Room-Temperature Operation of a p-Type Molecular Spin Photovoltaic Device on a Transparent Substrate

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The coupling of diverse degrees of freedom opens the door to physical effects that go beyond each of them individually, making multifunctionality a much sought-after attribute for high-performance devices. Here, the multifunctional operation of a single-layer p-type organic device, displaying both spin transport and photovoltaic effect at the room temperature on a transparent substrate, is shown. The generated photovoltage is almost three times larger than the applied bias to the device which facilitates the modulation of the magnetic response of the device with both bias and light. The device shows an increase in power conversion efficiency under magnetic field, an ability to invert the current with magnetic field and under certain conditions it can act as a spin photodetector with zero power consumption in the standby mode. The room-temperature exploitation of the interplay among light, bias, and magnetic field in the single device with a p-type molecule opens a way toward the development of efficient high-performance spin photovoltaic cells.

Vertical spin valve (SV) structures are widely used to study spin transport through organic semiconductors (OSCs).[1–3] Unlike inorganic semiconductors, OSCs are composed of light chemical elements resulting in a weak spin–orbit coupling and hyperfine interaction, which leads to long spin diffusion times.[4–8] Recently, and in spite of the relatively low carrier mobility of the materials studied, long distance spin transport has been achieved in several organic semiconductor based spin valves.[3,9] OSCs also offer a large degree of tunability in their mechanical, electrical, and optical properties over their inorganic counterparts, which can be used to add multifunctionality in a single device.[10–17] One such example is the observation of a photovoltaic effect in an electron transporting (n-type) C_{60} based spin valve, in which the magnetic and optical responses are coupled and this leads to several novel functionalities in a single device at low temperature.[16] In spite of this advancement, a basic standard small molecule organic photovoltaic cell is composed of both an electron (n-type) and a hole transporting (p-type) layer.[18–20] In order to achieve a high photovoltaic response of the SV toward its room-temperature multifunctional operation, devices with a hole transporting material have to be realized as a necessary step.

Here in this manuscript, we present the room-temperature operation of a p-type molecular spin photovoltaic (MSP) device on a transparent glass substrate. Our device has a simple vertical SV geometry composed of a bottom ferromagnetic (FM) electrode cobalt (Co) capped by a leaky AlO_{x} barrier, a p-type organic molecule (hydrogen phthalocyanine; H_{2}Pc) acting as the spin transporting channel and a top FM electrode (Ni_{80}Fe_{20}).[2,3] H_{2}Pc is a commonly used p-type material for small molecule organic photovoltaic cells and is also known for its stability in ambient conditions.[20–22] Figure 1a presents the schematic diagram of an H_{2}Pc molecule, while Figure 1b shows the transfer characteristic of a 30 nm thick H_{2}Pc based lateral organic field effect transistor (LOFET) respectively, which indicates the p-type operation with a lateral hole mobility of 3.3 \times 10^{-5} \text{ cm}^{2} \text{ V}^{-1} \text{ s}^{-1}.[23] The growth of the H_{2}Pc molecule on the glass substrate is amorphous and we thus expect isotropic charge transport (see Figures S1 and S2, Supporting Information). Information regarding the absorbance of the different layers is provided in Figure S3 (Supporting Information).

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no external magnetic field is applied to the device. The values of $I_{SC}$ and $V_{OC}$ are relatively small as compared to other conventional photovoltaic cells since in our case the device is composed of a single photoactive layer.\cite{14,15,25–29} Under an applied external magnetic field, the photovoltaic response of the device increases, yielding a higher $V_{OC}$ value when the orientation of the FM electrodes is antiparallel as shown in Figure 2b. The power conversion efficiency increases $\approx 12\%$ when the relative orientation of the FM electrodes changes from parallel to antiparallel state.\cite{16} The mechanism of the photovoltaic effect under the absence of applied magnetic field and for parallel and antiparallel orientation of the electrodes under magnetic field is schematized in Figure 2c,d in the rigid band approximation at equilibrium. We infer from the $I$–$V$ response of our device that, at equilibrium, there is an interface dipole formed at the H$_2$Pc/Ni$_{80}$Fe$_{20}$ interface despite the apparently good energy level alignment. On the contrary, the bottom interface is less affected because of the presence of the AlO$_x$ layer which isolates the molecule from highly reactive Co electrode underneath. In our model (Figure 2c), the photogenerated holes at the molecule–Ni$_{80}$Fe$_{20}$ interface are collected by the Ni$_{80}$Fe$_{20}$ electrode due to the in-built potential, before recombining with the electrons. The electrons then can either be transported to the bottom Co electrode by the in-built potential or lost due to partial recombination. Since H$_2$Pc is a p-type organic semiconductor, the generated photocurrent is mainly dominated by the collected holes at the molecule–Ni$_{80}$Fe$_{20}$ interface. In the open-circuit mode, the injected spin-polarized carriers must compensate the photogenerated carriers or in other words, the applied bias must be equal and opposite to the photo-generated voltage. In the parallel configuration of the electrodes, the photogenerated voltage ($V_{OC}$, P) is the same as in the case without applied magnetic field while in the antiparallel case, the injected spin-polarized holes are reflected by the bottom Co electrodes and can only be compensated by an enhanced photovoltage $V_{OC,AP}$ (Figure 2d,e).

