Selectivity at Surfaces

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Chiral Selective Chemistry Induced by Natural Selection of Spin-Polarized Electrons**

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Abstract: *The search to understand the origin of homochirality in nature has been ongoing since the time of Pasteur. Previous work has shown that DNA can act as a spin filter for low-energy electrons and that spin-polarized secondary electrons produced by X-ray irradiation of a magnetic substrate can induce chiral selective chemistry. In the present work it is demonstrated that secondary electrons from a substrate that are transmitted through a chiral overlayer cause enantiomeric selective chemistry in an adsorbed adlayer. We determine the quantum yields (QYs) for dissociation of (R)- or (S)-epichlorohydrin adsorbed on a chiral self-assembled layer of DNA on gold and on bare gold (for control). The results show that there is a significant difference in the QYs between the two enantiomers when adsorbed on DNA, but none when they are adsorbed on bare Au. We propose that the effect results from natural spin filtering effects cause by the chiral monolayer.*

Most biomolecules can be synthesized in two different mirror-image (chiral) shapes, namely two enantiomers. The enantiomers are recognized by their ability to rotate the polarization of linear polarized light either to the left (L) or to the right (D). In bioorganisms, sugars are always D and amino acids are always L. How this enantiomeric preference originated remains a mystery. Investigations into possible avenues of prebiotic chiral selectivity have been pursued since the time of Pasteur, and much of the effort in this area has been summarized in a number of reviews.[1] So-called determinate mechanisms presuppose that interaction of a chiral physical force with relevant organic molecules led to an enantiomeric excess (*ee*). Many investigations in this area have been devoted to pathways that involve preferential destruction of a particular isomer in an initially racemic mixture (equal quantities of both enantiomers), through the interactions of chiral particles such as circularly polarized UV radiation[2] or longitudinally spin-polarized electrons.[3]

It has been shown that low-energy (0–10 eV) spin-polarized secondary electrons, produced by irradiation of a magnetic substrate, can induce chiral-selective chemistry in an adsorbed adlayer.[4] Additional work has demonstrated that organized, double-stranded (ds) DNA, adsorbed on a gold substrate, acts as a natural spin filter for initially unpolarized, low-energy (0–1.2 eV) electrons, resulting in net polarizations as high as 60%.[5] This selectivity arises from the tendency of the electrons moving in a left- or right-handed chiral potential to have their spin orientations aligned parallel or antiparallel to their velocity.[6] Experiment and theory indicates that this spin filtering effect should be effective for higher energy ($E < 15$ eV) electrons as well.[7] In the present study, we probe whether low-energy secondary electrons, produced by X-ray irradiation of a gold substrate, and transferred through the chiral monolayer, induce enantiomeric selective chemistry in an adsorbed adlayer.

To test this, (*R*)- or (*S*)-epichlorohydrin (C_3H_5ClO, Epi) was adsorbed on a self-assembled monolayer of 70 base-pair-long dsDNA (Figure 1). The secondary electron-induced reaction was monitored by following changes in the Cl 2p X-ray photoelectron spectroscopy (XPS) spectra. By kinetic modeling of the reaction, quantum yields (QYs) were determined. For (*S*)-Epi, the QY was about 16% greater than for the *R* enantiomer, while the QYs were the same for the two enantiomers when they were adsorbed on bare Au.

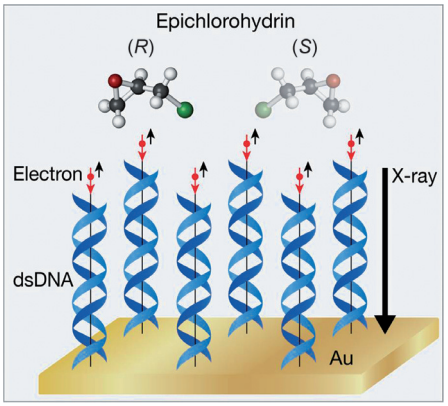

Figure 1. Diagram showing how the secondary electrons produced by X-ray irradiation become spin-polarized, with their spins aligned antiparallel to their velocity, and induce chiral selective chemistry in adsorbed (*R*)- or (*S*)- epichlorohdydrin.

