ≈ 3.4 Å.[18]

2) ESR lineshape definitely changes following the hydration conditions; the wet and the dry, as will be discussed in § 4.2.2.[21]

3) Mn ions could be incorporated not only into A-T and G-C pairs, but also into A-C and G-T pairs, which could never been joined by hydrogen bonds.[21]

4) If once Mn-DNA is dried enough, with a probable structure of A-form, similar to the hydrogen bonded natural DNA, Mn-DNA never return to the B-form, even with excess H_2O, making Mn-DNA gel-form. B-form comes back from A-form, only after complete dissolution in water.

5) Fe-DNA film could not be dissolved in water. If Fe ions locate outside of DNA, they could be hydrated and soluble.[21]

6) Mn-DNA is soluble in water. If Mn-DNA is dissolved into aqueous solution of excess quantity of NaCl to exchange the Mn counter ions in Mn-DNA to Na, a distinct change in magnetic property was not observed in the recrystallized film.

7) With STM, the images with periodic bright spots in the center part of the flat-ladder M-DNA were observed with reasonable measures, the wider distance between straight DNA backbones in M-DNA than in salmon DNA

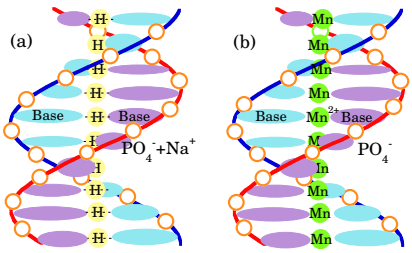


Figure 6. The schematic double helix structure of B-form DNA and Mn^{2+} ion inserted Mn-DNA. Lee and coworkers have proposed that metal ions are incorporated in between the bases of a base pair, instead of the hydrogen bonds.[20]

and longer periodicity of 0.8 nm along the DNA backbone, which is compared with 0.7 nm in salmon DNA. These increased dimensions might be caused by the insertion of divalent metal ions in between the bases of a base pair.

All these features support the proposed structure depicted in Fig. 6. The ratio of the number of divalent metal ions to phosphor was estimated with X-ray fluorescence analysis to be ≈ 0.5 and Na ions were not observed. On Mg-DNA and Ca-DNA, unfortunately, we have not direct structural evidence if Mg locates a similar position to the Mn and Zn cases, as shown in Fig. 6. STM study on these compounds will be undertaken in the near future.

4.2 Magnetic and Electronic Properties

If we have been successful to induce the charge carriers by the incorporation of divalent metal ions into the base pairs of DNA, we could expect the corresponding ESR spectra of electrons, such as π-electrons on the base pair. In this meaning, ESR is a useful technique to check the charge injection by doping. We will discuss details of the metal ion insertion to DNA.

4.2.1 Ca-, Mg-, and Zn-DNA

Kino and coworkers have proposed a possible charge injection mechanism to DNA on the basis of density functional theory (DFT) calculation for the metal ions of Ca, Mg, and Zn doped DNA.[36] They suggested that the hydrated metal ions located near the phosphate anions of the DNA backbone are stabilized as M^{2+}. However, in the anhydrous conditions, missing the hybridization of metal ion with the oxygen $2p$-orbitals of H_2O molecule, Zn and Mg ions become mono-cation, giving rise to hole doping to guanine base, but Ca ion does not.[36] Fig. 7 demonstrates ESR spectra for the dry state of M-DNA with M = Zn, Mg, and Ca, which is consistent with this theoretical suggestion; Zn and Mg doping seems to successfully induce new ESR signal, but Ca doping does not. However, we finally concluded these small ESR signals around $g \approx 2$ are impurities in origin, since the ESR intensities were not affected with any change of humidity, that is, any change of hydration.

