Magnetic fringe field control of electronic transport in an organic film

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Abstract

Random, spatially-uncorrelated nuclear hyperfine fields in organic materials dramatically affect electronic transport properties such as the electrical conductivity, photoconductivity, and electroluminescence1–8. The influence of these nuclear hyperfine fields can be overwhelmed by a small (∼10 mT) uniform external applied magnetic field, even at room temperature. As a result, in such applied magnetic fields at room temperature the kinetics of exciton formation, bipolaron formation, and single-carrier hopping are all modified, leading to changes in room-temperature electrical transport properties in excess of 10% in many materials. Here we demonstrate a new method of controlling the electronic transport in an organic film, using the spatially-varying magnetic fringe fields of an unsaturated ferromagnetic electrode. The effect of these magnetic fringe fields on electronic transport is hysteretic, anisotropic, occurs on a magnetic field scale larger than the nuclear hyperfine fields, and depends sensitively on the distance of the organic material from the ferromagnetic electrode.
Most spintronic devices use a change in the relative magnetizations of two magnetic electrodes to control the flow of electronic current through a nonmagnetic material\textsuperscript{9–11}, such as by spin-selective scattering (as in current-in-plane giant magnetoresistance)\textsuperscript{12,13}, or spin injection (as in current-perpendicular-to-plane giant magnetoresistance)\textsuperscript{14}. For the even simpler geometry of a single magnetic electrode, spin-orbit effects in the materials can permit control of the injection process of carriers at the interface between magnetic and non-magnetic materials, through differences in the tunneling matrix element for magnetizations parallel to or perpendicular to the interface (tunneling anisotropic magnetoresistance, or TAMR)\textsuperscript{15}. The magnetoresistive effects from a single magnetic electrode that we find, however, are closely related to the magnetoresistance of a bulk organic layer, and thus are substantial ($\sim 10\%$) at room temperature, can be engineered by controlling the domain structure of the magnetic electrode, and are not sensitive to injection at the magnetic-metal/organic interface. Our devices, which do not rely on spin injection\textsuperscript{16,17} or spin-valve behavior\textsuperscript{18–22}, may provide a simple approach to integrating magnetic metals and organics for hybrid spintronic devices.

Figure 1 summarizes the well-known magnetoresistance of organic layers at room temperature and the central features of the new magnetoresistive effect, which depends on the fringe field of a single magnetic electrode. Shown are the typical magnetoresistance measurement (Fig. 1a) and physical regimes of an organic device with two nonmagnetic electrodes (Fig. 1bc), along with the magnetoresistance (Fig. 1d) and physical regimes of an organic device with one ferromagnetic and one nonmagnetic electrode (Fig. 1efg), referred to here as a “half” spin valve, or semi spin valve. Transport through the organic film occurs by a sequence of hops along a path connecting the top electrode to the bottom electrode (Fig. 1, brown lines), and the rate of transport is dramatically affected by variations in the local magnetic field along the path, as found in numerous experimental and theoretical studies\textsuperscript{1–4,7}. If the source of that inhomogeneous field is a nuclear hyperfine random field, shown in Fig. 1be, then the field is intrinsic, random and spatially uncorrelated. An applied magnetic field $B$ that exceeds this random hyperfine field $B_{\text{HF}}$, as shown in Fig. 1c, will change the resistivity uniformly through the film; thus the magnetoresistance (Fig. 1a) is independent of distance from the nonmagnetic electrode as well as applied magnetic field angle.

