Chirality-Induced Spin-Selective Properties of Self-Assembled Monolayers of DNA on Gold

S. G. Ray,[1] S. S. Daube,[2] G. Leitus,[2] Z. Vager,[3] and R. Naaman[1,*]

[1]*Department of Chemical Physics, The Weizmann Institute, Rehovot 76100, Israel*
[2]*Chemical Support, The Weizmann Institute, Rehovot 76100, Israel*
[3]*Department of Particle Physics, The Weizmann Institute, Rehovot 76100, Israel*

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Here we show that self-assembled monolayers on gold of double-stranded DNA oligomers interact with polarized electrons similarly to a strong and oriented magnetic field. The direction of the field for right-handed DNA is away from the substrate. Moreover, the layer shows very high paramagnetic susceptibility. Interestingly, thiolated single-stranded DNA oligomers on gold do not show this effect. The new findings are rationalized based on recent results in which high paramagnetism was measured for diamagnetic films adsorbed on diamagnetic substrates.

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Chiral molecules are defined as those molecules that lack mirror image symmetry. Molecules that are chiral have two types of enantiomers that can be described as left-handed and right-handed species. Because of broken mirror image symmetry, when a charge moves within a chiral system in one direction it creates a magnetic field. The relation between chirality and magnetism has attracted the attention of many, including Pasteur [1] and Lord Kelvin [2]. Recent studies have focused on the related magnetochiral effect in which the magnetic field can give rise to an enantiomeric excess in photochemical processes [3–5]. Since the electron spin can also interact with a magnetic field, the relation between chirality, the magnetic field, and the electron spin has been recognized in the past (see, for example, Ref. [6]). Here we report on spin-selective transmission studies of electrons through self-assembled monolayers of double-stranded DNA (dsDNA) oligomers adsorbed on gold, which indicate that the monolayers interact with polarized electrons similarly to a strong and oriented magnetic field. The direction of the field for right-handed DNA is away from the substrate. Moreover, the layer shows very high paramagnetic susceptibility. Interestingly, thiolated single-stranded DNA (ssDNA) oligomers on gold do not show this effect. The new magnetic properties and the difference between ssDNA and dsDNA can be understood in terms of the properties of the charge transferred at the interface upon assembly [7].

It has been suggested that many of the mutagenic or lethal effects of ionization radiation can be attributed to the interaction of low-energy electrons with the DNA [8]. This interaction depends on the organization of the DNA [9] and its higher order structure [10]. While dsDNA monolayers on gold are well organized and have a repeating structure that leads to close packing, the single-stranded molecules do not have uniform conformation [see Fig. 1(c)].

In the present study, spin selectivity in electron transmission through DNA monolayers was determined by using circularly polarized light for ejecting spin-polarized electrons from gold substrate covered with the DNA layer (see Fig. 1) [11]. The magnetization of the monolayers was measured using a MPMS_2 SQUID-type magnetometer. For these measurements the monolayer was prepared on a pure polycrystalline gold foil. The magnetic response of the slide was measured separately and then subtracted from the signal obtained for the monolayer-coated gold.

For the electron transmission studies, self-assembled DNA monolayers were prepared according to a standard procedure [12,13] by depositing 15-mers of 3’ thiolated DNA on clean 200 nm thick polycrystalline gold film evaporated on glass slides. The dsDNA was produced by hybridization of 3’ thiolated ssDNA *ex situ* with its complementary nonthiolated DNA oligomer by combining

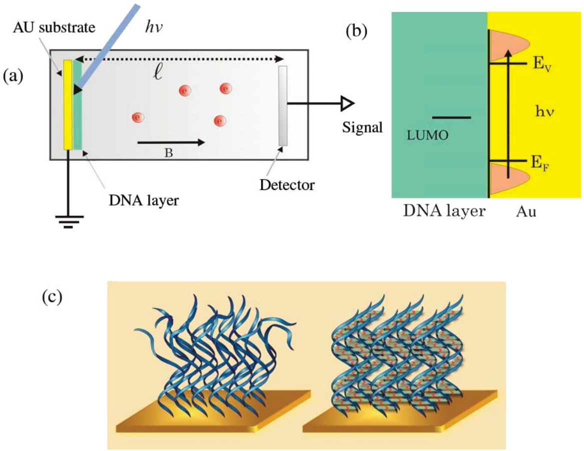

FIG. 1 (color). (a) The experimental setup in which a circularly polarized laser is used to eject photoelectrons from a gold substrate coated with a structured monolayer consisting of either ssDNA or dsDNA oligomers. (b) The energetics involved in the photoemission process. Electrons are excited from below the Fermi level to above the vacuum level. The lowest unoccupied molecular orbital (LUMO) on the DNA is schematically presented. (c) Scheme of the organized layers of the (left) ssDNA and (right) dsDNA. Because of the rigid nature of the double strands, the monolayer is better organized.

