

# Chiral Induced Spin Selectivity Gives a New Twist on Spin-Control in Chemistry

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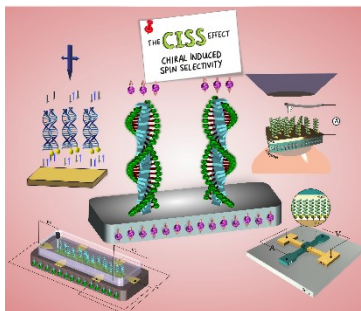
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## Conspectus

The electron's spin, its intrinsic angular momentum, is a quantum property that plays a critical role in determining the electronic structure of molecules. Despite its importance, it is not used often for controlling chemical processes, photochemistry excluded. The reason is that many organic molecules have a total spin zero, namely all the electrons are paired. Even for molecules with high spin multiplicity, the spin orientation is usually only weakly coupled to the molecular frame of nuclei, hence to the molecular orientation. Therefore, controlling the spin orientation usually does not provide a handle on controlling the geometry of the molecular species during a reaction. About two decades ago, however, a new phenomenon was discovered which relates the electron's spin to the handedness of chiral molecules and is now known as the Chiral Induced Spin Selectivity (CISS) effect. It was established that the efficiency of electron transport through chiral molecules depends on the electron spin and that it changes with the enantiomeric form of a molecule and the direction of the electron's linear momentum. This property means that, for chiral molecules, the electron spin is strongly coupled to the molecular frame. Over the past few years, we and others have shown that this feature can be used to provide spin-control over chemical reactions and to perform enantioseparations with magnetic surfaces.

In this account we describe the CISS effect and demonstrate spin polarization effects on chemical reactions. Explicitly, we describe a number of processes that can be controlled by the electron's spin, among them the interaction of chiral molecules with ferromagnetic surfaces, the multi-electron oxidation of water, and enantiospecific electrochemistry. Interestingly, it has been shown that the effect also takes place in inorganic chiral oxides like copper oxide, aluminum oxide, and cobalt oxide. The CISS effect results from the coupling between the electron linear momentum and its spin in a chiral system. Understanding the implications of this interaction promises to reveal a previously unappreciated role for chirality in biology, where chiral molecules are ubiquitous, and opens a new avenue into spin-controlled processes in chemistry.

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*The first direct measurement of spin exchange interactions with chiral molecules is presented here.*

Electron spin is essential for understanding chemical bonding, but the use of spin-control in synthetic chemistry is not widespread.<sup>5</sup> Although the field of “Spin Chemistry” is growing,<sup>6</sup> spin effects are usually associated with radical pair reactions. Even though radical chemistry represents a general class of chemical reactivity and radical pair reactions display significant magnetic field effects,<sup>7</sup> spin considerations do not typically provide stereospecificity in bimolecular reactions or in reactions between radicals and surfaces. As two molecular radicals react, it is usually not possible to control the relative orientation of the interacting spins and their orientation with respect to the reaction coordinate, because of the weak coupling of the electron spin with the molecule’s nuclear geometry. Even if an external magnetic field is applied to orient the spins in the laboratory frame, they are largely decoupled from the molecular frame. In addition, it is often assumed that spin control is not of importance for synthetic chemistry because of the small energy associated with spin flipping. This latter reasoning is less rigorous, however, as electron spin relaxation timescales are long compared to typical electronic and vibrational timescales in molecules and often commensurate or as long as rotational timescales.

Hence, it is often assumed that spin considerations are of little relevance to most bimolecular interactions or for the interaction of molecules with surfaces. It must be appreciated that support for this notion arises from the small spin-orbit coupling typical of organic molecules. This small value means that spin does not contribute significantly to the total angular momentum of molecular collisions, even in cases where angular momentum might be used to control chemical processes.<sup>8</sup> While this view holds for achiral molecules, recent experiments (*vide infra*) show that chiral molecules and chiral catalysts display prominent spin selectivity effects.<sup>9</sup>

An important and well-known exception to the above claim is the case of photodissociation, as well as other photochemical reactions.<sup>5-10</sup> Especially one should notice the role of spin in the electron transfer dynamics in Photosystem I<sup>11</sup> and the role spin may play in the avian compass.<sup>12</sup> In photochemistry and photoinduced reaction dynamics studies, it often becomes possible to prepare the reactant electronic state so that the electron spins on the product fragments are oriented.<sup>13,14</sup> It is important to note that what maintains the relative orientation of the two spins is the “spin exchange interaction” which can be many times  $k_B T$  at room temperature.