The strength and spatial correlation length of magnetic fringe fields induced by a ferromagnetic electrode, however, depend sensitively on the distance from the electrode to the
organic film as well as the magnetic domain structure of the electrode (Fig. 1f)\textsuperscript{23}. For a magnetic electrode with a well-defined magnetic anisotropy, this domain structure will be highly anisotropic and hysteretic, and can also be controlled using traditional approaches for engineering the magnetic anisotropy and coercive fields of magnetic media\textsuperscript{23,24}. Specifically the domains will be present for magnetic fields greater than the domain generation field $B_N$ and less than the saturation field $B_{\text{sat}}$. If $B_N > B_{\text{HF}}$ then a new region of modified resistivity will occur for magnetic fields between the domain generation field and the saturation field, causing the magnetoresistance to exhibit a replica of the resistivity at $B = 0$, but now at higher field range (Fig. 1d). For a sufficiently distant ferromagnetic electrode the magnetic fringe fields will be smaller than the nuclear hyperfine fields; for such a semi spin valve the organic film’s electronic transport should resemble that for a device with two nonmagnetic electrodes. A ferromagnetic electrode with very large domains would also likely have little effect on the electronic transport in the organic material, as the fringing field resulting from large domains should be close to spatially uniform and resemble that of an applied external magnetic field. Thus the length scale for magnetic field effects on electronic transport could be inferred from the dependence of the organic film’s conductivity on domain structure; measurements here indicate that length scale to be larger than 50 nm. The hysteretic behavior of the magnetic domains, whose spatial size is smallest at intermediate applied magnetic fields, can cause these semi spin valves to exhibit similar magnetoresistance curves to true spin valves, even though no spin injection is required for the semi spin valve to function.

The organic semiconductor semi spin valve device consists of the following thin-film layers, starting from the Si/SiO$_2$ substrate (for additional details see Methods). A Co/Pt multilayer film with perpendicular magnetic anisotropy (PMA) is the bottom electrode and source of magnetic fringe fields. This PMA magnetic electrode can be magnetized by large perpendicular magnetic field and demagnetized by large in-plane magnetic field (see supplementary information), and is terminated with (nonmagnetic) Pt. A conducting polymer layer (also referred to as a synthetic metal) consisting of the material poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS, referred to as simply PEDOT from now on) was deposited on top of this electrode and serves as the hole-injecting layer. PEDOT is commonly employed for this purpose in organic light-emitting diode devices\textsuperscript{25}. The combination of Pt termination of the electrode and conducting PEDOT exclude tunneling from the ferromagnetic metal to the PEDOT, thus eliminating TAMR. The next layer consists of a thin ($\approx$
30 nm) film of the organic semiconductor tris-(8-hydroxyquinoline) aluminum (Alq3). Alq3 is one of the most common organic semiconductors used in organic light-emitting diodes26. Alq3 also has a particularly large organic magnetoresistive effect (Ref. 27 and references within), and the magnetoresistive response to either the random hyperfine fields or magnetic fringe fields reported here occurs inside the Alq3 layer. The lack of spin-orbit interaction in PEDOT and Alq3 eliminates TAMR at the PEDOT/Alq3 interface as a source of the observed effect. Finally, Ca covered by Al was used as the top electrode, taking advantage of the favorable work function of Ca for electron injection. The contributions of the PEDOT and Ca electrodes to the device resistance (and magnetoresistance) are negligible, since they are metals, whereas Alq3 is an intrinsic semiconductor. In summary, the current path in our devices is: Bottom ferromagnetic electrode → PEDOT → Alq3 → Ca/Al. The PEDOT hole-injecting layer also, importantly, serves as a spacer layer of variable thickness (see Methods) to separate the magnetoresistive material, Alq3, from the bottom electrode that is the source of the magnetic fringe fields. All measurements reported here are at room temperature.

Figure 2a shows a typical magnetoconductivity trace for an organic device that uses two non-magnetic electrodes and whose magnetoconductivity is caused by random hyperfine fields. This device will serve us as a reference when, later on, we will discuss fringe-field induced magnetoconductivity. Panel a shows that the hyperfine induced magnetoconductivity response has a magnitude of ≈10% in our Alq3 devices. The effect essentially saturates for fields in excess of 0.1 T, is non-hysteretic, and has a full-width-at-half-maximum of approximately 20 mT (see inset). The effect is also independent of the direction of the applied magnetic field, and nearly independent of the Alq3 layer thickness.

