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Spintronics

Spin Selectivity in Electron Transfer in Photosystem I**

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***Abstract:** Photosystem I (PSI) is one of the most studied electron transfer (ET) systems in nature; it is found in plants, algae, and bacteria. The effect of the system structure and its electronic properties on the electron transfer rate and yield was investigated for years in details. In this work we show that not only those system properties affect the ET efficiency, but also the electrons' spin. Using a newly developed spintronic device and a technique which enables control over the orientation of the PSI monolayer relative to the device (silver) surface, it was possible to evaluate the degree and direction of the spin polarization in ET in PSI. We find high-spin selectivity throughout the entire ET path and establish that the spins of the electrons being transferred are aligned parallel to their momenta. The spin selectivity peaks at 300 K and vanishes at temperatures below about 150 K. A mechanism is suggested in which the chiral structure of the protein complex plays an important role in determining the high-spin selectivity and its temperature dependence. Our observation of high light induced spin dependent ET in PSI introduces the possibility that spin may play an important role in ET in biology.*

Electron transfer (ET) is a basic process in chemistry in general and in biological systems in particular. Therefore, much experimental[1] and theoretical[2,3] attention has been given to the subject. Most of the effort was focused on understanding the molecular properties that affect the ET. Photosystem I (PSI), which is part of the natural photosynthesis machinery, is among the most investigated systems[4] both because of its importance and because of the ability to apply various experimental methods for its study.[5–9] Despite the enormous efforts, there are still unresolved dilemmas as for the high efficiency of the ET in PSI. In recent years, it has been suggested that in the first stage of the ET process, that involves the photoexcitation and energy harvesting, there is a quantum coherent process that enables efficient energy transfer by coupling of electronic excitation with vibrations.[10,11] This means that the first stage of energy transfer, in which electronic excitation is coupled to vibrational motion, is an important parameter in determining the overall ET efficiency in PSI.[12]

Here we present evidences that in PSI not only the system structural and electronic parameters affect the ET, but also the electrons'. Namely, the electron spin defines its transfer rate. The spin selectivity is on the order of unity in the ET through the large (10 nm long) protein complex that functions in biological organisms. The spin of the transferred electrons is aligned parallel to its velocity. The spin selectivity peaks at room temperature and vanishes at about 150 K. The spin selectivity found is consistent with former observations that photoelectrons transmission through chiral monolayers[13] and electrons conducted[14,15] through chiral molecules are both spin dependent.[16] In another study small spin selectivity effect was also observed in electron transfer through chiral porphyrins.[17]

Electron transfer in PSI involves photo excitation which produces a singlet excited state of the primary electron donor P700. An electron is then transferred from the heterodimer to the primary acceptor, chlorophyll *a* (A_0), and then to a tightly bound phylloquinone molecule (A_1). The terminal acceptors in PSI consist of a series of three [4Fe-4S] clusters: F_X, F_A, and F_B (see Figure 1 C). The kinetics of these electron transfer processes has been intensively studied.[18,19]

In order to evaluate the spin selectivity, PSI-based monolayers were adsorbed on metal surface. The oriented monolayer was fabricated by the formation of direct sulfide bond between unique cysteine mutants of PSI and the metal surface linkers (see Figure 1 A and Supporting Information (SI)). The adsorbed PSI is in its native form and it displays photo-induced ET.[20,21] The robust PSI, used in these experiments, is isolated from the thylakoid membranes of cyanobacteria and is stable and active when adsorbed in a dry environment.[22] The spin selectivity of the ET process and its temperature dependence were studied by applying a new type of capacitance device[23] (see Figure 1 B–D, and details in SI).

This device is based on monitoring the electric potential between ferromagnetic nickel and silver layers, on top of which the PSI molecules are self-assembled. When the PSI is photo-excited, charge separation occurs. If the donor (P700) is in proximity to the silver, electrons from the silver will be transferred to the now positively charged donor. However, if the final acceptor (F_B) is closer to the substrate, the reduced F_B^- will transfer the electrons to the silver. The electron transfer process results in a change in the electric potential between the grounded Ni and the silver. The potential is positive when electrons are transferred from silver to the oxidized $P700^+$, and it is negative when electrons are transferred from F_B^- to silver. If the charge transfer is spin selective, the electric potential between nickel and silver will depend on the direction of magnetization of nickel, since the