Thus, the electronic states of M-DNA with Ca, Mg and Zn were interpreted to be semiconducting even with the divalent metal ion insertions, keeping the energy gap unchanged as observed in optical spectra (§4.2.4). The only effect in the divalent metal ion insertion is an ion exchange from two monocations, $2Na^+$, to single divalent cation, M^{2+}, to compensate two anions, $2PO_4^-$, in the DNA backbone. This conclusion contradicts the Ohmic charge transport observed in Zn-DNA.[18,26]

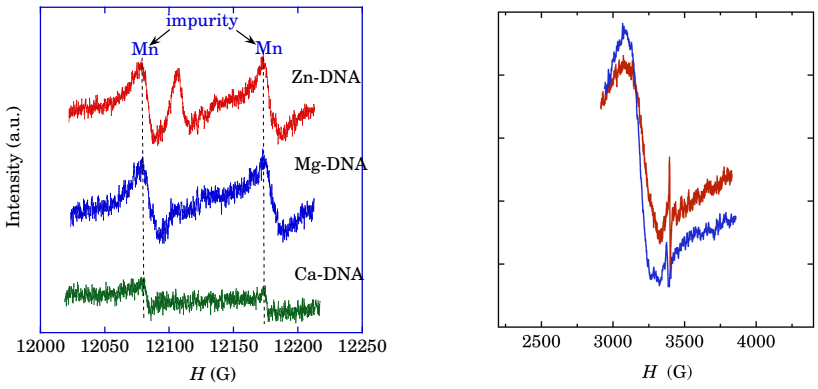


Figure 7. (Left) ESR derivative spectra in the dry state of Zn-DNA, Mg-DNA and Ca-DNA taken at Q-band (≈ 35 GHz) in the limited magnetic field range. Two signals around 12,080 G and 12,180 G might be the hyperfine structure of Mn ESR with the nuclear spin $I = 5/2$, originated from $MnCl_2$ impurity contained in the chemicals used to prepare M-DNA. Note the signals around 12,110 G with almost free electron g-value, prominent in Zn-DNA, only a trace in Mg-DNA and nothing in Ca-DNA.[18] This tendency is consistent with the proposed theoretical model,[36] but not with the humidity dependence of these signals.[18]
Figure 8. (Right) ESR derivative spectra in the dry state for two Zn-DNA samples at X-band.[18] This signal was understood as originated from the Cu^{2+} impurity spins because of small number of spins ≈ 0.2 %/bp. The sharp signal at $g \approx 2$ is unclear in origin.

When one observes ESR spectra of Zn-DNA in the wider magnetic field range, one frequently finds weak but broad ESR signals with larger g-factors than the free electron value $g \approx 2$ as shown in Fig. 8.[21] However, since it has been confirmed with the X-ray fluorescence analysis that the insertion rate of the divalent metal ions into DNA was nearly 100 %/bp, the ESR intensity for Zn-DNA was still enough weak, less than 1%/bp, compared with the expected ESR intensity.[18] However, there still remains a possibility that the strong electron-electron correlation effect might suppresses the induced susceptibility by the charge modification of the bases caused by the insertion of the divalent metal ions into DNA. Therefore, anyway, we have to conclude that the formation of metallic DNA would not be realized with the divalent metal ion insertion with Zn, Mg and Ca.

Very recently, Omerzu and coworkers have reported new results on Zn-DNA with a special sample preparation by a freeze-dry technique.[28] They insist that ESR spectra behave as almost temperature independent, like Pauli susceptibility in the usual metals, that is, the strongly correlated electron systems. They discussed that the spin carriers located not on the Zn^{2+} ions, thus, should be on DNA bases. Their result on the valence +2 for Zn ion is consistent with the absence of ESR spectrum corresponding to the full number of Zn ions and the UV/VIS absorption spectrum for Zn-DNA almost the same as that for the salmon DNA. Though this is a really interesting data and interpretations, the most important point should be answered what provides the spin carrier to DNA? The reason why is that Zn^{2+} plays no role for a modification of the electronic state in DNA.