We define this change in open-circuit voltage ($\Delta V_{OC}$) as $V_{OC,AP} - V_{OC,P}$. Figure 3a presents the modulation of $\Delta V_{OC}$ with respect to magnetic field and light. At stronger light intensities, the photogenerated carriers can be compensated with the application of a higher device bias in the parallel configuration and hence, even a higher applied bias is needed for the compensation in the antiparallel configuration. We observe that the value of $\Delta V_{OC}$ increases linearly with increasing light intensity (Figure 3b). This can be useful for a spin photodetector with zero power consumption since in the open-circuit mode of operation the current through the device is zero.\cite{30–32} In the short-circuit mode, the photogenerated current remains constant over the range of applied magnetic field simply because the photogenerated carriers are not spin-polarized (Figure 2c).

In dark conditions, we define the magnetocurrent (MC) (in percentage) as $(I_P - I_{AP})/I_{AP} \times 100\%$, where $I_P$ and $I_{AP}$ are
Figure 2. a) Current–voltage ($I$–$V$) response of the MSP device in dark and light (7.5 mW cm$^{-2}$) irradiation conditions without the application of any magnetic field. b) $I$–$V$ response of the device in dark and during light irradiation when the electrodes are in parallel or antiparallel configuration. c) Mechanism of electron–hole transport upon light irradiation under zero bias conditions. d,e) Spin-dependent charge carrier transport through the molecular layer under light irradiation in both parallel and antiparallel configurations of the electrodes in the open-circuit mode.

Figure 3. a) Modulation of the open-circuit voltage with magnetic field at various light intensities. The net current through the device is zero. b) The difference in open-circuit voltage ($\Delta V_{OC} = V_{OC, AP} - V_{OC, P}$) as a function of light intensities. $\Delta V_{OC}$ is linear with respect to the light intensities. c) $I$–$B$ response of the device with zero applied bias in dark and light irradiation conditions. The photogenerated current is unaffected on the application of magnetic field as it is not spin-polarized. d) Magnetocurrent (MC) response of the device at 300 K.
the currents in the parallel and antiparallel configuration of the electrodes, respectively. We observe an MC of 7% for an applied bias of 10 mV at room temperature (Figure 2d). Since the photogenerated voltage (of around 27 mV) with a light irradiation of 7.5 mW cm\(^{-2}\) is larger than the applied bias (10 mV), in these conditions the output current of the device can be modulated on both side of the zero-current level by varying the light intensity. The light modulation of the output current does not affect the spin-polarized charge transport through the device as the photogenerated carriers are non-spin-polarized, and the photocurrent only shifts the baseline of the magnetocurrent response of the device. Figure 4a shows the output current versus magnetic field (\(I-B\)) response of the device under various light irradiation conditions at an applied bias of 10 mV. The overall device current decreases with increasing light intensity. The \(I-B\) responses of the device moves from an overall positive current to an overall negative current through a point in which for a particular light intensity the antiparallel state current can be set to zero. Similarly, for a slightly higher intensity, the parallel state current across the device can be set to zero. This effect could be used to realize a switch having zero power consumption in the standby state. Moreover, at yet another light intensity, the parallel state current can exactly be set equal and opposite of the antiparallel state current (\(I_P = -I_{AP}\)) (see Figure S2, Supporting Information). This can act as a magnetic current converter. However, in all light intensities the value of \(\Delta I = I_P - I_{AP}\) remains the same for the applied bias of 10 mV.

We now focus on the response for a particular fixed light intensity (in the case shown of 7.5 mW cm\(^{-2}\)). Here, the \(I-B\) response of the device can be modulated around the zero-current level with a modified \(\Delta I\) under different applied bias (Figure 4b). The modification of \(\Delta I\) with both light and bias is summarized in Figure 4c. \(\Delta I\) remains constant with increasing light intensity for a fixed device bias. This again confirms that the photogenerated carriers do not affect the spin-transport properties through the device. At a fixed bias the amount of spin-polarized charge carriers flowing through the device remains constant whereas for a change in applied bias, this amount changes owing to the change in \(\Delta I\). The current level in the parallel state of the device can be tuned both by applied bias and light. The applied bias to the device injects spin-polarized carriers into the molecular layer through molecule–Ni\(_{80}\)Fe\(_{20}\) interface and thereby the spin-valve operation of the device is determined by the transport of the spin-polarized carriers through the channel and its detection. On the other hand, the light intensity modulates the spin-polarized charge carriers through the device.

