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# Electronic states of DNA and M-DNA studied by optical absorption

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To unveil the electronic states of divalent metal ion incorporated M-DNAs, where M is Mg, Mn, Ni, Co or Fe, optical absorption spectra have been studied in aqueous solutions of single-stranded (SS) 30-mer DNA of poly(dA) (adenine), poly(dG) (guanine), poly(dT) (thymine) and poly(dC) (cytosine), salmon-sperm DNA (B-DNA) and M-DNA. The absorption spectrum of the double-stranded (DS) B-DNA can be reproduced with the sum of the four absorption spectra of the SS oligo-DNAs in the ratio corresponding to the composition of B-DNA. This observation suggests that the interactions between complementary strands of DS DNA are negligibly weaker than the bandwidths of the optical spectra. In the metal-incorporated M-DNAs except for Fe-DNA, the absorption spectra show no significant qualitative change from that of B-DNA. Quantitatively, however, the absorption intensity decreases by ≈15 % uniquely in a DS poly(dA)-poly(dT) solution with adding $MCl_2$, while nothing happens quantitatively and qualitatively in any SS oligo-DNA and DS poly(dG)-poly(dC) solutions, suggesting some suppression of the electronic excitation only in the A-M-T complex. In contrast, remarkable differences have been observed in Fe-DNA, prepared with $FeCl_2$ and B-DNA. New absorption bands appear in the intra-gap energy of Fe-DNA, in addition to the suppression of the inter-band absorption peak of DNA at 4.8 eV. The intra-gap absorption is attributed to the appearance of $Fe^{3+}$ species with the same spectral feature as that of $FeCl_3$, that is, purely ionic $Fe^{3+}$ species. This observation suggests that $FeCl_2$ + B-DNA forms Fe-DNA with hydrated $Fe^{3+}$ ions with ionic bonds. Thus, it is concluded that the charge transfer from $Fe^{2+}$ to DNA has occurred in Fe-DNA and that the transferred charges are expected to be located in the nearby bases.

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## I. INTRODUCTION

Physical properties of natural deoxyribonucleic acid (DNA), and M-DNA inserted with divalent metal ions have attracted much interest in recent years because of scientific curiosity and potential applications to self-assembled nanostructure, nanowire for nanoelectronics, *etc.*[1–16] The reports of direct measurement with nanotechnology on the electronic properties of natural DNA extracted from λ-phage, calf thymus and salmon-testis, concluded diverse nature to be insulating,[8] semiconducting,[3,5,10,13] metallic,[1,7,11,14] and induced superconducting.[7] Such diversity would result from salt residues, electron bombardment by an electron microscope, effective doping, *etc.*[17] Consequently, there is a consensus that the nature of charge carriers in the natural DNA is semiconducting with $E_g \approx 4$ eV.

Several efforts to introduce charge carriers into the base π-band of DNA have been reported so far. One is the insertion of a divalent metal ion between each complementary base pair of a DNA double helix, adenine-thymine (A-T) or guanine-cytosine (G-C), as schematically shown in Figs. 1 and 2. The resulting DNA structure is called as M-DNA, where M is the divalent metal ions.[6,10–14,18–21] The other strategy is the chemical doping with iodine or oxygen[22–25] and FET configurations.[26] Rakitin and coworkers reported that Zn-DNA have a Ohmic *I-V* characteristics, which is in sharp contrast with the natural DNA and concluded that Zn-DNA is engineered conducting DNA nanowire.[6] However, it is also reported with a non-contact measurement study free from contact and contamination problems that M-DNA with Zn, Ca, Mg or Mn does not carry the paramagnetism accompanying the charge injection to DNA, suggesting no charge injection was established with these divalent metal ions.[10,13–15,20] This fact means that the divalent ions in M-DNA simply replace two sodium ions in $Na^+$-DNA, keeping the charge balance unchanged as shown in Fig. 2. In contrast, it has also been reported that the charge transfer from $Fe^{2+}$ to DNA actually occurred in Fe-DNA.[15,27,28] The conductivity enhancement in Fe-DNA has not been found probably because of too much strong correlation of the π electrons. On the other hand, Omerzu *et al.* have reported a new sample preparation technique of a freeze-drying method applied to

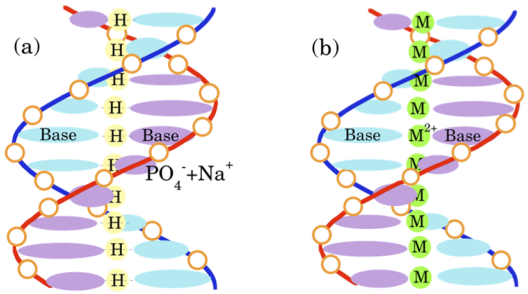


FIG. 1: (Color online) Schematic structures of (a) B-DNA and (b) M-DNA in B-form, where the ovals represent the bases. Each divalent metal ion M is inserted between the bases of a base pair as described in Fig. 2.[18]