4.2.2 Mn-DNA

Mn-DNA with $S = 5/2$ and $L = 0$ is a useful system with a good magnetic probe for ESR study. As demonstrated in Fig. 9, the single ESR spectrum at $g = 2.0$ is observed in Mn-DNA. Here, note the strong hydration effect to the ESR lineshape; sharp cutoff for the wet condition, and long tail for the dry. This finding might be understood with the isomeric structural transformation caused by hydration. It is well known that DNA transforms its double helix structure from B-form, as shown schematically in the bottom part of Fig. 11 familiar in the living cells, to A-form, the upper part of Fig. 11 stable in anhydrous circumstance.[4] If Mn-DNA shows a similar phase transformation to the natural DNA as in Fig. 11, the hydration change in Fig. 9 is consistent with the proposed M-DNA structure of Fig. 6 where the divalent metal ions locate in between the bases of a base pair, instead of the imino hydrogen bond.[20]

Fig. 10 provides an easy way to analyze visually the ESR lineshape. When the lineshape is Lorentzian, typical of the 3D network spin systems, the inverse of the normalized intensity holds the relation,

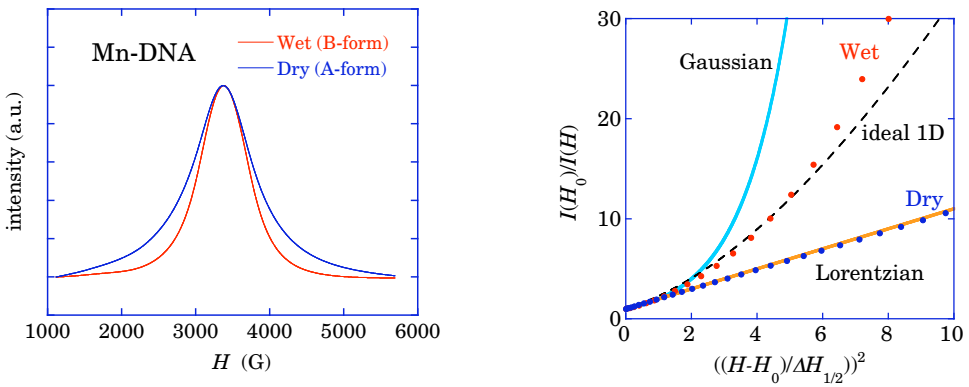


Figure 9. (After Ref.[21]) (Left) The ESR absorption spectra of Mn-DNA both in the wet and the dry conditions taken at X-band around 9.4 GHz. Note the definite difference in lineshape caused by the hydration conditions.
Figure 10. (After Ref.[21]) (Right) The characteristic plot for ESR lineshape analysis. The abscissa is a square of the magnetic field deviation from the resonance field H_0 normalized by the half width at half height $\Delta H_{1/2}$ of the absorption spectrum. The ordinate is the inverse signal intensity $I(H)$ normalized by the center height $I(H_0)$. The wide spectrum for the dry condition is reproduced well with the Lorentzian lineshape, but that for the wet condition with the characteristic lineshape for the 1D exchange narrowing case.[21,37] See the Fig. 11 and text in detail.

$$\frac{I(H_0)}{I(H)} = 1 + ((H - H_0)/\Delta H_{1/2})^2. \quad (1)$$

Thus, $I(H_0)/I(H)$ shows a straight line against the square of the field deviation for Lorentzian, as in the lowermost line assigned to "dry" in Fig. 10. In contrast, we have the intermediate lineshape in between Lorentzian and Gaussian for the spins confined in the 1D chains separated by more than 2 nm from each other as in "wet" Mn-DNA,[21,37] corresponding to "ideal 1D" in Fig. 10. These features ideally correspond to the structural transformation caused by the hydration, as described in Fig. 11. The wet Mn-DNA with the B-form, equivalently 1D array of $S = 5/2$ spins, shows almost "ideal 1D" lineshape. In contrast, the dry Mn-DNA with the A-form or a helical structure of spins gives Lorentzian lineshape, because the helical spin chains could form a 3D network of spins.