Now we turn our attention to the magnetoconductive response of the organic semi spin valve. Fig. 2b shows the effect of magnetizing the electrode on the semi spin valve device conductivity. The device was initially in a demagnetized state. The conductivity is initially low, and increases by almost 10% as the magnetizing magnetic field is applied. Upon removing the magnetizing field, the conductivity decreases again, but remains significantly above the level for the demagnetized device. This hysteretic behaviour is in contrast to the hyperfine induced magnetoconductivity of the reference device and clearly demonstrates an effect of the magnetic electrode on the device conductivity. Panels c and d are for perpendicular and in-plane applied magnetic fields, respectively, and show the magnetoconductivity as the
applied magnetic field is swept smoothly from large negative to large positive fields (black lines) and back (red lines). For both applied field configurations magnetoresistive effects of \(\approx 5\%\) are achieved for large fields, but the functional dependence of the magnetoconductivity on the applied field is anisotropic. Fig. 2 c and d contain several data sets offset along the y-direction that show the dependence of the semi spin valve effect on the thickness of the PEDOT spacer layer, i.e. distance between magnetic electrode and the magnetoresistive organic semiconductor. The hysteretic response of semi spin valve effect gradually decreases with increasing PEDOT spacer layer thickness, and for a spacer layer thickness of 100 nm the magnetoconductivity curves are similar to those measured in non-magnetic organic semiconductor devices (see Fig. 2a). In the following discussion we focus on the case of a perpendicular applied field, where it is possible to directly correlate the semi spin valve effect with the magnetic response and domain dynamics in the magnetic electrode.

We examine the relation between the electrode magnetic response and the magnetoconductivity by fabricating two devices on ferromagnetic electrodes with different perpendicular magnetic anisotropy. Fig. 3 shows magnetoconductivity curves and their correlation with magnetic hysteresis loops on the same devices. Hysteresis loops were measured using the magneto-optic Kerr effect (MOKE) technique. The electrode shown in Fig. 3a has a smaller coercive field (0.1 T), than the one presented in Fig. 3b (0.2 T). In both cases the magnetoconductivity (upper panels) changes are maximum at the coercive field and the conductivity is suppressed between the nucleation field and saturation field of the ferromagnetic electrode. However, in the device with the electrode with the larger coercivity (Fig. 3b) both the effect of the hyperfine induced magnetoconductivity variations (near zero applied field) and those induced by the ferromagnetic electrode (near the coercive field) are seen to occur in the same device in separate applied magnetic field ranges. This data shows that the hysteretic magnetoresistance of the organic layer is directly associated with hysteretic magnetization of the ferromagnetic electrode. This demonstrates that the conductance of the semi spin valve is suppressed when there are magnetic domains in the ferromagnetic electrode, i.e when the electrode is not magnetically saturated.

In order to further analyze the relation between the magnetoconductance and the magnetic domain structure, we imaged the domain structure of the electrode as a function of applied field using a transmission x-ray microscopy (TXM) and the x-ray magnetic circular dichroism (XMCD) effect\textsuperscript{28}. Fig. 4a shows an XMCD image of the magnetic electrode, with
the x-ray energy tuned to the Co L\textsubscript{3} absorption edge and incident normal to the sample surface. The measurements were conducted at the coercive field of the electrode (\(M \approx 0\)) and show ‘up’ (white) and ‘down’ (black) magnetized domains with sizes of about 200 nm in a labyrinth pattern (see supplementary material for images at different applied fields and videos of the domain dynamics).

These images have been used to determine the fringe magnetic fields at different distances above the ferromagnetic electrode. The four panels of Fig. 4\textbf{b} correspond to the fringe fields at four different distances above the electrode, calculated from image Fig. 4\textbf{a} using micromagnetics. Two-dimensional representations of the field magnitude are shown in Fig. 4\textbf{c} on a color scale for a \(3 \times 3 \ \mu\text{m}^2\) square area. Close to the electrode, the fringe fields mirror the magnetic-domain structure, with large values close to domain boundaries. At larger distances the fringe fields are reduced and vary on larger spatial scales. Fig. 4\textbf{c} plots the lateral correlation function of the fringe fields. This figure shows that the correlation length of the fringe fields increase with increasing distance from the surface while the root-mean-square (rms) amplitude of the fields decay rapidly with distance (inset, Fig. 4\textbf{c}). Higher Fourier components of the fringe field decay more rapidly with distance from the electrode surface, leading to a smoother variation in the fringe field and a larger field correlation length. Two effects play a role: the decrease in the fringe field strength with distance from the magnetic electrode, and the increase in the field correlation length. The strength alone is insufficient to explain the results in Fig. 2, as the fringe field strength still exceeds that of the nuclear hyperfine field at distances of 100 nm from the organic layer, whereas the magnetoresistive curves do not show any effect from the magnetic electrode.