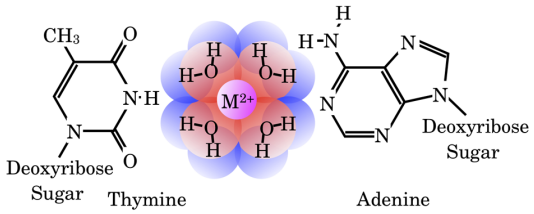


FIG. 2: (Color online) Model structure of metal ion incorporated base pair, Adenine-M-Thymine (A-M-T).[20] Hydrogen atoms have remained, but two hydrogen bonds are disconnected by the insertion of a large hydrated metal ion. Counter anions are located on the two DNA backbones, which are linear polymer chains with alternatively connected $PO_4^-$ anion and deoxyribose sugar.

Zn-DNA, which provides ESR spectra typical of strongly correlated electron systems.[29] They reported that the microwave conductivity of the mixture sample in a powder form is enhanced a little. This finding contradicts the reported results obtained by a conventional sample preparation technique,[15,20,27,28] suggesting that the electronic states of M-DNA are not unique but are dependent on the sample preparation conditions. Although several theoretical approaches to obtain the electronic states of M-DNA have been reported, the experimental results for the electronic states of the divalent metal ions are still crucially important for predicting theoretically the actual properties of M-DNA.[16,30,31]

In this report, we demonstrate optical absorption spectra of DNA and M-DNA to unveil the electronic states of the metal incorporated DNA, as a candidate of engineering materials. It is definitely confirmed that Fe-DNA is the first example of the charge transfer from the divalent metal ions to DNA.

## II. EXPERIMENTAL

Salmon-sperm DNA (B-DNA) and single-stranded (SS) oligo-DNAs (poly(dG), poly(dA), poly(dC), and poly(dT) with 30 base pairs) are provided from Wako Pure Chemical Ind. Ltd. and Hokkaido System Science Co., Ltd., respectively. M-DNA is prepared from an aqueous solution of DNA with $MCl_2$ in the molar ratio of 1:10. Here, note that $MCl_3$ with $M^{3+}$ did not form M-DNA composite. Except for Fe-DNA, excess cold ethanol at -20 °C is poured into the DNA-$MCl_2$ solution resulting in precipitate. The residual $MCl_2$ in the precipitate is washed out thoroughly with pure ethanol where DNA is insoluble. After that, dried in air and stored in a refrigerator. Optical absorption measurements were carried out in an aqueous solution of the stored precipitate with concentrations around 0.05 mM/L. For Fe-DNA, this technique was not applicable because the precipitate is insoluble in water again. Dialysis is used to remove excess $FeCl_2$ from an aqueous solution of Fe-DNA and $FeCl_2$ for optical measurements. Shimazu UV-1700 spectrometer was used for optical absorption measurements. X-ray fluorescence analysis indicated that the ratios of phosphorous and metal is approximately 2 to 1 as expected for the metals located in the center of a base pair substituted for two sodium ions compensating two phosphoric anions in DNA backbone.

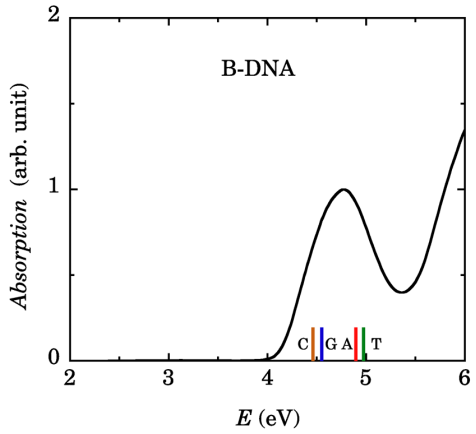


FIG. 3: (Color online) Absorption spectrum in an aqueous solution of B-DNA. The small bars in the bottom represent the HOMO-LUMO gaps for the four bases, cytosine (C), guanine (G), adenine (A) and thymine (T) from the left to the right, calculated by Iguchi with the Hückel approximation.[32]

## III. RESULTS AND DISCUSSION

### A. B-DNA and oligo-DNAs

Figure 3 shows the absorption spectrum of B-DNA. The energy gap $E_g$ is 4 eV from the absorption edge, and the gap energy of HOMO (Highest Occupied Molecular Orbitals) and LUMO (Lowest Unoccupied Molecular Orbitals) bands is 4.8 eV from the peak energy. The HOMO-LUMO gaps estimated from the Hückel calculation[32] for each base, G, C, A and T are also plotted in the bottom of Fig. 3, which are consistent with the absorption band of B-DNA.