Mn-DNA shows the Curie-Weiss behavior with $\Theta \approx$ -1 K for the wet and $\approx$ -2 K for the dry. The increase of interaction in the dry Mn-DNA would be consistent with the increase in the number of neighboring Mn spins because of the helical spin structure. As expected in the 3D coupled spin system, we observed a peak of the specific heat around 0.4 K as shown in Fig. 12, which would correspond to antiferromagnetic long-range ordering of the Mn ions, consistent with the steep increase of ESR line width below 50 K.[21] In the "wet" Mn-DNA, no definite change of the ESR line width was found down to 2 K, reasonable for the 1D magnetic systems.

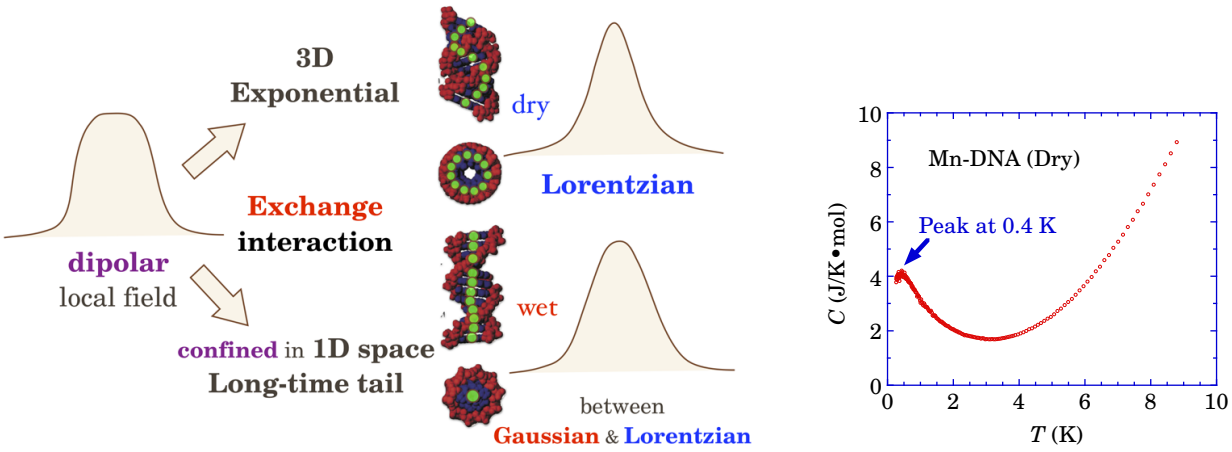


Figure 11. Schematic description of the exchange narrowing in the B-forn and the A-form Mn-DNA.
Figure 12. Specific heat of the "dry" Mn-DNA at low temperatures. In the lower temperatures below 4 K, where the lattice heat capacity disappeared, a peak around 0.4 K is found, due to some long range magnetic ordering.

4.2.3 Hyperfine splitting: Electronic states of Mn ion in Mn-DNA

In the aqueous solution of Mn-DNA, ESR spectrum in Fig. 9 splits into six peaks by the hyperfine interaction with $I = 5/2$ of a Mn nucleus, as demonstrated in Fig. 13. With a rapid tumbling motion of Mn-DNA in a solution, only the anisotropic dipolar interaction is averaged out, resulting in six hyperfine split spectra, because the hyperfine interaction is isotropic, insensitive to the tumbling motion. The separation of the center two peaks gives a hyperfine parameter, A_0,

$$H = A_0 \mathbf{I} \cdot \mathbf{S}. \quad (2)$$

The parameter A_0 reflects the ionicity of Mn bonding with surrounding atoms. For the Mn ions with ionic bonding in CaF_2 matrix, $A_0 \approx 100$ G, but in CaS with increased covalent bonding nature, A_0 reduces down to 80 G. In the Mn-DNA case, $A_0 = 96$ G, much close to the CaF_2 case, suggesting the bonding nature of Mn ions in Mn-DNA would be highly ionic. This analysis will be appear elsewhere.