Figure 2 presents XPS spectra of both bare Au and Au/dsDNA samples taken before and after dosing with Epi.

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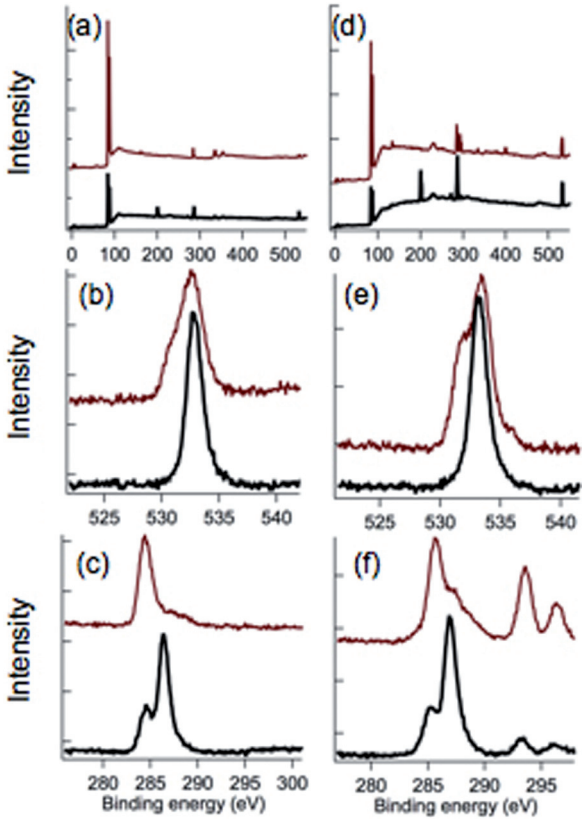

Figure 2. a), d) Survey, b), e) O 1s, and c), f) C 1s XPS spectra before (top spectrum, red) and after (bottom spectrum, black) dosing with Epi. Results for the bare Au substrate are shown in Figure 2 (a–c) and those for the dsDNA/Au sample are shown in Figure 2 (d–f). Data was obtained during the second running period using 740 eV X-rays.

Characteristic peaks are observed at 84 eV (Au $4f_{7/2}$), 200 eV (Cl 2p), 285 eV (C 1s), and about 532 eV (O 1s). For the surface without the Epi, the peaks position and relative intensities are similar to what has been reported previously.[8] Following adsorption of Epi on the bare gold, new peaks are observed in the C 1s (286.4 eV) and O 1s (532.7 eV) spectra. For Epi adsorbed on the dsDNA-coated gold, the same peaks appear at 0.5 eV higher binding energy. Two of the carbon atoms in Epi are bound to O, while the other is bound to Cl, so it might be expected that two chemically shifted C 1s peaks would be seen. However, the C–Cl and C–O chemical shifts are about the same, 1.3–1.4 eV,[9] so only one peak is observed. Oxygen is only bound to carbon, so indeed only one O 1s peak exists.

During irradiation of the adsorbed Epi, significant changes were observed in the C 1s, O 1s, and Cl 2p XPS spectra. Since C and O are also found in the substrate, we concentrated on monitoring changes in the Cl 2p peak. For each system, a series of XPS spectra was obtained. A typical Cl 2p XPS spectrum obtained for Epi adsorbed on DNA is shown in Figure 3, for the two running periods. The spectra in Figure 3 can be decomposed into two, spin–orbit split (1.6 eV) peak pairs (see Supporting Information). The main one at 200.6 eV is due to the unreacted Epi. X-ray irradiation produces dissociated Cl bound to the substrate with a binding energy lower by 2 eV than the unreacted species.[9,10]