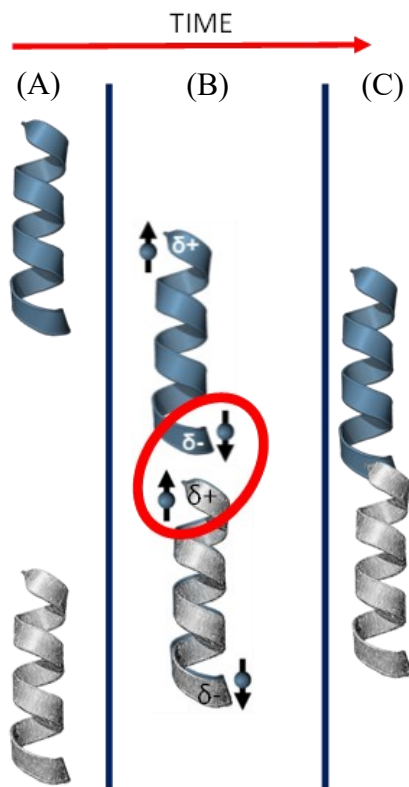
Below we discuss experiments which show that spin constraints can play a major role for reactions involving chiral molecules. Our discussion begins by describing the chiral induced spin selectivity (CISS) effect which provides the connection between a molecule's chiral structure and the electron spin. Next, we provide several examples for how the CISS effect leads to spin-controlled reactions and interactions. Because the spin degree of freedom is coupled to the linear momentum of the electron for chiral molecules, electron transfer and electron rearrangement of chiral reactants (and intermediates) are affected by the spin. These features mean that CISS is relevant also in biology.<sup>15</sup>

## 1. The CISS effect

About two decades ago it was found that the electron transmission through chiral molecules is spin dependent; i.e., chiral molecules can act as spin filters.<sup>16</sup> Since that time, the effect has been reported for many chiral molecules, chiral polymers, chiral organic-inorganic assemblies, and chiral inorganic materials, by numerous groups.<sup>17</sup> Important new insights about the importance of the CISS effect in Chemistry, and the enantiospecific interaction of molecules, arose recently when the CISS effect was also found to manifest as a transient spin polarization which accompanies charge polarization in chiral molecules.<sup>2,3</sup> While it is broadly appreciated that charge reorganization occurs for a molecule under an applied electric field, or when a molecule interacts with another molecule or with a surface, the concomitant spin polarization for chiral molecules has not been appreciated before.

Consider a closed shell molecule (total spin zero). Charge polarization of the molecule generates a dipole moment by creating excess charge density in one region of the molecule and a depletion of charge density in the opposite region, i.e., the positive and negative poles of the dipole. For chiral molecules, the electron displacement current generates a spin dipole. Which spin is associated with which electrical pole depends on the handedness of the molecule (see Figure 1). While the total spin of the molecule remains zero, the spin dependent charge reorganization (SDCR) arises from spin polarization with opposite signs at the two electric poles. The SDCR affects the reactivity of chiral molecules and may contribute to enantioselectivity in the interaction between chiral molecules. The SDCR also affects the interaction of chiral molecules with ferromagnetic surfaces<sup>18</sup> and it has been used for separating enantiomers.<sup>3</sup>

*The SDCR effect implies that closed shell chiral molecules can have their electron spin distribution polarized relative to the molecular axis, analogous to a “singlet bi-radical” but with no need for an external magnetic field. This property opens a new route into spin selective chemistry.*



**Figure 1: The Spin Dependent Charge Reorganization (SDCR) effect.** From left to right - (A) Two chiral reactant molecules are represented by helices. (B) As the chiral molecules approach each other dispersion forces generate induced dipoles on each molecule. Because of the SDCR effect the charge polarization is accompanied by a spin polarization. In the case of homochiral reactants, the spins on the opposite electric poles are antiparallel (singlet configuration) while if the molecules are of opposite handedness, the spins on the opposite poles will be parallel (triplet configuration). (C) The two chiral molecules react to give a product. If the spin polarization on the molecules are anti-parallel, then a singlet state is formed and if the spin polarizations are parallel, a triplet state is formed. Since commonly the singlet state is more energetically favorable, the reaction between homochiral molecules is more favorable as compared to reaction between heterochiral molecules.