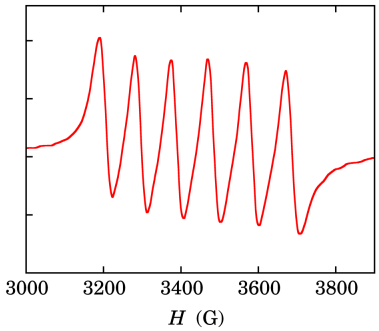


Figure 13. ESR spectra of Mn-DNA in a aqueous solution. The separation of the center two peaks contains useful information on the bonding nature of Mn ion.

With this conclusion, we have tried to form Mn-DNA with unrealistic pairing on the basis of the complementary rule, poly(dA)-poly(dC) and poly(dG)-poly(dT) with $MnCl_2$. The magnetic properties of Mn-poly(dA)-poly(dC) have been confirmed to reproduce all of the Mn-DNA results as reported here, including the hydration effect in Fig. 9, which strongly suggests that Mn ions actually work as the ionic binder for any bases to form base pairs.[21] This is one of the reasons for the heavy metal ions to disturb heredity information.

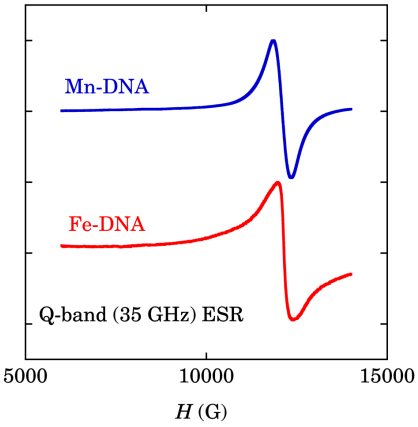
4.2.4 Optical absorption spectra in M-DNA

One of the basic parameters, optical absorption has been studied in aqueous solutions of M-DNA with several species of divalent metal ions, M. On the basis of the conclusions mentioned above, usual divalent metal ions in M-DNA are ineffective to modify the electronic states of DNA, such as charge injection to DNA. Actually, the optical absorption spectra for M-DNAs are the same as that of DNA in a aqueous solution; the definite semiconducting energy gap of 4.7 eV. Only the exception is Fe-DNA, where Fe^{2+} transforms to Fe^{3+} in Fe-DNA (§ 4.2.5). Characteristic features in Fe-DNA are the suppression of interband absorption and the tail into the energy gap. One possible reason why the interband absorption could be suppressed is due to the filling of π^* band of the nucleobases by the charges transferred from Fe^{3+} in Fe-DNA.

4.2.5 Fe-DNA

All the M-DNAs discussed in the former sections have never shown any traces of charge injection from the divalent metal ions to the DNA bases or backbones. Thus, no essential change in the electronic structures of M-DNA can be expected, keeping the energy gap unchanged, as confirmed in the optical absorption of M-DNA in § 4.2.4. Very interestingly, we found one exception to this category, Fe-DNA. Fe-DNA was prepared with the same procedure as the others: solution of DNA is mixed with $FeCl_2$ solution. The solution is transparent and very light greenish in color. However, the solution changes color to ocher typical of Fe^{3+} ions, with time or with pouring cold alcohol to precipitate the sample. Actually, other physical properties also suggested that Fe^{2+} ions in the solution were converted into Fe^{3+} ions in the dried Fe-DNA film with the color shown in Fig. 14.[21] Thus, it is really interesting where the charge released from Fe^{3+} transferred: nucleobases? or oxygens? The optical absorption spectrum of Fe-DNA suggests that the π^* band might be filled partly, because the interband transition was suppressed from that of DNA.