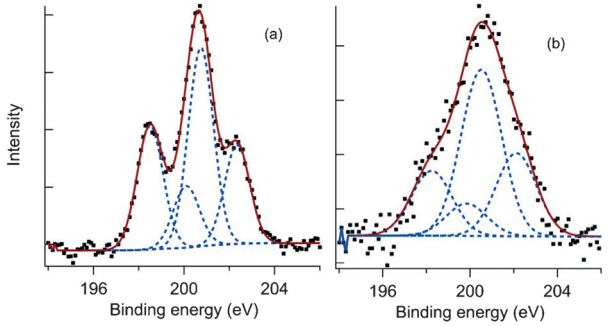

Figure 3. Cl 2p XPS spectra taken in the second run (a) and the first run (b) for Epi adsorbed on DNA. The points are the raw data; the dashed lines are the individual fitted components, and the solid line is the synthesized curve.

A typical series of XPS spectra, taken as a function of irradiation time, is shown in Figure 4. It is evident that, as a function of time, there is a loss of unreacted Epi and a rise in the concentration of dissociated Cl. The inset shows the area

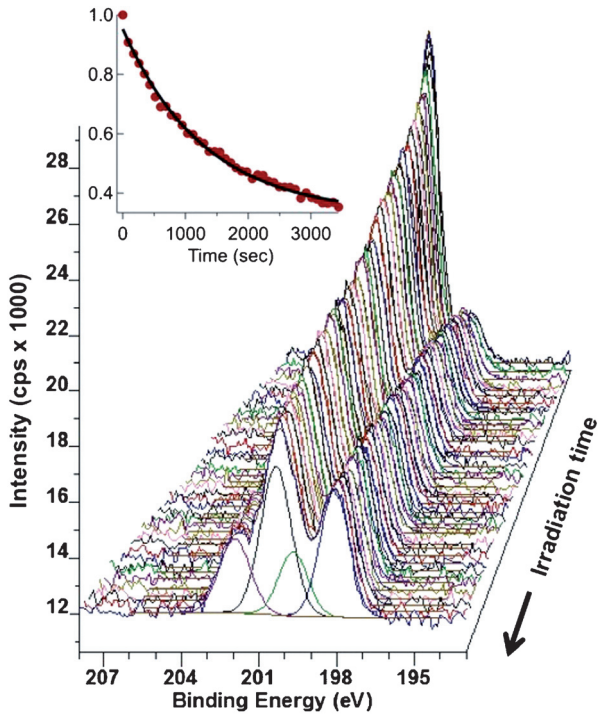

Figure 4. Series of 41 Cl 2p XPS spectra for *S*-Epi/DNA taken as a function of irradiation time with 740 eV X-rays. The time between each spectrum is 86 s. The inset shows the decay of the normalized area of the Cl $2p_{3/2}$ peak as a function of time (red dots) fitted with an exponential function (solid line).

of the unreacted Cl peak as a function of irradiation time. The points are the values of the peak areas and the solid line is a fit to a single exponential function, $A + B\exp(-t/\tau)$ (t is the time, A and B are constants) that yields the reaction time constant, τ. This procedure was done numerous times for each chirality and substrate by moving the illumination to a new spot.

Using the time constant results, it is possible to extract the reaction cross section, σ, by using the relationship, $\sigma = 1/\tau f$, where f is the flux density. As we assume that the reaction is induced by the secondary electrons rather than use the X-ray radiation itself, we use for f the flux density of the secondary electrons. Although it was not possible to measure f directly, the background of the Cl 2p XPS peak should be proportional to the flux of the secondary electrons. To obtain the quantum yield (QY) for the reaction we use the relationship, $QY = N\sigma$, where N is the concentration of Epi on the surface. As the coverage was not uniform, the total intensity of the Cl 2p peak from the initial spectrum in a photolysis series was used as a measure of it.

The results of the QY analysis for both experimental runs are shown in Figure 5 and summarized in Table 1. As it was not possible to maintain the same X-ray beam size and thus have the same flux density between the two sets of experiments, the results are normalized to 1 for the maximum QY (observed for *S*-Epi/DNA).