Figure 4 represents the absorption spectra of SS oligo-DNAs with characteristic features of the bases, which can be compared with the Hückel estimation of absorption energies for each base molecule.[32] Good agreement is found between the absorption spectra and the Hückel estimation except for poly(dT). This discrepancy would be related to a methyl function of thymine base, which is not taken into account in the Hückel estimation in ref. 32. Figure 5 demonstrates the absorption spectra of the DS poly(dG-dC) and the DS poly(dA-dT). The spectrum of each DS oligo-DNA can be reproduced well with a sum of the spectra for the corresponding SS oligo-DNAs, as demonstrated by the dotted curve in Fig. 5. This agree-

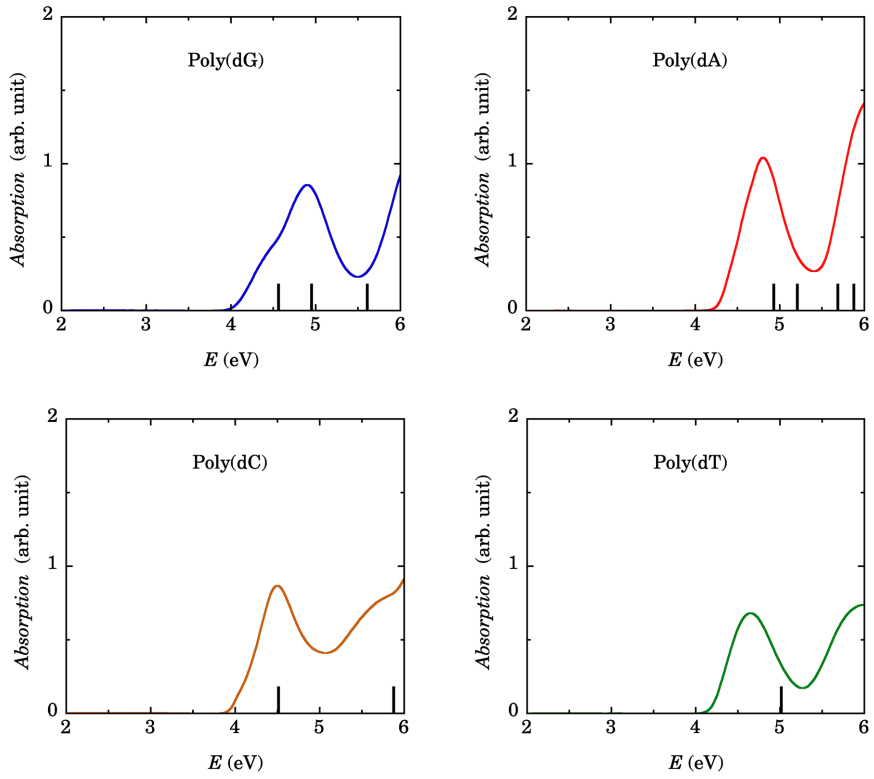


FIG. 4: (Color online) Absorption spectra in aqueous solutions of the four 30mer SS oligo-DNAs, poly(dG), poly(dA), poly(dC) and poly(dT). The bars in the bottom of each panel represent the Hückel estimation.[32] The leftmost bar represents the energy difference between LUMO and HOMO. The second bar represents the difference of LUMO and 2nd HOMO for poly(dG) and poly(dA), and 2nd LUMO and HOMO for poly(dC). The third bar shows that of LUMO and 3rd HOMO for poly(dG) and 2nd LUMO and HOMO for poly(dA). The forth bar for poly(dA) corresponds to the difference of LUMO and 3rd HOMO.