equal amounts of the two oligomers in 0.4 M phosphate buffer, *p*H 7.2, heating the mixture for 10 min at 80 °C, followed by slow cooling to room temperature over several hours. Complete hybridization was determined by nondenaturing gel analysis. The clean Au slide was uniformly covered with the oligomer solution (50 mM) and kept overnight in a clean and controlled humid environment. After deposition, the slides were washed thoroughly, first in phosphate buffer and subsequently in sterile deionized water (millipore), and then dried in N_2. The thickness of the monolayer, determined by ellipsometry, was 3.7 ± 0.2 nm. ^{32}P-labeled DNA oligomers were used to characterize the adsorption quantitatively and were found to be about 1×10^{13} molecules/cm^2.

The samples were inserted into an ultrahigh vacuum chamber at $<10^{-8}$ mbar. The polarized photoelectrons are ejected from the substrate by applying a laser beam at 193 nm (6.4 eV) using a $\lambda/4$ plate to create either left- or right-handed circularly polarized light. It has been established that right-handed circularly polarized light induces positive helicity [14] in the photoelectrons ejected from the gold substrate and that the reverse is true for left-handed polarized light. The spins of the photoelectrons are polarized [15] by about 15% [16–19]. After having been passed through the organic layers, the electrons' energy distribution is analyzed by using a time-of-flight spectrometer [20].

The laser energy is maintained very low (20 pJ/pulse, energy density ~2 nJ/cm^2) to avoid any nonlinear processes. To avoid damage from UV radiation, the sample is exposed to the laser beam for only 20 μs. The photon energy is above that of the gold work function (~5 eV); however, it is less than the ionization potential of the DNA bases (~8.4 eV) [21]. Therefore, all the photoelectrons originate from the metal substrate; they are transmitted through the DNA monolayer to the vacuum, where their energy is measured.

Control experiments showed [10] that no ssDNA breaks occur due to the UV laser light. In addition, we showed that there is a linear dependence of the electron signal on the laser flux and therefore the electrons that are ejected from the gold are indeed produced by single photons. Finally, we showed that DNA monolayers, prepared from ethyl alcohol solutions, behaved identically to monolayers made from aqueous solutions. Therefore, salt did not play a role in our measurements.

Figures 2(a) and 2(b) present the energy distribution of the transmitted photoelectrons when they are ejected from the gold by either clockwise (cw) or counterclockwise (ccw) circularly polarized laser and pass through a monolayer made either from single strand (a) or double strand (b) DNA. Within our signal-to-noise ratio, no spin selectivity could be observed in the ssDNA monolayers. In the case of monolayer made from dsDNA, the transmission is more intense for electrons ejected with a ccw polarized laser; namely, these electrons are polarized with their spin pointing antiparallel relative to their velocity [17]. The transmission selectivity [22] is, with very high confidence, positive. Its exact value varies somewhat from sample to sample and is estimated as $8 \pm 2\%$. The data is based on studying more than 20 samples. Assuming about 15% initial polarization of the electrons [11], the transmission results indicate a spin selectivity of at least 50%.

Figures 2(c) and 2(d) show the magnetic moment as measured for DNA adsorbed on 99.999% polycrystalline gold foil after subtracting the diamagnetic contribution of the gold. The foil is made as a ~20 mm^2 disk with a mass of 52.4 mg. While the signal for a ssDNA [Fig. 2(c)] is very weak, it is very pronounce for the dsDNA monolayer [Fig. 2(d)]. The magnitude of the signal, in this case, varies somewhat from sample to sample, as indicated in the figure. The magnetic moment was found to be temperature