## 2. Hall measurements

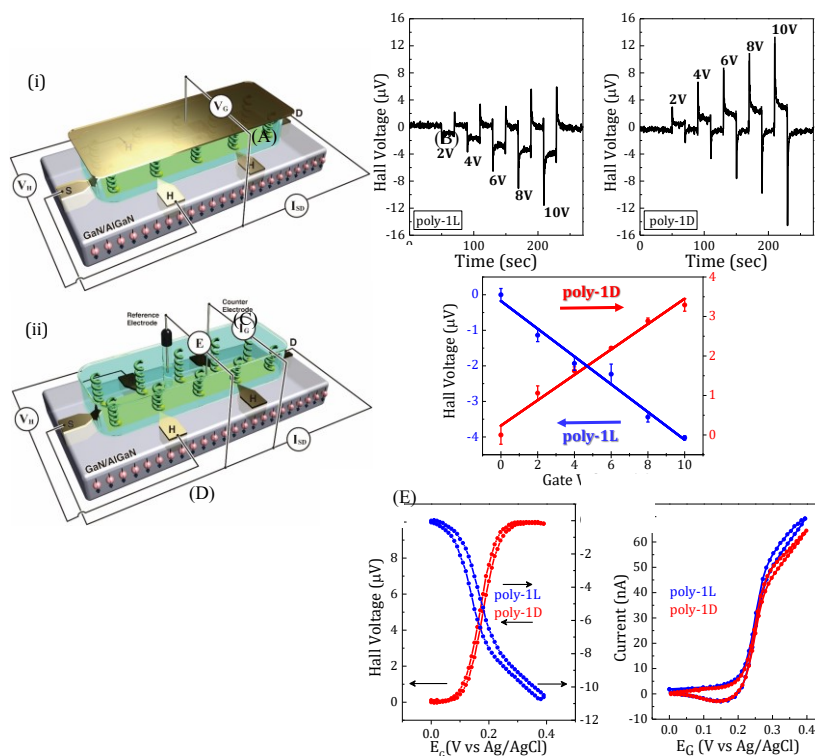
A Hall effect device<sup>19</sup> is commonly used to measure magnetic fields. In the device, current is flowing between source and drain electrodes and a magnetic field acts on the device. The magnetic field and the current generate a Lorentz force acting on the charges, which creates an electric potential (the Hall voltage) perpendicular to the current and the magnetic field. Thus the magnitude of the Hall potential reports on the strength of the magnetic field. In our case we used a Hall device to measure directly the SDCR effect, by placing a self-assembled monolayer film of alpha-helical peptide oligomers on the surface of a Hall device and measuring the film's magnetization as a function of the voltage applied across the peptides, the length of the peptide oligomer, and the chirality (L versus D) of the oligomer.<sup>20</sup> In these measurements no external magnetic field was applied, rather the

SDCR effect in the peptide monolayer generates a magnetic field at the Hall device surface producing a Hall voltage.

Figure 2 illustrates a Hall device, comprising a GaN/AlGaIn structure with a two-dimensional electron gas layer. The Hall bar circuit is buried under a protective 20 nm film so that it can be used as a working electrode in an electrochemical cell. This device is used to study the SDCR in the chiral polymers [poly(4-ethynylbenzoyl-L-alanine decyl ester) (poly-1L), poly(4-ethynylbenzoyl-D-alanine decyl ester) (poly-1D), and poly(4-ethynylbenzoyl-2-methylalanine decyl ester) (poly-2)].<sup>21</sup> By applying a constant current between the source and drain electrodes of the Hall bar circuit, one can monitor the magnetization on the working electrode. Although no external magnetic field is applied, a magnetic field is generated by the SDCR effect as a voltage is applied across the chiral polymers which are adsorbed on the surface of the device.

Two types of measurements are shown in Figure 2. In each case, the polymers are adsorbed on the device which is placed within an electrolyte solution and used as a ‘smart’ working electrode. In the first type of experiment, an inert electrolyte is used and a voltage is applied between the ‘smart’ working electrode and an Au counter electrode. Upon application of a voltage, the polymer charge polarizes and this charge polarization is accompanied by spin polarization. The spins that are exchanged between the polymer and the working electrode’s surface generate a magnetization (Figure 2i). The mechanism by which this device operates is described in detail in reference.<sup>22</sup> In the second type of experiment, the spin-dependence of the Faradaic current in a redox reaction was measured (Figure 2ii). Here, the Hall device served as the working electrode in a three-electrode electrochemical cell with a Pt counter electrode and a Ag/AgCl reference electrode. When Faradaic current flows to the working electrode through the chiral polymer’s film, the current is spin-polarized, thus generating a magnetization and a Hall voltage. In this scheme, one can simultaneously measure the charge current versus applied potential (cyclic voltammogram) and the magnetization versus applied potential (Hall potential versus voltage) for the redox reaction. It is important to appreciate the difference between the two modes of experiments using the Hall device. In the first type of measurement, the spin injected into the Hall device arises from transient charging (double-layer) current, whereas the second type of experiment has a steady-state current flowing from the Faradaic process.

Figures 2A and 2B show the Hall signal as a function of time that were obtained by the first type of measurement for poly-1L and poly-1D on the Hall device. The signals shown are the Hall voltages that were measured for different biases (gate voltages), applied between the counter electrode and the ‘smart’ working electrode. The magnitude of the measured Hall potential is proportional to the voltage applied (see Figure 2C) and the sign of the Hall potential depends on the handedness of the polymers. These results confirm the SDCR process.



**Figure 2:** Schematic presentation of the experimental set of Hall measurement in the polarization (i) and electrochemical mode (ii). Hall potential recorded in polarization mode as a function of time for (A) poly-1L and (B) poly-1D for various gate pulses. (C) The Hall voltage as a function of the gate voltage for monolayers of poly-1L (blue) or poly-1D (red). (D) Hall potential recorded in the electrochemical mode as a function of the voltage when the working electrode (the Hall device) is coated with monolayers of poly-1L (blue) or poly-1D (red). (E) The voltammograms are shown for a working electrode that is coated with monolayers of poly-1L (blue) or poly-1D (red). Note: All the electrochemical measurements were performed using ferrocene as a redox probe in water. A Pt wire was used as the counter electrode, the drain electrode of the Hall device was used as the working electrode, and a silver wire was used as a reference electrode. Reprinted with permission from Ref. 21. Copyright 2020 Wiley-VCH.