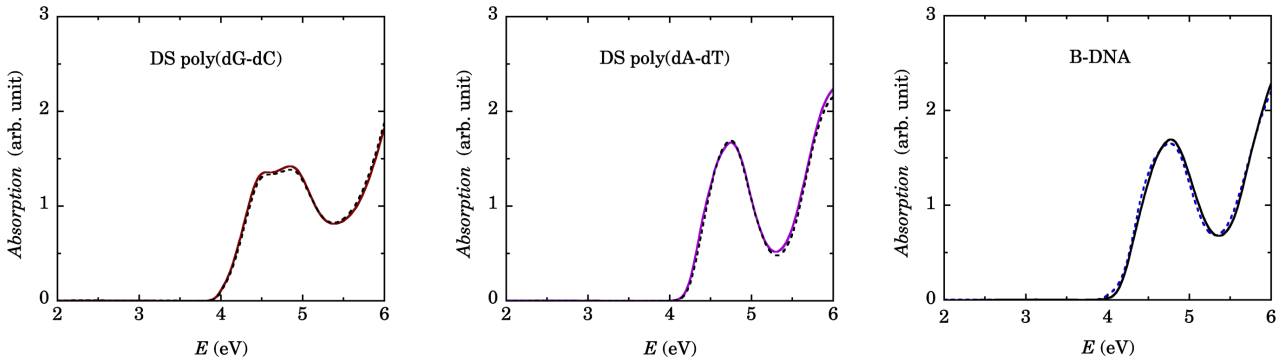


FIG. 5: (Color online) Absorption spectra in aqueous solutions of DS poly(dG-dC) (left) and DS poly(dA-dT) (center) are shown together with the sum of the corresponding spectra of SS oligo-DNAs in Fig. 4 by the dotted curves. The spectrum of B-DNA (right) is compared with the sum of the spectra of the DS poly(dG-dC) (left) and the DS poly(dA-dT) (center) with the ratio of 0.37:0.63 by the dotted curve, which is in good agreement with the experimentally observed ratio of 0.4 (GC) : 0.6 (AT) in the salmon-sperm DNA.[33]

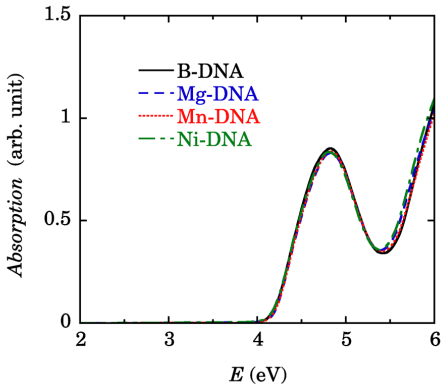


FIG. 6: (Color online) Absorption spectra in aqueous solutions of Mg-DNA, Mn-DNA and Ni-DNA, together with that of B-DNA. The peak intensity is normalized to compare the spectral shape. Co-DNA and Zn-DNA show almost the same spectra as these. However, Fe-DNA behaves differently as discussed in III C. Omerzu *et al*. reported red shifts of the peak position up to 0.1 eV in Zn-DNA.[19] Such a large shift is not found in the present study including Zn-DNA.

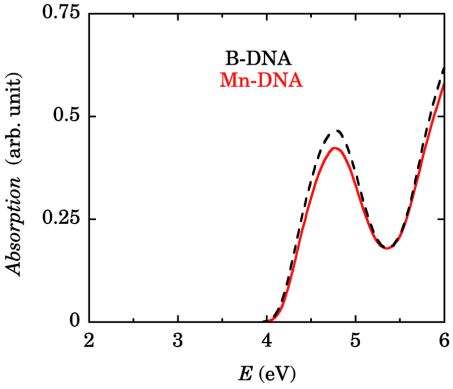


FIG. 7: (Color online) Absorption spectra in an aqueous solution of B-DNA (dashed curve) and Mn-DNA+unreacted $MnCl_2$ (solid curve) prepared by *in-situ* adding of $MnCl_2$ into the B-DNA.

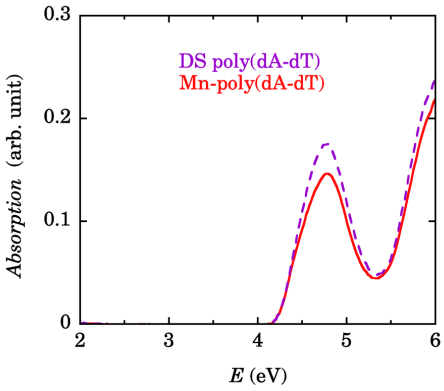


FIG. 8: (Color online) Absorption spectra in aqueous solutions of DS poly(dA-dT) (dashed curve) and DS poly(dA-dT) after *in-situ* $MnCl_2$ addition (solid curve). A definite suppression of the absorption area by 15 % below 5.5 eV was observed.

ment suggests that the interaction between the bases in a complementary pair is so weak. The full band width at half maximum of the SS oligo-DNA is about 0.5 eV and the interaction between the bases in a double stranded DNA is much smaller than 0.5 eV.

### B. Mg-DNA, Mn-DNA and Ni-DNA

#### 1. *Absorption spectra*

The absorption spectra of the metal incorporated DNAs are shown in Fig. 6. Any meaningful change of the spectra from B-DNA is not found in these complexes. Except for Fe-DNA, this observation is common to the M-DNAs with M = Mg, Mn, Zn, Ni or Co. This fact is consistent with the conclusion deduced from the magnetic study on M-DNA prepared by the same technique as the present study. The magnetic properties of M-DNAs with M = Mg, Ca, or Zn are basically diamagnetic, which is consistent with the proposed model of ionic bonding with the hydrated divalent metal ions in M-DNA.[20,27] In M-DNAs with transitional 3*d* elements of Mn, Ni, or Co, the observed magnetic properties are well understood only with 3*d* electron spins and without the spins of $\pi$ electrons transferred to the bases. This conclusion suggests that the charge injection from the divalent metal ions to DNA didn't occur, but a simple ion exchange took place.[10,13,15] As a result, any significant change of the electronic states of DNA was not attained by the divalent metal ions of Mg, Mn, Zn, Ni and Co incorporated into DNA with the ethanol precipitation technique applied in the present study. The other preparation technique of Zn-DNA samples proposed by Omerzu *et al*.[29] with a freeze-drying method is expected to provide some change of the electronic states of DNA. The investigation to unveil the electronic states of Zn-DNAs with the freeze-drying method is in progress.