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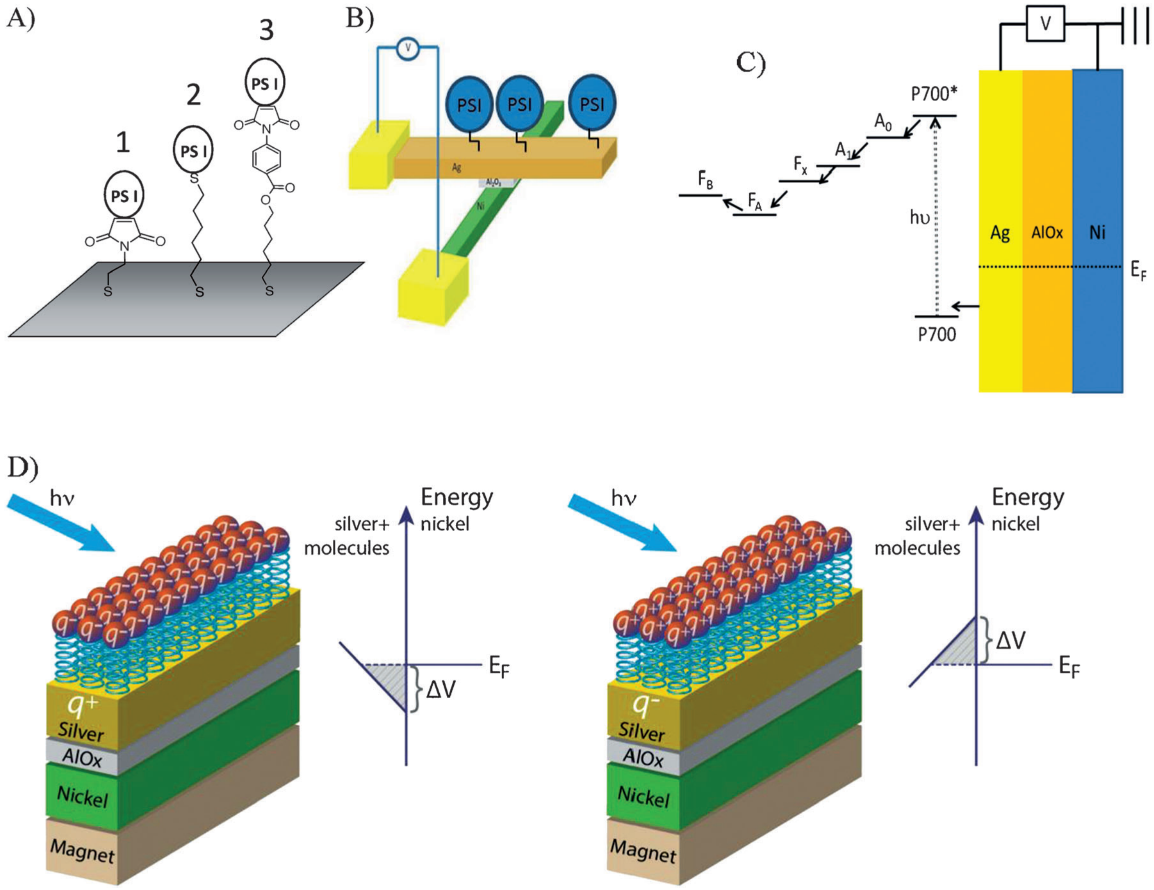

Figure 1. A) The linkers: 1) DTME; 2) 1,6-hexanedithiol; 3) 6-amino-1-hexanethiol coupled to sulfo-MBS. B) The capacitance device used for monitoring ET and spin selectivity. C) Energy level diagram for the electron transfer when the donor (P700) is located near the silver substrate. From each stage in the electron transfer process, electrons can decay back to P700 and charge recombination can occur. The excitation is proportional to the light intensity and the ratio between the charge separation and the recombination rates define the amount of charge located on the acceptor (F_B). The voltage, *V*, measured between Ni and Ag, is proportional to the amount of electrons transferred from Ag to the oxidized P700. D) A scheme of the device and its energy states. On the right: If the donor (P700) is at the far end of the complex, electron is transferred to the silver. At steady state, a dipole is formed with its negative pole on the silver and states above the Fermi level of the system are populated (gray area). If the electrons are spin aligned, they can be transferred to the nickel, only if the unpopulated states on the nickel, near the Fermi level, belong to this spin orientation. Otherwise, they will not be transferred and higher voltage will be measured between the nickel and the silver. On the left: If the donor group is placed near the silver substrate, upon photoexcitation electrons are transferred from the silver to the acceptor and at steady state a dipole is formed with its positive pole on the silver. If the transferred electrons are spin polarized, the empty states below the Fermi level of the system all belong to one spin state. Hence, if the nickel is magnetized so that its electrons are spin polarized and they can tunnel to the silver layer, the voltage will be low, while if it is magnetized in the opposite direction the measured voltage will be higher.