The field correlation lengths in Fig. 4 at different distances from the electrode can be correlated with the magnetoresistance measured in devices of different thickness (Fig. 2). Although controversy remains about the origin of the organic magnetoresistive effect with two nonmagnetic electrodes, most theories consider it a kinetic effect involving the spin-dependent recombination of two carriers or formation of two-carrier complexes. A simple model of the effect, which can be applied to many of these mechanisms\textsuperscript{3,4,7}, analyzes the kinetics for two sites\textsuperscript{29} which are considered to be bottlenecks in the percolative carrier transport, one at most and the other at least singly occupied. The radial size of a typical percolation cluster, and thus the typical distance between the two bottleneck sites in transport, is comparable to the thickness of the layer traversed (30 nm of Alq\textsubscript{3}). From Fig. 4 the
typical length scale of fringe field correlation is $\sim 50 - 100$ nm, which ranges from comparable to much larger than the Alq$_3$ layer thickness. For Alq$_3$ layers located more than 50 nm from the magnetic electrode the fringe field correlation length scale exceeds the typical separation of bottleneck sites, and thus the fields acting on both of the two bottleneck sites are typically parallel. In this situation the spatially-varying fringe field will not produce this magnetoresistive effect, as confirmed by Fig. 2.

We have shown that the structure of a spatially-varying magnetic fringe field originating from an unsaturated magnetic electrode dramatically modulates the magnetoresistance of an organic layer at room temperature, over the magnetic field range where an applied field overwhelms the spatially-varying fringe field. Thus patterning of the domain structure of the magnetic electrode should permit a detailed engineering of the magnetoresistive curves caused by the single magnetic electrode, producing the greatest magnetic field sensitivity in the field regime where domains are shifting in the magnetic electrode. In principle semi spin valve devices should work even if the current is not routed through the magnetic layer, suggesting a simple approach to solving the impedance mismatch problem between magnetic metals and organics for hybrid spintronic devices. The termination with Pt and use of a conductive PEDOT layer to eliminate tunneling rule out tunneling anisotropic magnetoresistance$^{30}$ as an explanation for our results. Our results also differ in trend and dependence on magnetization orientation substantially from that expected for TAMR, and do not require spin-orbit interaction to play a role in the device structure. We emphasize that the behavior of the magnetoresistive curves can strongly resemble spin-valve features, even though no spin valve is present, and no spin injection is occurring in the device.

**METHODS**

**Semi spin valve fabrication**

The organic semiconductor semi spin valve consists of a ferromagnetic layer, a hole-injecting layer, an organic semiconductor, and a top electrode. The ferromagnetic electrode is a Co$|$Pt multilayer (30 repeats and 24 nm in total thickness, terminated with 5 nm of Pt) deposited using electron-beam evaporation in ultra high vacuum on oxidized Si wafers for devices studies and Si supported Si$_3$N$_4$ windows for magnetic domain imaging studies using
an x-ray transmission microscope. Optical lithography is used to define the bottom electrode geometry. A hole-injecting layer, conducting polymer poly(3,4-ethylenedioxythiophene)poly(styrenesulfonate) (PEDOT:PSS), was deposited by spin-coating from an aqueous suspension (suspension purchased from H. C. Starck, CLEVIO P VP AI 4083). A 30 nm thick film of organic semiconductor Alq$_3$ (sublimed grade, purchased from HWSands Corp.) was deposited by thermal evaporation in high vacuum and at room temperature. The Ca (10 nm) layer, covered by a capping layer of Al (40 nm), was deposited by electron-beam evaporation at room temperature through a metal stencil to obtain a cross point device geometry of dimension 500 $\mu$m $\times$ 500 $\mu$m. The ferromagnetic electrodes were characterized by magnetic force microscopy (MFM), ferromagnetic resonance (FMR), vibrating sample magnetometry (VSM), and magneto-optical Kerr effect (MOKE).