#### 2. *Quantitative spectral change*

On the shape of the absorption spectra, any meaningful changes were not found in M-DNA except for Fe-DNA. However, the definite suppression of the inter-band absorption peak is found in Mn-DNA and Mn-poly(dA-dT), but is nothing in Mn-poly(dG-dC).

Quantitative change of the absorption spectrum of an aqueous DNA solution before and after *in situ* adding of $MnCl_2$ powder (approximately 0.5 mM, ten times of DNA concentration) into the solution is investigated for

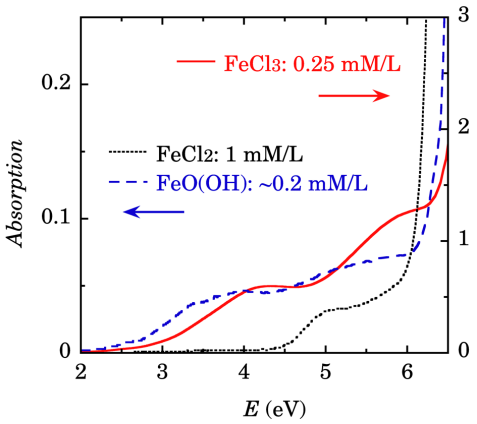


FIG. 9: (Color online) Absorption spectra in aqueous solution of $FeCl_3$, $FeCl_2$ and FeO(OH). The absorption intensity of $FeCl_3$ is stronger than the others more than 10 times. Although the valence of Fe is +3 in both of $FeCl_3$ and FeO(OH), the spectra differ qualitatively from each other, so that we can easily discriminate them.

B-DNA, SS oligo-DNAs and DS oligo-DNAs. Figures 7 and 8 show the suppression of the absorption spectrum in the Mn-DNA and the Mn-poly(dA-dT) solutions of approximately 0.05 mM. The dashed curves of B-DNA were taken before adding $MnCl_2$ and the solid curves describe the spectra of Mn-complexes after *in-situ* adding of $MnCl_2$. The spectral area below 5.4 eV in Mn-poly(dA-dT) is reduced to 85 % of the spectrum before adding $MnCl_2$.

It should be stressed that the addition of $MnCl_2$ to each of "SS" oligo-DNA has nothing of effect qualitatively and quantitatively. A simple sum of the absorption spectra of SS oligo-DNA and $MnCl_2$ is observed, which is substantially SS oligo-DNA because of transparency of $MnCl_2$ below 6 eV. The absorption spectrum of DS poly(dG-dC) also shows nothing of change with addition of $MnCl_2$. Thus, the spectrum is modified only in the A-Mn-T complexes, in which the inter-$\pi$-band absorption is suppressed by 15 %. This suppression in the A-Mn-T base pairs is fully accountable for the spectral suppression in B-DNA with $MnCl_2$ in Fig. 7. A similar suppression is also found in Fe-DNA. It is open question what is the suppression mechanism in the A-Mn-T base pair.

### C. Fe-DNA

One of the peculiar M-DNAs is Fe-DNA. An aqueous solution of B-DNA and $FeCl_2$ generates $Fe^{3+}$-DNA accompanied by the charge transfer from $Fe^{2+}$ to DNA. It was confirmed that a valence of Fe in Fe-DNA is +3 in terms of the ESR observations at the free electron $g$ value, $g \approx 2$, typical of $S = \frac{5}{2}$ spin systems such as $Fe^{3+}$.[15,28] X-ray fluorescence analysis indicated that the molar ratio of P and Fe was approximately 2 to 1 and that of Cl was less than 3 % against Fe, that is, only a trace. Thus, the transferred electron from $Fe^{2+}$ is expected to be located not on Cl ions, but on the bases.