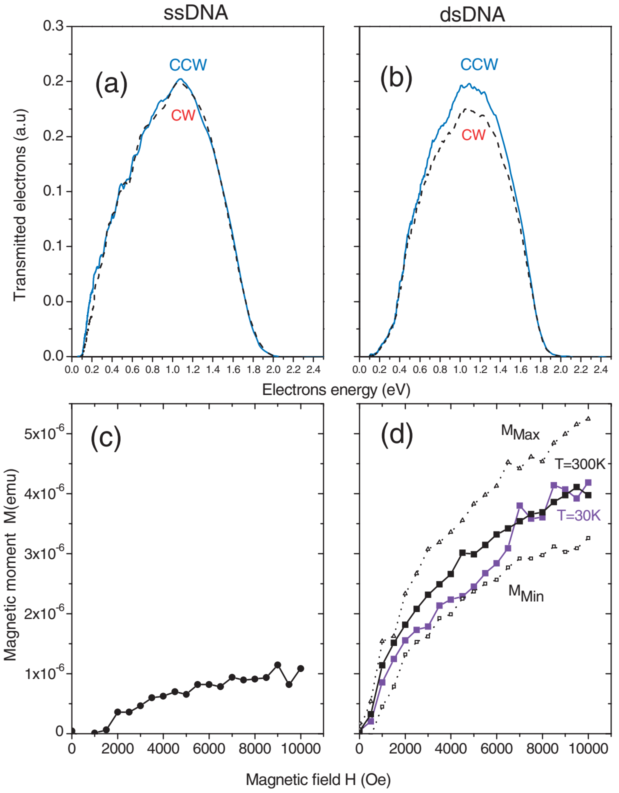

FIG. 2 (color). (a),(b) The energy distribution of the transmitted photoelectrons through a monolayer made from (a) ssDNA or (b) dsDNA oligomers. The electrons are ejected from the gold with a clockwise (cw, dotted line) or counterclockwise (ccw, solid line) circularly polarized laser. While in the first case, the electrons are spin polarized with the spin parallel to the electrons' velocity, for ccw circular polarized laser, the spin is polarized antiparallel to the velocity. (c),(d) The magnetic moment as measured for the DNA-coated gold after subtracting the diamagnetic contribution of the gold. The magnetic moment measured for monolayer made from (c) single strands or (d) double strands measured at 300 (solid line with squares) and 30 K (solid line with circles). The dotted curves indicate the range of variation in the magnetic measurements obtained for different samples. The extreme values are shown: maximum as triangles and minimum as squares.

independent and showed no hysteresis. At a field of 1 T, the signal corresponds to about 90 Bohr magnetons per adsorbed DNA molecule [23], and for most of the samples, the signal does not reach saturation at this value. These observations are consistent with previous studies performed on layers that were not necessarily chiral [24,25].

It is important to realize that the spin-selective electron transmission cannot be affected by *absorption* dichroism of the DNA monolayer. This is because the light passes through only a single monolayer resulting in less than 1% absorption of the incident light by the layer [26,27]. Therefore, adsorption cannot account for the 8% difference in the electrons signal observed. In addition, we performed circular dichroism (CD) absorption experiments at 193 nm (see Fig. 3) and found that, within our signal-to-noise ratio, no dichroism exists at this wavelength. Hence, one has to conclude that the observed effects are originating from other physical mechanisms.

Two effects were detected in the present study: the spin-selective electron transmission through monolayers made from dsDNA and the large magnetic moment measured for these layers. In addition, it has been found that there is clear difference between monolayers made from ssDNA and those made from dsDNA. This difference exists despite the fact that both types of molecules are chiral.

In trying to rationalize the observations, it is important to realize that chirality alone cannot explain spin selectivity and the same is true for the existence of magnetism by itself. In what follows, we will present a model that rationalizes qualitatively the results. The model is based on our previously proposed explanation for the magnetism in organized layers [7]; however, here it is expanded to include also the spin-selective electron transmission.

Our previous explanation for the magnetism is based on the fact that, upon organization of a self-assembled monolayer (SAM), charge is transferred, driven by the electrostatic repulsion between the parallel aligned dipolar molecules in the SAM. In the case of the dsDNA samples, holes have to be transferred from the substrate in order to explain the sign of the spin selectivity. It is important to realize that the charge transferred to each molecule is a fraction of a unit charge [28,29]. Thus holes, left on the monolayer, are squeezed on a two-dimensional net. Based on Hund's rule and as shown before [7], in each domain of the monolayer the spins associated with these holes must all be aligned parallel to each other. The charge squeezed in between the two-dimensional network of molecules in the monolayer may have large orbital magnetism [7].