In the second type of experiment, we measured the spin selective electron transfer through the polymers for a ferrocene redox couple in a phosphate-buffered saline (PBS)



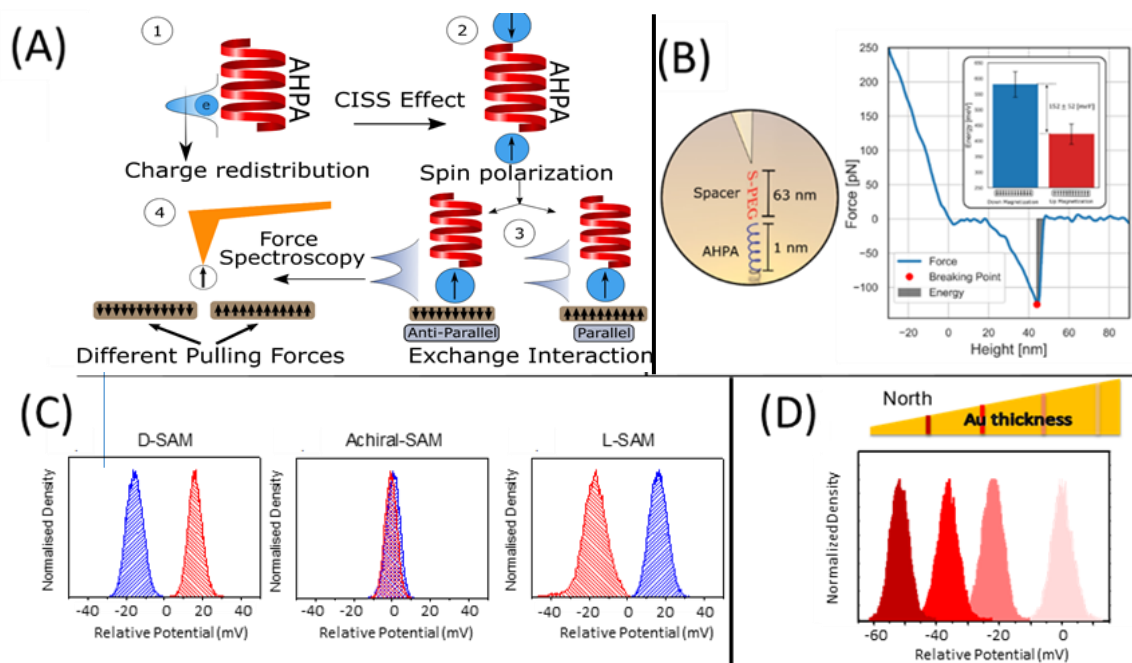
solution. Figure 2D shows the Hall potential obtained when the potential in the electrochemical cell was varied between 0 and 0.4 V. The corresponding cyclic voltammograms are shown in Figure 2E. While the voltammograms for the two enantiomers are very similar, the Hall potentials that are measured have opposite signs. Note the different axes for the L and D polymers. The small hysteresis observed in the Hall potential plots indicate an asymmetry between the spin polarization in the oxidation and reduction currents that may result from differences in the interfaces on the two sides of the polymers, one being the solid substrate and the other the electrolyte. These experiments, as well as others, demonstrate spin selective electron transport through chiral films adsorbed on electrodes. This approach for producing spin-polarized electron current opens a new way for performing spin selective electrochemical reactions, *vide infra*.

### **3. Interaction of chiral molecules with ferromagnetic surfaces.**

The spin-dependent charge reorganization observed in chiral molecules implies that the interaction between a chiral molecule and a magnetized surface should be enantiospecific. Consider a ferromagnetic metal that is magnetized along its surface normal so that the spin sub-bands of the conduction electrons are split in energy – presenting more filled orbitals of one spin direction and more empty orbitals of the other spin direction. Because of the spin-dependent metal orbital population, the chemisorption or physisorption of a molecule will depend on whether the molecule's orbitals have a preferred spin direction with respect to the metal. For example, the interaction energy for a molecule forming a chemisorption bond with a metal spin-orbital will depend on whether the spins are aligned anti-parallel (singlet) or parallel (triplet). For achiral molecules, the charge redistribution in the molecule as it approaches and binds to the surface is not spin-dependent and no apparent spin specificity is observed. As a chiral molecule approaches the surface, however, it undergoes a spin-dependent charge redistribution so that one enantiomer interacts along a singlet reaction coordinate and the other enantiomer interacts along a triplet reaction coordinate. This mechanism for enantiospecific interaction of chiral molecules and ferromagnetic surfaces was not appreciated previously.