#### 1. *Absorption spectra of $FeCl_2$, $FeCl_3$ and FeO(OH)*

Before discussing the absorption spectra of Fe-DNA, it is essential to study the spectra of Fe in several possible forms, $FeCl_2$, $FeCl_3$ and FeO(OH), as shown in Fig. 9. FeO(OH) is an oxidized product of $FeCl_2$ in "hot water" and prepared from an $FeCl_2$ aqueous solution by keeping it at the elevated temperature of 50°C for 30 min. Figure 10 shows the time evolution of the $Fe^{3+}$ concentration at room temperature in three aqueous solutions containing $FeCl_2$ only, DS poly(dG-dC) + $FeCl_2$, and DS poly(dA-dT) + $FeCl_2$. In the aqueous solution of $FeCl_2$ only, nothing happens for 30 min at room temperature, which is sufficiently long to prepare the samples in the present study. Thus, all the Fe incorporated DNAs in the present study do not contain FeO(OH) as an $Fe^{3+}$ source. It is noteworthy that *DS DNA* is essential for the creation of $Fe^{3+}$ in the aqueous solution of $FeCl_2$, and that the spectral shape of $FeCl_3$ reproduces well the incremental part of the absorption spectra. These observations suggest that the transformation of $Fe^{2+}$ into $Fe^{3+}$ requires the presence of base pairs, resulting in the complexes of A-Fe-T and G-Fe-C, which is consistent with the model structure of M-DNA: each metal ion is located between the bases of a base pair, as shown in Fig. 2 and the base pairs would work as a container of the charge, which has been transferred from $Fe^{2+}$.

Three spectra in Fig. 9 guarantee that we can discriminate the species of Fe ions from each other in terms of the spectral shape. The difference of $FeCl_3$ from FeO(OH) in the spectral shape for $Fe^{3+}$ can be attributed to the character of bonds: purely ionic character of $Fe^{3+}$ in $FeCl_3$ and covalent character in FeO(OH). Thus, it is concluded that $Fe^{3+}$ in Fe-DNA has also ionic character with spherical wavefunction, as $Fe^{3+}$ in $FeCl_3$. Then, the spectrum of $Fe^{3+}$ in $FeCl_3$ will be utilized as the reference spectrum for $Fe^{3+}$ in Fe-DNA.

#### 2. *Absorption spectra of Fe-DNA*

The absorption spectra of Fe-DNA prepared with the dialysis method from an aqueous solution of $FeCl_2$ and B-DNA is shown in Fig. 11. A definite change from that of B-DNA is clearly demonstrated: the suppression of the inter-$\pi$-band absorption similar to the Mn-DNA case in Fig. 7 and the appearance of the intra-gap absorption. These features depend on a kind of base pair, G-Fe-C or A-Fe-T, as demonstrated in Fig. 12. The solid curves represent Fe-oligo-DNAs at 30 min after adding $FeCl_2$ into the aqueous solutions of DS oligo-DNAs. The original spectra before adding $FeCl_2$ are shown by the dashed curves. The solid curves contain the spectra of unreacted $FeCl_2$ in addition to that of Fe-oligo-DNA cre-

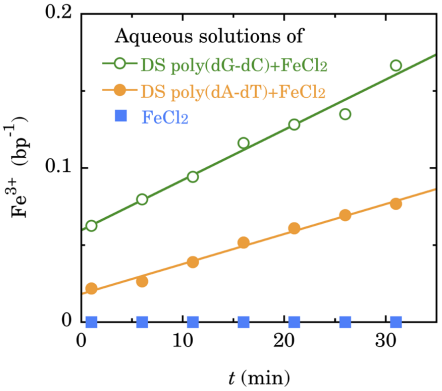


FIG. 10: (Color online) Time evolution of $Fe^{3+}$ concentration per base pair (bp) in aqueous solutions of $FeCl_2$, DS poly(dG-dC)+$FeCl_2$ and DS poly(dA-dT)+$FeCl_2$. $FeCl_2$ is principally transformed to FeO(OH) at elevated temperatures, but does not at room temperature for 30 min. The incremental spectra of DS oligo-DNAs with $FeCl_2$ are well reproduced by the spectrum of $FeCl_3$, suggesting the electronic states of Fe-oligo-DNA is of ionic in character.

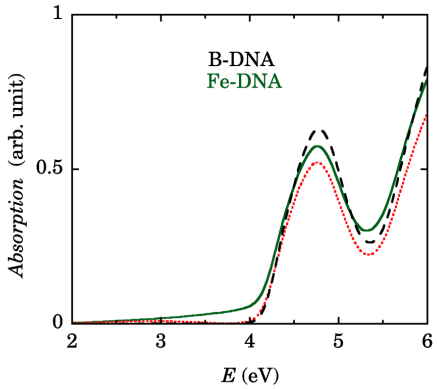


FIG. 11: (Color online) Absorption spectra in aqueous solution of Fe-DNA prepared with the dialysis method from B-DNA and $FeCl_2$ (solid curve). Dashed curve represents the spectra of B-DNA. Dotted curve represents the difference between the spectra of Fe-DNA and $Fe^{3+}Cl_3^{3-}$, which demonstrates the suppression of the inter-$\pi$-band absorption, as also found in Mn-DNA.

ated by the reaction with $FeCl_2$. If the spectra of unreacted $FeCl_2$ and the intra-gap absorption by the reference spectra of $FeCl_3$ are optimally subtracted from the solid curves, the spectral change from the DS oligo-DNA can be demonstrated, as shown by the dotted curves. In the Fe-poly(dG-dC) case, the original spectrum of the dashed curve is reproduced very well in both of the shape and intensity by the dotted curve. In contrast, the dotted curve in the case of Fe-poly(dA-dT) is strongly suppressed from that of DS poly(dA-dT). Characteristic features of the suppression in the inter-$\pi$-band absorption are summarized as follows.