electrons that enter the silver (from the PSI monolayer) or the holes left in the silver (after polarized electrons are transferred to the PSI layer) have well-defined spins. When nickel is magnetized such that its electrons' spins are aligned with the same spin polarization as in the excess electrons or holes in the silver, charge can tunnel between the nickel and the silver through the AlOx; however, if the electrons in the Ni are aligned opposite to the spin of the excess charge in the silver, then tunneling is inhibited until a higher voltage is reached between the nickel and the silver. The spin polarization is defined as the difference in the voltage, measured when the Ni magnetic dipole pointing towards or away from the surface divided by the voltage measured when no magnetic field is applied. More detailed on the device and on the data analysis are given in the Supporting Information.

To determine the effect of the linker, which binds the PSI to the surface, on the spin selectivity, the PSI complexes were bound to the silver surface through three different linkers: dithio-bis-maleimidoethane (DTME), 1,6 hexanedithiol, and 6-amino-1-hexanethiolcoupled to sulfo-MBS (Figure 1 A). The PSI complexes were bound either when the P700 is located near the surface, or in the opposite configuration, with the FeS clusters in proximity to the substrate. The binding configuration depends on the mutation made in the PSI complex. The PSI system is excited by a red (660 nm 10 mW) cw laser chopped at a frequency of 137 Hz with a duty cycle of 50%. The voltage between the silver and Ni layers is measured with a lock-in amplifier. The sample is housed in a vacuum chamber, placed within the gap of an electromagnet, and is attached to a cold finger that allows it to be cooled from room temperature down to 80 K. Each type of