If a ferromagnetic substrate is not yet magnetized, the surface comprises a mixture of domains magnetized up or down - on average the density of states for spin pointing “up” or “down” is the same. The electronic interaction at the interface between chiral molecules

and the ferromagnetic substrate, the spinterface,<sup>23</sup> breaks the spin degeneracy so that one spin is preferred over the other, depending on the handedness of the adsorbed chiral molecules. The exchange interaction of a chiral oligopeptide with a magnetic substrate is strong enough to switch and control the magnetization direction of the substrate.<sup>24</sup>



**Figure 3: The FM/ chiral molecule interactions.** Top panel: direct measurement of the exchange interaction between the FM and the chiral molecules. (A) An alpha helix polyaniline (AHPA) is adsorbed on a gold AFM cantilever. The system is immersed in ethanol to reduce capillary forces. The sample under study is an MBE grown Co-based nanostructure with an out-of-plane easy axis. When the tip is close to the sample, reorganization of the electric charges in the molecule (1) results in spin filtering due to the CISS effect (2), which is followed by an exchange interaction between the molecular wavefunction and the wave function of the substrate (3). This interaction is sensed by the deflection of the AFM cantilever (4). (B) left: Schematic of the tip with the adsorbed molecules. right: Typical force dependence on the tip-surface distance, the pulling point of the molecule and the integrated area represent the pulling energy of the molecule. Inset: The mean pulling energy for the up and down direction of perpendicular sample magnetization, showing a difference of 150 meV. The standard error of the mean is shown. Reprinted from Ref. 4 with permission. Copyright 2020 Wiley-VCH. Bottom panels: contact potential difference for chiral and achiral self-assembled monolayers on magnetized surfaces. (C) Histograms, obtained from Kelvin probe measurements of the contact potential difference (CPD) for chiral and achiral self-assembled monolayers on Ni/Au magnetized surfaces, reveal an enantiospecific response for chiral molecules and no magnetization response for achiral molecules. (D) Change in the CPD as a function of the Au layer thickness for Co magnetized films with adsorbed L-A5 (SH-(CH<sub>2</sub>)<sub>2</sub>-NH-(Ala-Aib)<sub>5</sub>-COOH) SAMs. The top diagram represents the Au wedge and the color of each plot corresponds to the region indicated on the gradient bar by the same shade. Reprinted with permission from ref. 18. Copyrights 2020 American Chemical Society.

A direct measurement of the exchange energies that control the interaction between a ferromagnetic substrate and chiral molecules was realized by atomic force mapping, as presented in the top panel of Figure 3.<sup>4</sup> In this experiment a helical (and chiral) polypeptide, alpha helix polyalanine, was adsorbed on the gold cantilever of an atomic force microscope and then used to measure the force between the molecule and a ferromagnetic substrate (Figure 3B left). As the cantilever (and molecule) approach the substrate, the spin dependence for the chiral molecule/surface interaction manifests in a different force acting on the AFM cantilever (Figure 3A). Integrating the force over the tip displacement provides an energy for the interaction, and the difference in energy for the two magnetization directions (up versus down) of the ferromagnetic (FM) substrate reports on the difference in the interaction energy of the chiral molecule and the magnetized sample. These experiments find an energy difference of  $\sim 150$  meV at short range, which is about  $6 k_B T$  and significantly larger than the expected Zeeman splitting (Figure 3B).