**Measurements**

Magnetoresistance measurements were done in a closed-cycle He cryostat positioned between the poles of an electromagnet. The measurements reported here are all at room-temperature. Magnetoresistance (MR) measurements were performed using a Keithley 2400 sourcemeter. X-ray measurements were performed at the Advanced Light Source (ALS) at the Lawrence Berkeley National Laboratory. Images were taken with XM-1 zone-plate microscope at beamline 6.1.2.

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FIG. 1. Comparison of magnetic fringe-field control of magnetoresistance with non-magnetic organic magnetoresistance. a Magnetoresistance for nonmagnetic organic device, showing a low-field regime and a high-field regime. b Transport along a hopping path (brown line) through the organic film is affected by variations in the local spin quantization axis along the path (local spin quantization axis shown by pink arrows). c An applied magnetic field that exceeds the hyperfine field provides a uniform local spin quantization axis in the film, enhancing transport. d Magnetoresistance for the semi spin valve, showing in addition an intermediate field behavior. e Low-field regime: the electrode magnetization is saturated, yielding negligible fringe fields. f Intermediate-field regime: domains in the electrode have nucleated, and a spatially inhomogeneous fringe field (red/blue arrows) causes variations in the local spin quantization axis. g High-field regime: saturated electrode, uniform spin quantization axis.

FIG. 2. Magnetoresistance in organic semiconductor devices: a Organic magnetoconductivity caused by random hyperfine fields in a device using two non-magnetic electrodes. b Hysteretic conductance in an organic semiconductor semi spin valve with a bottom ferromagnetic electrode. Initially the electrode is in a demagnetized state. At time 35 s a magnetizing magnetic field is applied (red curve). Even after the magnetizing magnetic field is removed, the device conductivity (black curve) remains several percent above its original value. cd Dependence of the magnetoconductivity on the thickness of the PEDOT spacer layer between the ferromagnetic electrode and magnetoresistive organic semiconductor for c perpendicular and d in-plane applied magnetic fields, respectively. The black curves are for sweeps from large negative fields to large positive fields, and the red curves for the return sweep. The numbers assigned specify the PEDOT spacer layer thickness (data offset along the y-axis for added clarity). The applied voltage biases are 4.5V, 7V, 7.2V and 7.5V for the 15nm, 20nm, 50nm and 100nm devices, respectively. At small spacer layer thickness the magnetoconductivity is dominated by the hysteretic fringe-field induced magnetoconductance, whereas for large spacer layer thickness we recover the hyperfine-induced magnetoconductance shown in a.
FIG. 3. Correlation between magnetoconductivity and magnetic switching for two different ferromagnetic bottom electrodes: ab show magnetoconductivity in semi spin valve devices, cd the magneto-optic Kerr effect (MOKE) measurements of the magnetic electrodes. The experiments were performed using a perpendicular applied magnetic field. The devices in top panels a and b used a 15 nm and 20 nm PEDOT spacer layer, respectively. This figure shows that the hysteretic magnetoresistance response correlates well with the magnetic state of the bottom electrode as determined by the MOKE data. Hysteretic magnetoconductivity is observed only in the regime where the ferromagnet is unsaturated and emits rapidly spatially varying fringe magnetic fields.

FIG. 4. Fringe fields from the magnetic electrode. a X-ray microscopy image of the magnetic electrode at the coercive field (corresponding to $M = 0$). The signal is due to the dichroic absorption of circularly polarized x-rays at the $L_3$ Co absorption edge incident normal to the film surface. The images are $5 \times 5 \mu m^2$. The fringe fields were calculated from these images using OOMMF. b Normalized in-plane correlation function of the fringe fields at different distances from the electrode, 12 nm blue, 36 nm red, 60 nm green and 84 nm purple. The inset shows the rms value for the fringe field versus distance from the electrode. c Magnitude of the fringe field in a $3 \times 3 \mu m^2$ area is plotted using a color scale at four different distances from the electrode. The lower panels correspond to the fringe field as a function of position at $y = 1.5 \mu m$, a profile through the center of the corresponding color images.
Figure 1
Figure 3

(a) Magn. Cond. (%) vs Magnetic Field (T)

(b) Magn. Cond. (%) vs Magnetic Field (T)