Figure 14. (Left) $FeCl_3$, (Center) $FeCl_2$, (Right) Fe-DNA



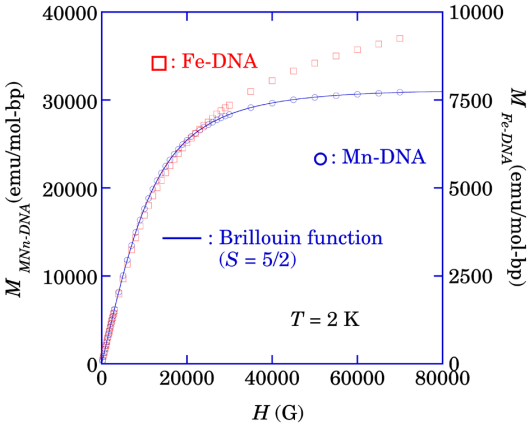


Figure 15. (After Ref.[21]) (Left) The ESR spectrum of Fe-DNA taken at Q-band ($\approx$ 35 GHz, corresponding to 12,500 G for $g = 2$), together with Mn-DNA spectrum. From g-factor nearly equal to 2, the electronic states of Fe ion are suggested to be Fe^{3+} with $S = 5/2$ for high spin state, as same as Mn^{2+} ion, and $S = 1/2$ for low spin state, depending on the crystalline field, where each Mn ion locates.
Figure 16. (After Ref.[21]) (Right) Magnetization curve at 2 K for Fe-DNA and Mn-DNA. M-H curve for Mn-DNA is nicely reproduced with a $S = 5/2$ Brillouin function, but not in Fe-DNA. Both of ESR spectrum in Fig. 15 and M-H curve in Fe-DNA could not be reproduced with a single species of spin, $S = 5/2$.

Figure 15 demonstrates one of the evidences for the charge transfer from Fe^{2+}. Since Fe^{2+} has six d-electrons, $S = 2$ and $L = 2$ are expected for the high spin state. Non-zero orbital angular momentum produces a resonance shift caused by the spin-orbit interaction. Thus, only Fe^{3+} ions provides ESR spectrum at $g = 2$, the free electron g value. Therefore, the observed signal at $g \approx 2$ in Fig. 15 is a strong evidence for the Fe^{3+} in Fe-DNA. It is not possible to reproduce the M-H curve of Fe-DNA only with the high-spin of Fe^{3+}, S=5/2, but the low-spin of Fe^{3+}, S=1/2 is also required. The origin of these spins is not clear now.

We do not have definite evidence for the location where the electron transferred from Fe^{2+}. One possible candidate is the base π band. In this case, ESR from π-electron might be observed around $g \approx 2$. The observed ESR signal in Fig. 15 suggests that the lineshape is not simply reproduced by a single Lorentzian, but composed of 3 components to reproduce the spectra successfully.[21] On the other hand, the electrical conductivity did not show any enhancement over B-DNA, which suggests the presence of the strong electron-electron correlation effect in the baes π-electron band.

5. SUMMARY

Magnetic and optical absorption studies have been applied to investigate the electronic states of B-DNA and M-DNAs incorporated with the divalent metal ions. The conclusion on B-DNA is that the electronic states are semiconducting with the energy gap of 4.7 eV. The issue on the magnetic behavior of the natural DNA was resolved by comparing the magnetic behaviors of DNAs from several different sources. The conclusion is that the ESR signals observed in natural DNA are impurity in origin. The DNAs from different origins with different extraction procedures provide different behavior in the ESR spectrum.

Almost all M-DNAs, inserted with the divalent metal ions, have still large energy gap as same as B-DNA. The first effect of the divalent ion insertion might be ion exchange from $2Na^+$ to one M^{2+}, keeping the electronic states less modified. Only the exception, Fe-DNA was found, where the charge transfer from Fe^{2+} to e^-+Fe^{3+} has occurred. From the suppression of the interband absorption, the location of the transferred electrons from Fe^{2+} has been suggested to be the nucleobase π band. Further investigation on the electronic states of M-DNA and other charge transfer doping mechanism will be proceeded in future.

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