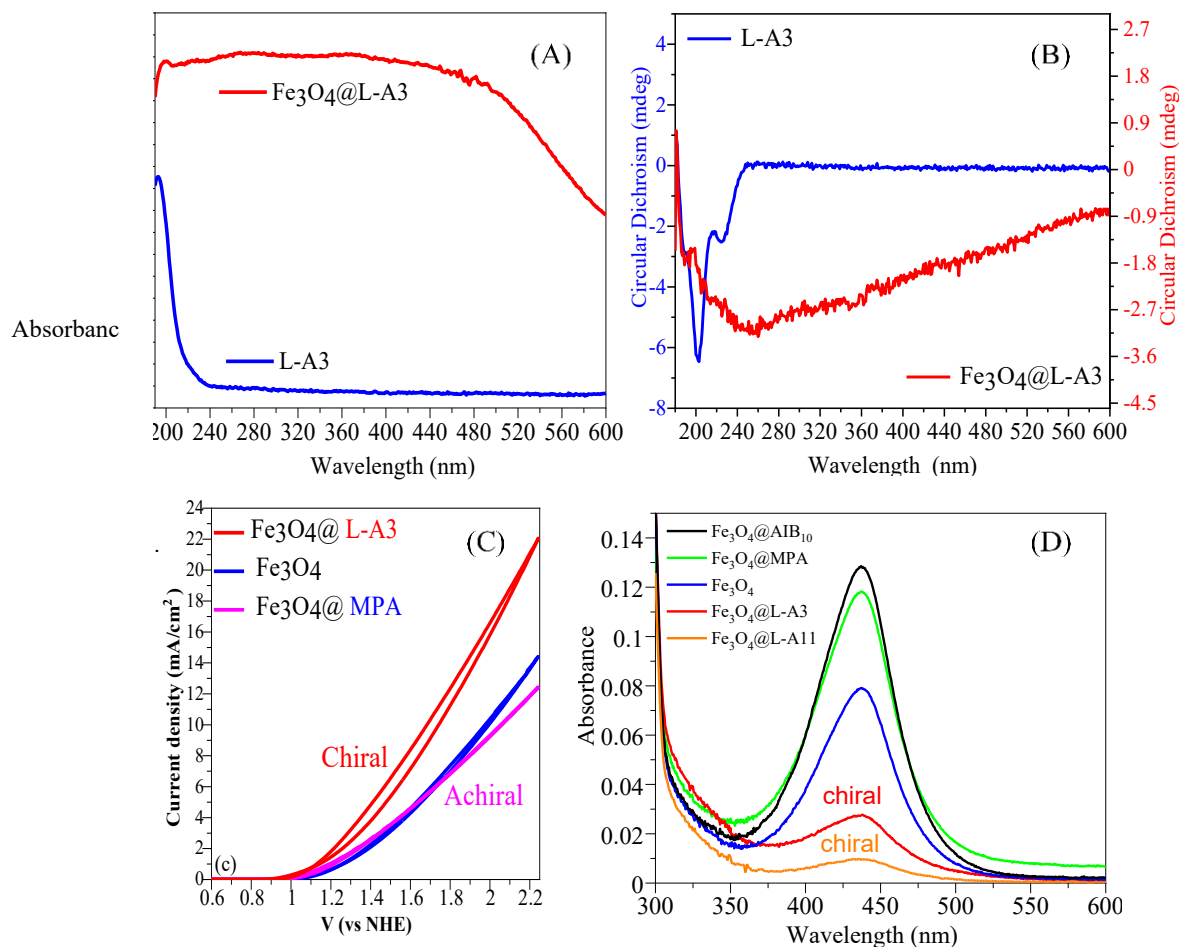
To quantify the work function differences in the chiral molecule-FM system, Kelvin-probe measurements on ferromagnetic thin film electrodes coated with self-assembled monolayers of chiral molecules were performed.<sup>18</sup> These measurements, which are presented in the bottom panel of Figure 3, reveal that the electron penetration from the metal electrode into the chiral molecules depends on the ferromagnet's magnetization direction and the molecules' chirality. The Kelvin probe microscopy data show that the extent to which the electron density from the ferromagnet penetrates into the chiral peptide monolayer is enantiospecific and changes with the sign of the magnetization; i.e., tunneling into chiral molecules is spin dependent (Figure 3C). Figure 3D shows that the enantiospecific interaction of chiral molecules with a ferromagnetic surface depends on the amplitude of the electron spin wave function penetration. Together, these data and other findings from these studies show that as chiral molecules adsorb on the surface of thin ferromagnetic films, a magnetization perpendicular to the surface is created, without the application of current or an external magnetic field.<sup>24</sup> Correspondingly, changes in the surface magnetization generate changes in the electrostatic field for chiral molecules. Although the energy difference has contributions from magnetic field (Zeeman) effects, it is dominated by the spin exchange energy.

#### 4. Controlling chemical reaction by spin- water oxidation.

Despite significant progress in recent years, inefficiencies in the oxygen evolution reaction (OER) remain an important barrier to the broad deployment of water electrolysis.<sup>25,26</sup> Three primary obstacles arising from the OER are i) overpotentials of about 0.6 V are required, ii) production of H<sub>2</sub>O<sub>2</sub> by-product,<sup>27-29</sup> and iii) the need to operate at high pH (>10) which can lead to chemical corrosion of device components. The H<sub>2</sub>O<sub>2</sub> production can be reduced and the energy efficiency improved by better controlling the spin of the electrons injected into the anode.<sup>30-33</sup>

Control over spin in the elementary electrochemical steps generates spin alignment in the unpaired electrons of the intermediate radicals ( $\bullet$ OH) that are adsorbed on the surface and combine along a triplet surface to form the ground-state triplet oxygen molecule ( $^3$ O<sub>2</sub>). Because hydrogen peroxide is a singlet species, polarizing the spin of  $\bullet$ OH inhibits H<sub>2</sub>O<sub>2</sub> evolution and reduces the overpotential. The benefits of spin control in the electrolysis have been shown by using chiral anode materials and by using magnetized anodes. Studies with a TiO<sub>2</sub> anode that was modified by a monolayer of chiral molecules, chiral supramolecular structures, or a chiral film, were reported, as well as anodes comprising chiral inorganic oxides of CuO<sup>34</sup> and CoOx (both paramagnetic and ferromagnetic).<sup>35</sup> Spin control has also been demonstrated for magnetic electrodes with high current density and low by-product yields.<sup>36</sup>