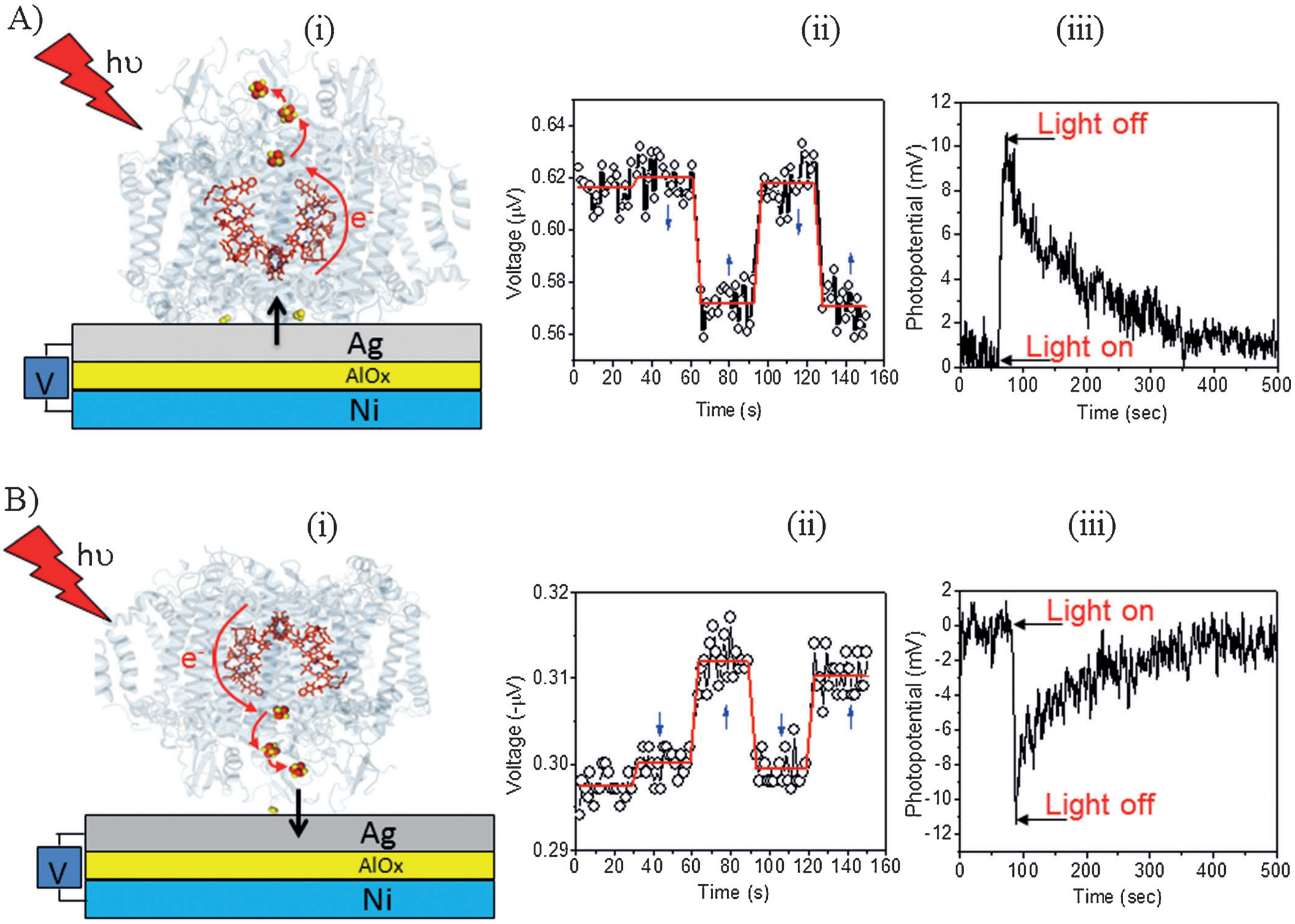

Figure 2. The two configurations studied (i). A) The PSI is adsorbed so that the donor group, P700, is in proximity to the surface, B) when the iron–sulfur clusters (the acceptors) are located near the surface. In (ii), the voltage measured at room temperature is shown when the magnetic field is flipped to point parallel or antiparallel relative to the surface normal (up and down, blue arrows, respectively). In (iii) the photovoltage signal is shown, as measured with a Kelvin probe, where positive and negative signals indicate increases or decreases in the workfunction upon illumination, respectively.

experiment was performed with ten different samples. The errors were determined based on the variation in spin polarization values obtained with these samples. Separately, room temperature surface photo-voltage (SPV)[24] measurements were conducted in which the work function of the silver, coated with the various PSI monolayers, was measured upon photo-excitation. The measurements were performed with a Kelvin probe (Delta Phi controller 07, KP-S).

Figure 2 presents the voltage change when the magnetic field direction is modulated (blue small arrows), for a PSI system bound to the silver either when P700 is in proximity to the substrate (Figure 2A) or when the iron–sulfur clusters are close to the silver substrate (Figure 2B). When P700 is close to the substrate, the photo-voltage measured with the capacitance device is positive, implying that electrons are transferred from the silver to the photoexcited P700. The SPV measurements show an increase in the silver's work function upon illumination, for this configuration. This result is consistent with the transfer of electrons from P700 to the iron complex and the formation of a dipole moment, with the negative pole pointing away from the surface. When the FeS clusters are closer to the silver substrate, the photo-excited electrons are transferred from P700 to the FeS clusters and from there to the silver. Hence, the silver becomes negatively charged (Figure 2B,i) and the work function is lowered. Remarkably, the magnetic field effect is opposite for the two different orientations of PSI relative to the surface; when P700 is close to the silver and the magnetic field of the Ni is pointing away from the surface, the voltage is higher. When the FeS is facing the silver, the opposite behavior is observed (Figure 2B).

The spin polarization is defined as the difference in the voltage measured with the Ni magnetic dipole pointing either towards or away from the surface divided by the voltage measured with no magnetic field applied. At room temperature, no significant dependent of the spin polarization on the linker was observed. The data shown in Figure 2 is not corrected for the loss of spin orientation in the silver and for the nickel not being an ideal spin injector (see SI). The uncorrected polarization is $-8\pm1\,\%$ when the P700 is near