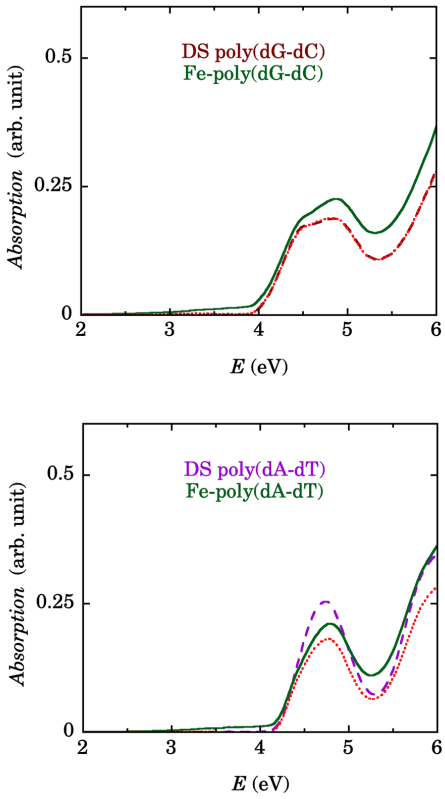


FIG. 12: (Color online) Absorption spectra in aqueous solutions of DS Fe-poly(dG-dC) and DS Fe-poly(dA-dT), which are measured at 30 min after adding $FeCl_2$ into DS poly(dG-dC) and DS poly(dA-dT), shown by solid curves. Dashed curves represent the spectra before adding $FeCl_2$. Dotted curves represent the difference spectra between the solid curve and the spectra of unreacted $FeCl_2$, and $FeCl_3$ as a reference spectrum for $Fe^{3+}$ in Fe-DNA, which is suppressed by $\approx 30$ %. In Fe-poly(dG-dC), the dashed curve overlaps entirely with the dotted curve.

1. The suppression occurs only in the A-M-T complex, but not in the G-M-C.

2. The suppression was observed both in M = Mn and Fe, under the presence of AT base pairs.

3. SS poly(dA) or SS poly(dT) with $FeCl_2$ produces intra-gap absorption caused by $Fe^{3+}$ ions, but no suppression of the inter-$\pi$-band absorption was observed.

Here, it is noteworthy that the HOMO-LUMO gaps of the electron orbitals of DNA backbones are much larger than the observed energy range, thus only the $\pi$ electron orbitals of the bases contribute to the observed absorption spectra. On the first and the second, since any qualitative change of the spectra was not observed, the magnitude of the HOMO-LUMO gap seems to be unchanged. The suppression has no connection with the charge injection to the LUMO band from the metal ions, because no charge

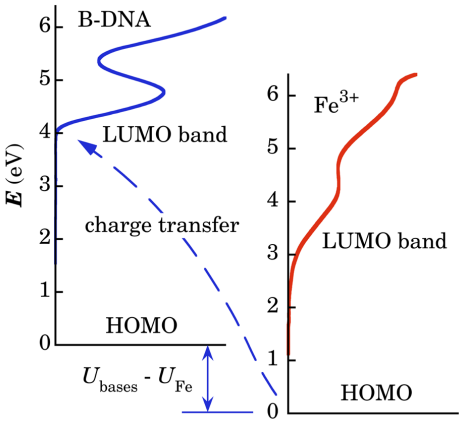


FIG. 13: (Color online) Schematic description of the promotion energy from HOMO of $Fe^{3+}$ to LUMO of DNA bases.

injection occurs in Mn-DNA. Furthermore, in both of Fe-poly(dG-dC) and Fe-poly(dA-dT), the quantity of $Fe^{3+}$ increases with time as an evidence for the charge injection up to 0.1-0.17 electron in Fig. 10, while the suppression increases up to 30 % only in Fe-poly(dA-dT). This suppression is too large to interpret by the charge injection to the three LUMO levels substantial for the absorption spectrum.[32] One electron injection to the LUMO levels of bases results in the maximum suppression of 1/6, that is, 1/60 for 0.1 electron in the Fe-poly(dA-dT) case. As one possibility, the suppression of the inter-$\pi$-band absorption would be concerned with the decoupling of the intra-AT base pair interaction by the insertion of a large hydrated metal ion.[20] One related fact is that the peak energy of the inter-$\pi$ band absorption of poly(dA) and poly(dT) in Fig. 4 are overlap each other, but those of poly(dG) and poly(dC) are separated by 0.5 eV in their peak position, comparable with the full width of absorption band 0.5 eV of SS oligo-DNAs. The mechanism of the suppression only in the A-M-T complex would be a very interesting issue and there should be some interesting mechanism in it. The third fact suggests that A-Fe-A or T-Fe-T complexes can be formed by the Coulomb attraction between the $Fe^{3+}$ situated between the bases of a base pair and $PO_4^-$ in the DNA backbones.