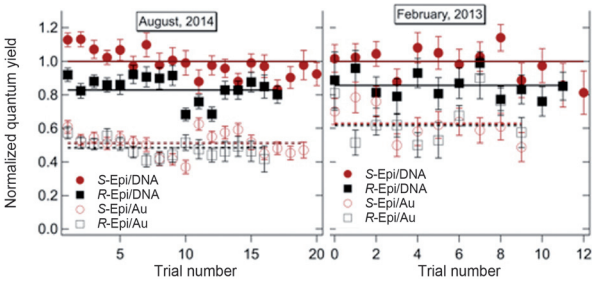

Figure 5. Results of the QY determinations for the two runs. Each data point represents the extraction of the QY from one series of data such as shown in Figure 4. The lines represent the average values from Table 1.

Table 1: Summary of the normalized quantum yield (Norm QY) determinations for the two different experimental runs.

System	Norm QY Run 1	Norm QY Run 2
S-Epi/DNA	1.00 ± 0.05	1.00 ± 0.03
R-Epi/DNA	0.86 ± 0.05	0.83 ± 0.02
S-Epi/Au	0.62 ± 0.05	0.51 ± 0.02
R-Epi/Au	0.62 ± 0.05	0.49 ± 0.02

Figure 5 and Table 1 show that there is a significant difference of about 16% in the QY for the two enantiomers adsorbed on DNA, but none when they are adsorbed on Au. For Run 1 and Run 2 the ratio of the *R*-Epi/*S*-Epi QY is the same within experimental error (ca. 0.85). However, for Epi/Au the ratio of *R*- or *S*-Epi QY to that of *S*-Epi/DNA is 0.62 for Run 1 and about 0.5 for Run 2. This may be due to the fact that the preparation of the Au surface was not carefully controlled between the two sets of samples. It is interesting to note that the QY is significantly lower for the Au surface as opposed to the DNA/Au system. This is reasonable because the excited states of the negatively charged Epi, which leads to the dissociation, will be quenched when the molecule is directly adsorbed on the metal substrate.[11]

It is possible that electron-induced reactions in the DNA, or direct X-ray absorption in the Epi, could have influenced the results. Using the measured sample current as a gauge of the total (secondary and primary) emitted electron flux density, we can calculate a cross-section for the electron-induced reaction in Epi, which results in a σ of 45–55 Mb. The electron induced σ in DNA (determined in a similar manner) has been determined to be about 5 Mb,[8b] while the gas-phase X-ray absorption cross section is < 1 Mb,[12] so neither reaction should play a significant role in this process.

We have no way to determine the exact nature of the interaction between the DNA and the adsorbed Epi. The C 1s, O 1s, and Cl 2p XPS spectra show no evidence of Epi dissociation before irradiation. It is possible that there are differences in bonding between the two enantiomers and DNA, which could also lead to some chiral selective interactions. Previous studies have shown shifts of up to 0.2 eV in the N 1s and S 2p binding energies between D- and L-cysteine adsorbed on a chiral gold surface.[13] Since we made numerous measurements of the Cl $2p_{3/2}$ binding energy for the initially bound molecule, we were able to determine accurate binding energies for *S*-Epi and *R*-Epi adsorbed on DNA, which are 200.66 ± 0.13 eV and 200.60 ± 0.06 eV, respectively (200.2 eV for Epi on Au). The fact that these values are the same may indicate that chiral-selective adsorption is not a major factor in determining the reactivity.

The inset in Figure 4 shows that the concentration of the unreacted Epi decreases by about 65% during a typical photolysis series, which lasts about 2.5τ and does not approach 0. One possible reason for this is that the Cl fragment reacts with residual C on Au or in DNA to form a species with a similar binding energy as the unreacted Epi. However, temperature-dependent measurements (Supporting Information) indicate that this is at most a minor process. As there is up to two monolayers coverage of Epi (which could be susceptible to islanding), it is possible that the photolysis occurs primarily in the outermost layers, which could lead to the observed effects.