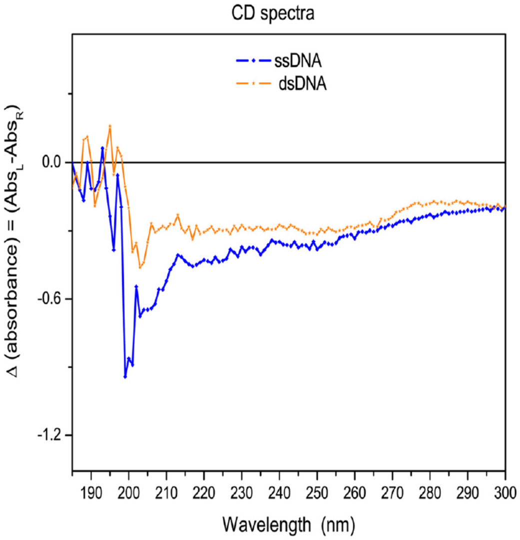

FIG. 3 (color online). Circular dichroism absorption spectra of ssDNA and dsDNA in buffer solution.

Hence, in each domain, except for the spin order parameter, there is an internal angular momentum order parameter that depends on the external magnetic field. However, if the adsorbed molecules are not chiral, then in each domain the spins can be oriented either towards or away from the substrate and the net magnetism with no magnetic field is therefore zero.

The situation is different, however, when the adsorbed molecules are chiral. Here the charge transfer process, occurring upon organization, is directly related to the preferred direction of the angular momentum of the transferred electrons. Hence, upon electron transfer, the direction of the transient magnetic field is well defined and energetically favors a unique direction to the spin order parameter. Thus, for chiral molecules, the spins of the transferred holes are aligned in the same direction for all domains. The preferred direction of the spin depends on the handedness of the DNA. The polarization of the spins can be detected by the magnetoresistance effect, namely, spin-dependent electron transmission. This effect is similar to the spin transmission preference observed in electron transmission through an ultrathin magnetic cobalt layer [30]. Indeed, spin-selective electron transmission was observed only for chiral monolayers. For monolayers made from nonchiral alkylthiols, paramagnetism was measured [24], but no spin selectivity in electron transmission could be observed [11].

The difference between single and double strands of DNA monolayers may be explained if one considers that dsDNA monolayers form well-organized layers and that the molecules themselves are rigid double helices with a right-handed helicity. In the case of ssDNA monolayers, the layer is much less organized and the molecules have no well-defined helix-type structure [see Fig. 1(c)], hence the monolayers are not well packed and therefore the electrostatic repulsion between the molecules can be reduced by their bending and reorientation rather than charge transfer. For dsDNA monolayers, the only way the system can reduce the electrostatic repulsion is by charge transfer.

Hence, our model involves a three stage process: (a) Charge transfer that reduces the electrostatic repulsion within the monolayer (this occurs in the dsDNA and not in the unorganized ssDNA). (b) For monolayer made from chiral molecules, the extra charge is spin polarized, hence it acts as a spin filter in the electron transmission experiment. (c) Upon application of external magnetic field, the charge has a magnetic moment due to orbital magnetism.

In this context, it has been reported that electronic reconstruction occurs on the interface between two insulators, and that electrons are transferred. These electrons were found to be conductive and ferromagnetic in nature [31]. A similar phenomenon occurs with a closely packed organic layer adsorbed on metal. In this case the charge transferred to the layer from the substrate has unique and surprising properties, among them very strong magnetization consisting of hundreds of Bohr magnetons or adsorbed molecules [24]. In several recent works, gold nanoparticles coated with an adsorbed organic layer were found to possess magnetic properties [32,33] and surprisingly, magnetic properties at other interfaces were found [34,35]. It is interesting to note that, when the magnetic response of a single isolated closed loop has been measured, the magnetism found was between 1 to 2 orders of magnitude larger than predicted theoretically. Namely, it seems as if each electron contributes many Bohr magnetons, similarly to the situation described in the present study [36,37].

The results presented here demonstrate an advance in the ability to use molecular spintronic devices. The combination of chiral molecules and a molecular organization incorporating a two-dimensional dipole layer makes the DNA monolayer special and opens the possibility of applying these newly discovered properties in futuristic SAM-based devices.

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*Electronic address: ron.naaman@weizmann.ac.il

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