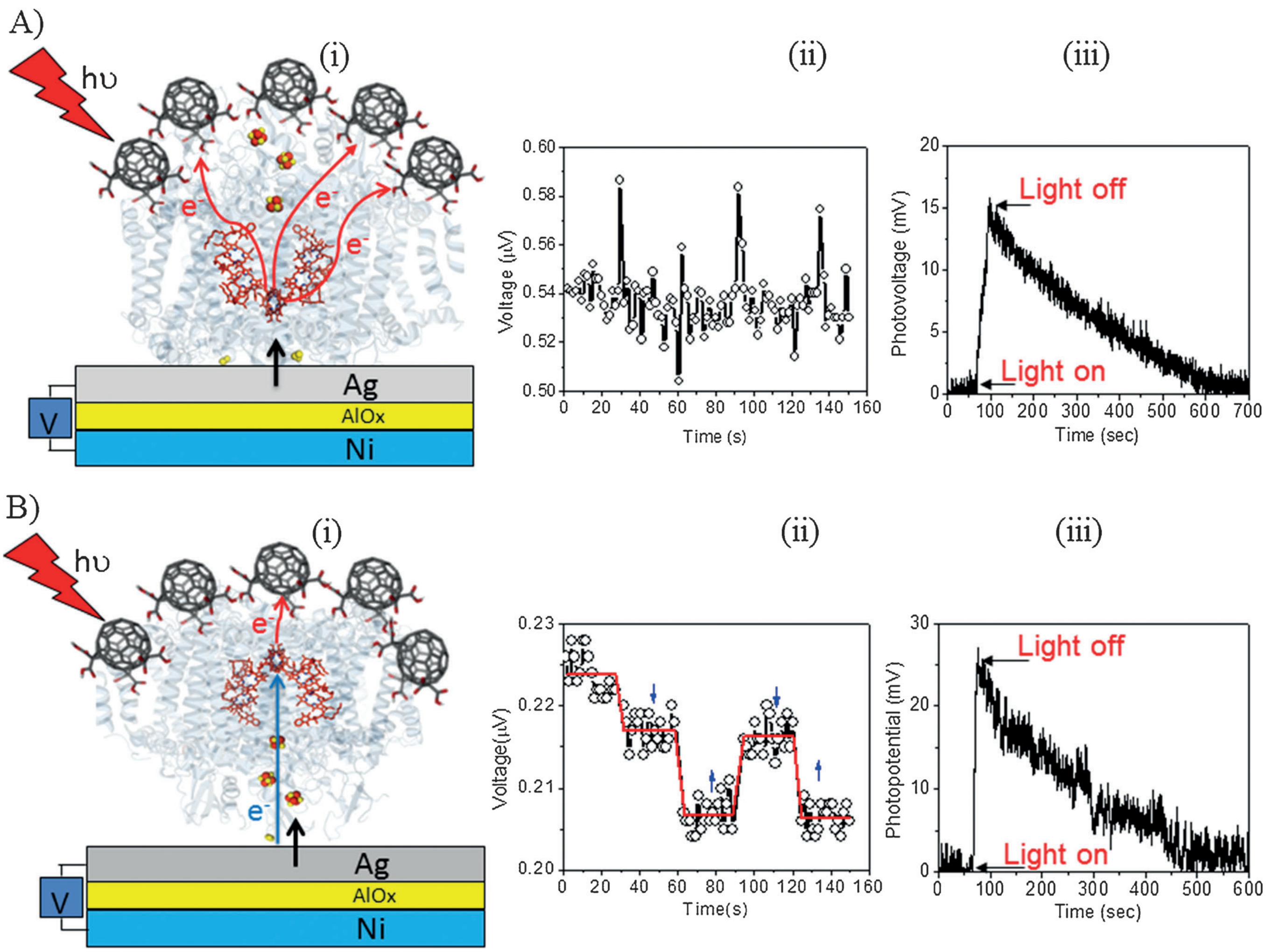

Figure 3. A,B) The PSI decorated with fullerenes on the acceptor or the donor side, respectively. In (ii), the voltage measured at room temperature is shown when the magnetic field is flipped to point up relative to the surface (up, blue arrows) or down (down, blue arrows). In (iii) the photovoltage signal is shown, as measured with a Kelvin probe, where positive signals indicate increase in the workfunction upon illumination.

the surface and $+4\pm1\,\%$ when the FeS cluster are in proximity to the surface. When corrected for the two factors, as described in the Supporting Information, the polarization is $-80\pm20\,\%$ when P700 is facing the surface and $+40\pm10\,\%$ when the FeS clusters are near the surface. Since in the first case the electrons are transferred "away" from the surface, whereas in the second they are transferred towards the surface, these results indicate that in both cases the spin of the transferred electrons is aligned parallel to their velocity. The values obtained for the polarization, at room temperature, are extremely high and exceed those measured for ET through 78 base long DNA with the same device.[23] The correction procedure, as described in the SI has two parameters, the non-ideal spin polarization of the nickel and the silver's Debye temperature. While the error in the first parameter is very small, the actual Debye temperature may vary from sample to sample by about 10%, as probed in ref. 23. This factor introduces large error in the values obtained for the corrected polarization.