During a photolysis series, the total area of the Cl peaks decreased by about 30%, which indicates that about half of the loss of the Epi is due to desorption. Electron-beam-induced chiral-specific desorption has been observed for *R*/*S*-methyl lactate adsorbed on a chiral Cu(643) surface.[14] The selectivity was postulated to result from the large differences in binding energy ($3.92\ kJ\,mol^{-1}$) for the two enantiomers bound to a chiral kink site. Since there are no chiral sites on the surface of the self-assembled dsDNA, there should be no differences in bonding energies between *R*- And *S*-Epi bound to it. To check this hypothesis, cyclic voltammetry measurements were performed on the adsorption of *R*- or *S*-ferrocene adsorbed on dsDNA and compared to measurements on a chiral polymer.[15] A significant enantioselective effect was observed for the chiral polymer, but none in the case of dsDNA (Supporting Information). These results rule out the possibility that the results are due to different interaction between the self-assembled monolayer of DNA and the two enantiomers.

Recently it has been demonstrated that thin double monolayers of organic enantiomers adsorbed on a surface

can affect the direction of the spin of the electrons emitted from a magnetized substrate.[16] This dramatic effect, in which the chiral adsorbent is more significant than the magnetic alignment, indicates that even very thin chiral layers, like those in the present work, can determine the spin of the electrons. The spin direction depends on the handedness of the enantiomer.

In summary, we have presented results showing that there is a significantly higher quantum yield for dissociation of adsorbed (*S*)- as compared to (*R*)-epichlorohydrin when the molecules are adsorbed on a self-assembled monolayer of chiral dsDNA. Based on former studies, we suggest that the effect results from secondary electrons produced by X-ray irradiation of the substrate. These electrons become spin-polarized when transmitted through the DNA, which acts as a natural spin filter. Hence, the enantioselectivity observed is a result of different quantum yields for reaction of spin polarized electrons with the two enantiomers. Such a mechanism may have played a role in the formation of chiral molecules in the prebiotic world. An enantiomeric excess (*ee*) of a molecule with a particular chirality, formed in an inner layer, could act as a spin filter producing an excess of electrons with spins that are polarized so as to preferentially dissociate molecules with an opposite chirality. Thus, the initial *ee* could be propagated throughout the ensemble even in the absence of a chiral force.

Experimental Section

The experiments were performed at the Advanced Photon Source (APS) during two different running periods separated by 1.5 years. During the first period XPS was performed using 950 eV X-rays and a VG CLAM2 electron energy analyzer, while in the second period, measurements were performed using 740 eV X-rays and an Omicron Argus analyzer. In both cases the angle of incidence between the X-rays and the sample normal was 60 degrees. All binding energies are referenced to the Au $4f_{7/2}$ peak at 84 eV.

The samples were prepared at the Weizmann Institute following a procedure described previously (see Supporting Information).[5] They consisted of 3′ thiolated DNA (70 base pairs long) adsorbed on a clean 200 nm thick polycrystalline gold film on a Si substrate. Bare gold samples were also tested. The samples were shipped in sealed vials under a nitrogen atmosphere to the APS and not opened until shortly before they were loaded into a load lock chamber, which was immediately evacuated. After transferring onto the manipulator in the analysis chamber (base pressure $= 1.5 \times 10^{-10}$ Torr), they were cooled to about 90 K and dosed with (*R*)- or (*S*)- Epi with a micro-channel plate doser. Owing to the directionality of the doser, the coverage was not uniform, but ranged between 0.5 to 1 nm as determined by the attenuation of the Au 4f peak in the XPS spectrum. Based on the liquid density (1.18 $g\,cm^{-3}$) and assuming a simple cubic structure, the intermolecular distance between the adsorbed chiral molecule should be about 0.5 nm, which results in coverages corresponding to 1–2 monolayers.

Keywords: chirality · DNA · enantioselectivity · photoelectron spectroscopy · surface chemistry

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