The intra-gap absorption has been successfully reproduced by the reference spectrum of $FeCl_3$ with ionic character. This result is consistent with the ionic character of Mn in Mn-DNA, deduced from the hyperfine splitting of Mn ESR in an aqueous solution of Mn-DNA.[20,27] Thus, it has also been concluded that Fe ions are hydrated by several water molecules, probably octahedrally, between the bases of a base pair in Fe-DNA, as in Mn-DNA, which prevents from forming covalent bondings with the nitrogen atoms in the bases.

The observation of the intra-gap absorption originated from $Fe^{3+}$ strongly suggests that one electron transferred from $Fe^{2+}$ to the bases of a base pair. This transfer requires the promotion of the electron from the HOMO $d$ band of Fe to the LUMO $\pi$ band of the bases. The HOMO band of Fe ions is triply degenerated $t_{2g}$ under the octahedral $H_2O$ configuration and filled by 6 electrons in $Fe^{2+}$ and 5 in $Fe^{3+}$. To roughly estimate the promotion energy, it should be known the relative potential difference between the HOMO bands of Fe and the bases. We have no information on it, but can estimate one limit of the maximum difference of 2 eV as $U_{\rm base} - U_{\rm Fe}$, since the LUMO band of Fe, 2 eV above HOMO in Fig. 9, should be higher than the HOMO level of the bases, as described in Fig. 13. If not, the charge will flow from the HOMO band of bases to the LUMO of Fe. Thus, the promotion energy is less than 6 eV (2 eV + 4 eV for the HOMO-LUMO gap of the bases). This energy should be supplied by the Coulomb attractive potential $U_{{\rm C},\pi-{\rm Fe}}$ between the LUMO $\pi$ electron of the bases and $Fe^{3+}$,

$$\frac{U_{{\rm C},\pi-{\rm Fe}}}{-e} = -\frac{3e}{4\pi\epsilon_0 d} \quad ({\rm eV}), \tag{1}$$

where $e = 1.6 \times 10^{-19}$ C is the electron charge and $d$ is the distance between the $\pi$ electron and the $Fe^{3+}$ ion. Assuming the distance $d = 0.6 \times 10^{-9}$ m between the centers of $Fe^{3+}$ and the hexagon of bases, we obtain $U_{{\rm C},\pi-{\rm Fe}}/(-e) = -7.2$ eV as the stabilizing energy for the charge transfer, which is enough large to compensate the estimated promotion energy of 6 eV. Thus, we conclude that the electron transfer reasonably occurs from $Fe^{2+}$ to the bases and $U_{\rm base} - U_{\rm Fe}$ should be smaller than 2 eV. Unfortunately, the observed conductivity of Fe-DNA is smaller than that of B-DNA, which would be caused by the strong electron correlation along the base stacking.

## IV. CONCLUSION

The absorption spectra in DNAs were investigated. The absorption spectrum of B-DNA is reproducible with the sum of the spectra in DS poly(dG-dC) and DS poly(dA-dT). Each spectrum of the DS oligo-DNAs are also reproducible with that of the SS oligo-DNAs. Thus, both of the intra-strand and the inter-strand interactions between the bases are small enough in comparison with the fullwidth of the inter-band absorption spectra of $\approx 0.5$ eV for the SS oligo-DNAs. The energy gap of 4 eV and the HOMO-LUMO gap of 4.8 eV are reproduced well by the Hückel estimation with the resonance integral of $\beta_{BB} \approx 0.1\beta$ between the bases.[32]

Incorporation of metal ions into DNA with the ethanol-precipitation method cannot generate any change of the electronic states of DNA, except for Fe-DNA. It is clearly demonstrated that $Fe^{2+}$ incorporated into the base pairs of DNA is transformed into $Fe^{3+}$, and that the intensity of the inter-band absorption of G-M-C complex shows nothing of change from that of the G-C pair, but the formation of A-M-T complex strongly suppresses the inter-band absorption of the A-T pair. The ionic character of $Fe^{3+}$ in Fe-DNA, as same as the Mn-DNA case, is

confirmed from the appearance of almost the same spectra as that of $FeCl_3$ with ionic character upon insertion of the Fe ions into DNA, which suggests that the ionic character of M in M-DNA is the common feature in M-DNAs prepared with the ethanol-precipitation method. It is expected that the electronic states of M-DNA will be unveiled by the theoretical approaches on the basis of the present findings. The investigation of the second type of M-DNA prepared with the freeze-drying method proposed by Omerzu *et al.*[29] is intensively in progress.

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