The large spin polarization observed is an indication for the spin selectivity in the electron transfer process in the PSI. The results indicate that the electron that leaves the P700 donor has a well define spin (Figure 2A) and the electrons arriving at the acceptor are also polarized (Figure 2B). The results in Figure 2 also serve as an additional verification that the effect is induced by the molecules and not simply by the magnetic field. Since changing the orientation of the PSI relative to the surface affect the direction of spin polarization.

For probing the effect of the ET path on the spin polarization, carboxyfullerenes (CF) were attached to the PSI. In Figure 3A,B the results are presented for PSI covered with CF either on the FeS complexes' side or on the P700 side, respectively. Results from two types of experiments are shown, for the PSI adsorbed on the capacitance device (Figure 3,ii) and SPV measurements (Figure 3,iii). When P700 is close to the substrate, the photo-voltage measured with the capacitance device is positive, implying that electrons are transferred from the silver to the photoexcited P700. The SPV measurements show an increase in the silver's work function upon illumination, for this configuration. This result is consistent with electrons transferred from P700 to the iron complex and the formation of a dipole moment with the negative pole pointing away from the surface. Coating of PSI complexes with carboxyfullerenes (CF), either on the side of P700 or on the side of the acceptors, alters the outcome of the measurements. Because of the very high electron affinity of the fullerenes, they are the best electron acceptor in the system (see Figure 3).[25] The results from the capacitance device and from the SPV measurements indicate that in both cases the electrons are transferred to the fullerenes. No polarization is measured when the fullerenes are close to the iron–sulfur complexes, but when the fullerenes are located near P700, some spin polarization is apparent although it is weaker than in the unmodified system.

Temperature-dependent measurements were performed on a PSI system bound to the substrate via three different linkers. The results indicate that the temperature dependence of the charge separation efficiency results from the linker and that it is only weakly temperature dependent in PSI, within the range of the temperatures studied (see Figure 4A). However, this situation is different when the spin selectivity of the charge separation is measured, which was found to be very sensitive to temperature. Independent of the linker, we have found that the spin selectivity peaks at about 300 K and decreases rapidly with a decrease in temperature. The exact temperature dependence of the spin selectivity is linker dependent (see SI); however, at 150 K it decreased to zero for all linkers (Figure 4B).

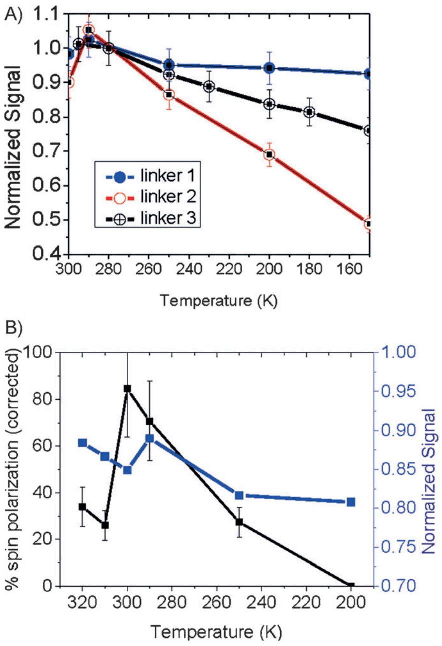

Figure 4. A) Temperature-dependent normalized voltage signal, as measured for PSI adsorbed with its P700 (donor) near the silver surface for three different linkers. The signal was normalized relative to the maximum voltage measured. The linkers are: 1) dithio-bis-maleimidoethane (DTME), 2) 1,6-hexanedithiol, and 3) 6-amino-1-hexanethiol coupled to sulfo-MBS. B) Temperature-dependent normalized signal (blue) and the corrected spin polarization (black) for the same PSI orientation bound by linker 1.