To illustrate the benefit of spin control on the performance of an OER anode, we chose a well-established and efficient OER catalyst, Fe<sub>3</sub>O<sub>4</sub>, and converted it into a chiral catalyst by chemisorbing chiral molecules onto it.<sup>37</sup> Figure 4 shows the absorption (4A) and the circular dichroism spectra (4B) of the peptide SH-(CH<sub>2</sub>)<sub>2</sub>-NH-(Ala-Aib)<sub>3</sub>-COOH (L-A3) and the Fe<sub>3</sub>O<sub>4</sub>@L-A3 NPs in solution. The CD spectrum of L-A3 in (Figure 4B) exhibits two CD peaks at 201 nm and 226 nm. Attaching L-A3 to Fe<sub>3</sub>O<sub>4</sub> results in a CD spectrum in the range of the Fe<sub>3</sub>O<sub>4</sub> NPs' absorption. This effect of induced chirality in NPs, as a result of the adsorption of chiral molecules, is well documented<sup>38,39,40</sup> and is demonstrated here for the Fe<sub>3</sub>O<sub>4</sub> NPs.<sup>41,42</sup> It was observed for all chiral molecule@Fe<sub>3</sub>O<sub>4</sub> NPs studied in the present work. In the past, it has been shown that electron transfer through semiconducting NPs coated with chiral molecules is spin dependent.<sup>43,44</sup>



**Figure 4: Spin controlled water splitting.** The results obtained using 20 nm  $\text{Fe}_3\text{O}_4$  nanoparticles and nanoparticles coated with achiral or chiral molecules, which are supported on an FTO substrate to make the OER anode. (A) Absorption spectra of a 1 mM L-A3 solution (blue line) and  $\text{Fe}_3\text{O}_4@\text{L-A3}$  (red line); (B) CD spectra of a 1 mM of the molecules (blue line) solution and  $\text{Fe}_3\text{O}_4$  particles to which the chiral molecules were attached (red line). (C) The current density of  $\text{Fe}_3\text{O}_4$  NPs linked with L-A3 (chiral)  $\text{Fe}_3\text{O}_4$  NPs linked with MPA (3-mercaptopropionic acid, achiral) and pure  $\text{Fe}_3\text{O}_4$  NPs. (D) Visible absorption spectra from the titration of the electrolyte used (0.1 M  $\text{Na}_2\text{SO}_4$ ) with o-tolidine of bare  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_3\text{O}_4@\text{L-A11}$  (chiral),  $\text{Fe}_3\text{O}_4@\text{L-A3}$  (chiral),  $\text{Fe}_3\text{O}_4@\text{MPA}$  (achiral), and  $\text{Fe}_3\text{O}_4@\text{AIB}_{10}$  ( $\text{NH}-(\text{CH}_2)_2\text{-SH}-(\text{Aib})_{10}\text{-NH}_2$ , achiral). Reprinted with permission from ref. 37. Copyright 2018 American Chemical Society.

Figure 4C shows that the anode currents of  $\text{Fe}_3\text{O}_4$  NPs coated with chiral molecules are much larger than for  $\text{Fe}_3\text{O}_4$  NPs modified by the achiral molecules. Thus, chiral molecules enhance the anode current for water splitting. As expected, there is little difference in performance if L or D enantiomers are used, because either of these choices lead to spin alignment of the radical intermediates on the surface; the correlation of the spin alignment among the radicals is important, not the specific direction of the spins in the laboratory frame.

To confirm the role of CISS-based spin polarization for the anode reaction, we investigated the formation of  $\text{H}_2\text{O}_2$  during water electrolysis with these anodes. In these studies, o-tolidine was used as a redox indicator for the presence of  $\text{H}_2\text{O}_2$ , as it displays an absorption peak at about 436 nm upon reaction with  $\text{H}_2\text{O}_2$ . Figure 4D shows spectra taken of solutions after the reaction was carried out in a 0.1 M  $\text{Na}_2\text{SO}_4$  electrolyte solution. A strong absorbance appeared at 436 nm when the anode was coated by achiral  $\text{Fe}_3\text{O}_4$  NPs, namely, the  $\text{Fe}_3\text{O}_4@\text{MPA}$  NPs and  $\text{Fe}_3\text{O}_4@\text{AIB}_{10}$  NPs, and the absorbance was much weaker when the chiral  $\text{Fe}_3\text{O}_4$  NPs ( $\text{Fe}_3\text{O}_4@\text{L-A11}$  and  $\text{Fe}_3\text{O}_4@\text{L-A3}$ ) were used on the anode. Thus, the chiral imprinted  $\text{Fe}_3\text{O}_4$  NPs inhibit  $\text{H}_2\text{O}_2$  formation. Moreover, Figure 4D shows that  $\text{Fe}_3\text{O}_4@\text{L-A11}$  exhibited better performance in suppressing the production of  $\text{H}_2\text{O}_2$  than does  $\text{Fe}_3\text{O}_4@\text{L-A3}$ . This phenomenon demonstrates that the L-A11 molecules have a stronger CISS response than the L-A3 molecules; their longer chains provide higher spin selectivity.<sup>15</sup>

The data in Figure 4 demonstrate the importance of spin control for reducing the reaction barrier and reducing by-product formation in the OER reaction. In this example, the chirality was imprinted on the NPs by a chiral molecule ligand shell, which also facilitates spin-polarized intermediates because of the CISS-based spin filtering. The concepts illustrated by the results in Figure 4, and our earlier work, have been corroborated in other studies<sup>45,46</sup> and for anodes operating at much higher current densities. For example, Garces-Pineda and coworkers showed that an external magnetic field increases the current densities by two times at  $100 \text{ mA cm}^{-2}$  under high applied bias.<sup>47</sup> and other workers have shown that the magnetization state of ferromagnetic catalysts affect the OER efficiency.<sup>48,49</sup> In a recent study, significant improvements were demonstrated in current density for chiral CoOx films over their achiral analogues at current densities of  $50 \text{ mA/cm}^2$ . Lastly, a number of theoretical studies have identified the importance of spin considerations during  $\text{O}_2$  ( $^3\Sigma_g^-$ ) generation.<sup>50-53</sup> It must be appreciated that the spin selectivity is a result of the reactants being adsorbed on the electrodes and therefore not being able to rotate freely.