**Figure 4.** a) Modulation of output current of the device as a function of the magnetic field with varying light intensities at a constant bias of 10 mV. b) \(I-B\) responses of the device under constant light irradiation but varying the bias from 10 to 70 mV. c) The difference in current in parallel and antiparallel state (\(\Delta I\)) as a function of light intensity for a constant bias of 10 mV and as a function of applied bias for a constant light intensity of 7.5 mW cm\(^{-2}\). d) Electro-optical modulation of the device under varying applied bias and light intensity to have zero output current in the parallel state, meaning that the generated open-circuit voltage cancels exactly the applied bias.
hand, the incident light creates non-spin-polarized carriers responsible for the photocurrent generation. The spin-polarized current modulation in the device is mediated by these photon-generated non-spin-polarized carriers without the loss of spin polarization of the injected spin-polarized carriers. The interplay between light and applied biases can lead to certain states where for an applied bias equal to the open-circuit voltage, the parallel state current can be set to zero. At those particular light intensities and applied biases, spin-polarized current can be generated for the antiparallel orientation of the electrodes as shown in Figure 4d. This complex electro-optical modulation of the device can lead to the operation of a spin valve that consumes negligible power in the stand-by state and can act as a spin photodetector.[16,33,34]

In conclusion, we have illustrated the room-temperature operation of a spin-photovoltaic device based on a thin film of hole transporting small molecule H$_2$Pc on a transparent glass substrate. The photovoltaic power conversion efficiency was enhanced as a result of the enhanced photocurrent generation with the application of a small applied magnetic field. The device can act as a perfect magnetic current converter, as a spin photodetector, and can generate spin-polarized current under certain applied bias and light irradiation conditions. Our approach opens the door toward the generation of a more complex and highly efficient spin-photovoltaic device, e.g., a p-n heterojunction device, which is a necessary building block for future devices operating at room temperature on transparent substrates.

Experimental Section

Device Fabrication: Vertical spin valves with Co/AIO$_x$/H$_2$Pc/Ni$_{80}$Fe$_{20}$ were fabricated in situ in an ultrahigh vacuum (UHV) chamber with base pressure less than 10$^{-9}$ mbar. The pyrex glass substrates were cleaned in an ultrasonic bath using acetone and isopropanol subsequently and then dried with a N$_2$ flow. The substrates were cooled down to liquid N$_2$ temperature before the deposition of the materials. At first, eight 12 nm thick Co lines were deposited through shadow masking technique to define the bottom electrodes. A 1.5 nm Al layer was then deposited everywhere on the sample and semi-oxidized to form a leaky AIo barrier. A 90 nm thick H$_2$Pc was then deposited again with shadow masking technique to form the molecular layer on Co/AIO$_x$ while leaving one junction without the molecular layer as reference. Finally, the top Ni$_{80}$Fe$_{20}$ layer was deposited using another shadow mask to complete the device. The area of the cross-bar geometry devices was ranging from 1 µm$^2$ to 5000 µm$^2$. Co, Ni$_{80}$Fe$_{20}$, and Al were evaporated from Lesker (purity: 99.95%) and were used as received. Co and Ni$_{80}$Fe$_{20}$ were evaporated from an e-beam evaporator in one of the UHV chambers with a rate of 1 Å s$^{-1}$ (for the top Ni$_{80}$Fe$_{20}$ deposition, the starting rate was 0.1 Å s$^{-1}$ for the first 2 nm to protect the soft organic layer). Al was thermally evaporated from a Knudsen cell at a rate of 1 Å s$^{-1}$. H$_2$Pc was purchased from Sigma Aldrich (with 99.99% purity) and was used without further purification. The molecules were evaporated at a rate of 0.1 Å s$^{-1}$ from another Knudsen cell from a separate chamber.

Thin Film Characterization and Electrical Measurements: Both the metal and the organic materials were calibrated using the quartz crystal monitor during the evaporation. The film thicknesses were measured using X-ray reflectivity (XRR) technique and the morphologies were checked by atomic force microscopy (AFM) technique. The devices were measured in a standard four-probe configuration in a variable temperature Lakeshore probe station (equipped with magnetic field) under high vacuum.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

molecular spintronics, organic spin valves, spin-photovoltaics, transparent substrates

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