The results indicate that when electrons are transferred from the silver towards P700 and then to the iron–sulfur complexes, the spin selectivity is extremely high, approaching unity. In this case, our experiment probe to what extend the unpaired electron left on the P700 maintains its spin alignment after the second electrons was transferred from the initial singlet state. The observation that the correlation between the spins of the two electrons is maintained for relatively long time is consistent with EPR studies performed on PSI in solution.[26–28] Those studies indicate correlation between the spins, however in the present study we show that the spins are not only correlated but that each electron has a well define spin orientation. Namely, the spin of the electron being transferred is always aligned parallel to its momentum, while the spin of the electron left on the P700 is always aligned antiparallel. Hence, by the fabrication of oriented PSI monolayer's we are able to determine the degree of spin polarization as well as the spin alignment.

When the spin polarization of the process is measured for PSI adsorbed with the iron clusters near the silver, the spin polarization value is about half of that measured in the other configuration. This reduction in the measured polarization may result from the large spin–orbit coupling in the FeS clusters that contribute to some spin depolarization, before the electrons enter the silver. It is also possible that while the electron resides on the FeS cluster, it completely loses its spin polarization and the polarization we observe results from the electron being transferred through chiral environment from the cluster to the silver substrate.

When the fullerenes are attached on the side of the iron–sulfur complexes, in accordance with the CPD results, they attract the electrons and no spin polarization is observed. In this case, the electrons can bypass the iron sulfur clusters (Figure 3A) and they are transferred from P700 in different directions. Hence, there is no specific direction of spin alignment. On the other hand, when the fullerenes are attached near P700, the sign of the voltage indicates that electrons are transferred from the silver towards the fullerenes (opposite to the case with no CF) and spin polarization is present. These observations can be rationalized if upon photo-excitation, an electron is transferred from P700 directly to the nearby fullerenes (red arrow, Figure 3B), leaving the P700 positively charged. In a second step, the positively charged P700 is neutralized by electrons coming from the silver substrate (blue arrows Figure 3B). These electrons are transferred in a well-defined direction and hence they exhibit spin polarization. Namely, by substituting of fullerenes we were able to probe the dependence of the spin polarization on the ET path and prove that spin polarization is highly dependent on the ET path in PSI.

The observed spin orientation is consistent with the chiral induced spin selectivity (CISS) effect observed recently in other chiral system.[16] The effect depends on the chirality of the medium through which the electron is transferred and on the molecular electric field acting on the electron.[29] The CISS is a dynamic effect that induces spin alignment when the electron is in motion and therefore even if spin polarization is partially lost when the electron resides on the cofactor, it will be realigned again in the next hopping event.

The CISS effect can rationalize also the temperature dependence of the spin polarization. Reduction in spin selectivity upon cooling was directly observed in the case of polyalanine, where it was correlated to changes of the electric dipole moment of the system.[30] Namely since the spin selectivity depends on the electric field applied on the electron, temperature dependent structural changes which are known to occur in the proteins, may affect the spin selectivity. Unlike some proteins that undergo "cold denaturation"[31] upon cooling, PSI underwent evolutionary adaption that enables it to function at cold temperatures.[32] Hence, we suggest that the drop in the spin polarization observed at low temperatures is related to changes in charge distribution in the PSI and not to cold denaturation. Interestingly, the reduction in spin selectivity upon cooling does not correlate with a similar drop in the charge separation efficiency, indicating that the electron transfer and the charge recombination processes are less sensitive to local modifications of the electric field in the molecule than the spin selectivity. Hence, spin-sensitive measurements may serve as a new tool for monitoring changes in charge distribution in proteins.

Applying a newly developed spintronic device and a novel technique that utilizes two different PSI mutants, it was possible to control the orientation of the PSI monolayer relative to the device (silver) surface, and to evaluate for the first time the direction and degree of spin polarization in ET through PSI. It was demonstrated that light-induced electron transfer through PSI is highly spin selective and that the electrons' spin are aligned parallel to the ET direction. We propose that the CISS effect is responsible for the high spin polarization observed and its temperature dependence. An open question is whether the spin selectivity serves any biological function. It is known from solid state studies that coupling of the electron's spin to its linear momentum enhances electron transport, due to the elimination of back scattering.[33–35] Therefore, the spin selectivity observed may enhance the efficiency of the electron transfer in PSI. Independent of the existence of this effect in biology, it is still striking that an electron's spin is preserved in electron transfer through such a complex system like PSI.

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