The studies of chiral catalysts on the oxygen evolution reaction show that the spin polarization of intermediates (which arises because of CISS effects) can be used to select the desired reaction pathway(s) over others.

## 5. CISS and enantioselective electrochemistry

In addition to improved product selectivity because of spin selection rules, CISS concepts can be applied to enantioselective electrochemical reactions. Recently, we showed that magnetized film electrodes can be used to perform enantioselective electrochemistry.<sup>54</sup> In one case, we used magnetized electrodes to selectively decompose one enantiomer over the other in a racemic mixture. In a second case, we showed that the spin polarization that is introduced into an achiral monolayer film by a magnetized substrate enantiospecifically binds one enantiomer from a racemic mixture, thus creating a chiral adduct between molecules in a racemic mixture and a magnetized substrate. The methods illustrated by these two approaches could be used in enantioselective synthesis as well as chiral resolution. In a third case, we used a magnetized substrate to electropolymerize chiral polymer films on a magnetized electrode. In this case the monomer reactants in the electropolymerization are achiral and the CISS selectivity is believed to arise during the propagation phase of the polymer growth rather than in the initiation phase. A more detailed review/perspective on this work has recently appeared and the reader is referred to that for more details.<sup>9</sup>

### **Future perspective.**

The field of spin selective Chemistry with chiral molecules is in its infancy. As illustrated by the water electrolysis studies with chiral electrodes, controlling the electron spin polarization of adsorbed intermediates affects the reactivity and changes the reaction product outcomes. As an extension of the work performed on the oxidation of water, other multi-electron reactions should be studied, in which the product is in its triplet state, like oxygen, or when the by-product is oxygen. Controlling the spin in these reactions may affect the reaction barriers and change the ratio between different products. Particularly interesting and important examples for such reactions may prove to be the reduction of CO<sub>2</sub> and/or N<sub>2</sub> because of their importance to solar fuels chemistry.

The work described above makes clear that the conventional wisdom as to the electronic nature of a “closed shell” molecular system is misleading when applied to chiral molecules. Spin control has the potential to transform the synthesis of chiral molecules. Although not yet tested, the enantioselective reduction of prochiral molecules to chiral products on a ferromagnetic surface that is coated with chiral molecules which serve as an

asymmetric catalyst could prove to be a general strategy. It is interesting to note that the chiral molecules attached to the surface need not be enantiopure, because the selectivity will be achieved by the direction of magnetization of the substrate which causes the emission of electrons with their spins polarized either parallel or antiparallel to their momentum (see Figure 1).

The findings described here should also change the way one calculates interactions between chiral molecules. As a result of the SDCR effect the interaction between two chiral molecules, or between chiral molecules and a ferromagnetic surface, one should include the spin exchange interaction. Because of the large magnitude of this term, even relatively small spin polarizations of a few percent may result in significant interaction energies. This can be important for Biology as most interaction and conformational adjustments are associated with chiral structures.

## **Biographies**

**Ron Naaman** is Professor Emeritus from the Weizmann Institute. He received his PhD from the same institute and spent two years at Stanford as a postdoctoral fellow and an additional year at Harvard University. His research involves the study of the interaction of electrons with organic molecules and bio-systems like proteins, oligopeptides, and DNA. His research group discovered the chiral induced spin selectivity effect in collaboration with David Waldeck. This effect is the focus of his research for the last two decades.

**Yossi Paltiel** is a Professor in the Applied Physics Department in the Hebrew University of Jerusalem Israel. Prof. Paltiel has worked for both leading high-tech industry groups and in the academic world. Paltiel's group's goal is to establish a way to incorporate quantum mechanics into room temperature devices mimicking Biology and Chemistry processes. In this sense the group also works on spin interfaces using chiral molecules and materials. Paltiel has two startup companies.

**David H. Waldeck** is a Professor of Chemistry and the Academic Director of the Petersen Institute of NanoScience and Engineering at the University of Pittsburgh. He received his PhD in Chemistry from the University of Chicago and then held an IBM postdoctoral fellowship at U.C., Berkeley before moving to Pittsburgh. His research uses methods of spectroscopy, electrochemistry, and microscopy to investigate primary processes in



molecules, supramolecular assemblies, and nanomaterials. Currently, his research is focused on the fundamental understanding of the chiral induced spin selectivity (CISS) effect, as well as its role in electron transfer reactions and electron transport in supramolecular structures.

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