Polaron spin current transport in organic semiconductors

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A. Sample preparation

The main experiments were performed on a trilayer structure of Ni$_{80}$Fe$_{20}$/PBTTT/Pt. The Pt layer was sputtered onto a cleaned SiO$_2$ (300 nm)/Si substrate at a base pressure of $1 \times 10^{-6}$ mbar with a rate of 2 Å s$^{-1}$. The resulting 7 nm-thick Pt film was further cleaned via plasma processing in order for PBTTT to form a highly-ordered crystalline structure. PBTTT used in the present study was synthesized and purified by Dr. Martin Heeney of Imperial College, London. Molecular weight and polydispersity of the used PBTTT were measured to be 21 kDa and 1.6, respectively. The PBTTT film was spin-coated onto the Pt layer from a 10 mg ml$^{-1}$ 1,2-dichlorobenzene solution in a nitrogen glovebox. The films
were annealed inside the glovebox at 180 °C for 10 mins, then slowly cooled down to room
temperature. We varied the spinning speed from 500 to 5,000 r.p.m. for controlling the film
thickness of PBT TT, and also employed a drop-casting method from 0.2, 1.0, 2.0, and 10
mg ml\(^{-1}\) solutions to make thicker films. A thin film of Ni\(_{80}\)Fe\(_{20}\) (10 nm) was thermally
evaporated on the top of the PBT TT layer at a rate of 0.2 Å s\(^{-1}\) with a shadow mask.
The thicknesses of the PBT TT and metallic layers were determined by a combination of
various methods, such as surface profilometry, atomic force microscopy (AFM), ellipsometry,
scanning electron microscopy and transmission electron microscopy. Control experiments
were performed on the same device structure Ni\(_{80}\)Fe\(_{20}\)/PBT TT/non-magnetic metal(NM),
where the Pt layer was replaced by NM = Au and Cu. To prepare the control devices, thin
films of Au (40 nm) and Cu (300 nm) were thermally evaporated onto the SiO\(_2\)(300 nm)/Si
substrate. The lateral dimensions of the Ni\(_{80}\)Fe\(_{20}\) layer and bottom NM layers were 2.0 × 
2.5 mm\(^2\) and 2.0 × 5.0 mm\(^2\), respectively. Ferromagnetic resonance (FMR) in Ni\(_{80}\)Fe\(_{20}\) was
excited by using both an X-band electron paramagnetic resonance (EPR) apparatus and
another setup based on a coplanar waveguide. For the X-band EPR, the trilayer device was
placed at the center of a TE\(_{011}\) microwave cavity with a resonance frequency of \(f = 9.45\,\)GHz.
For the measurement with the coplanar waveguide, the trilayer device was mounted onto a
strip line that was designed to propagate microwaves, for which \(f\) and the input microwave
power were set to 3 GHz and 20 dBm. The FMR absorption spectrum was determined by
measuring both the microwave transmission and reflection components. To determine the
mobility of PBT TT, current-voltage (\(J-V\)) characteristics were measured on Ni\(_{80}\)Fe\(_{20}\) (30
nm)/PBT TT (120 nm)/Pt (7 nm) cross-bar architectures. The details are shown in section
D.
B. Surface profile of PBTTT

PBTTT is a widely studied organic semiconductor because it exhibits a high field-effect mobility up to 1.0 cm$^2$ V$^{-1}$ s$^{-1}$ as well as a good stability$^{22}$, which originates from its highly crystalline lamellar structure. Various spectroscopic measurements have revealed that the $\pi$-conjugated backbones of PBTTT adopt a highly ordered, lamellar structure with in-plane $\pi-\pi$ stacking and out-of-plane side chain orientation$^{81}$. As a result, a clear and molecularly flat terrace morphology can be seen in AFM micrographs. Figure 1a,c shows 15 $\mu$m $\times$ 15 $\mu$m and 3 $\mu$m $\times$ 3 $\mu$m AFM images of the PBTTT (40 nm) films that were spin-coated on a SiO$_2$(300 nm)/Si substrate. The observed surface is homogeneous in the large-area scan shown in Fig. 1a with an r.m.s. surface roughness of 2.1 nm, which is flat enough for distinguishing different devices that were employed for thickness-dependence measurements. The terrace morphology can be seen in a small-area scan shown in Fig. 1c, exhibiting 1.85 nm molecular steps between individual polymer lamellae, as shown in the height distribution histogram (Fig. 1b). This strongly suggests that the present PBTTT film forms a highly-ordered lamellar structure. No significant differences were observed between the surface of PBTTT films on SiO$_2$(300 nm)/Si (Fig. 1c) and those on Pt (Fig. 1d), indicating that a terraced structure can be realized even on the Pt layer.
Figure 1: Surface image of PBTBB. a, 15 µm × 15 µm and c, 3 µm × 3 µm AFM images of PBTBB spin-coated on a SiO₂(300nm)/Si substrate. b, A typical height distribution histogram. d, A 3 µm × 3 µm AFM image of PBTBB on a Pt (7 nm) layer. The film thickness and r.m.s. surface roughness were measured to be approximately 40 nm and 2.0 nm.
C. X-ray photoelectron spectroscopy (XPS) analysis of elemental composition of PBTTT

X-ray photoelectron spectroscopy (XPS) measurements (Fig. 2) were performed to investigate the chemical composition and a possible contamination of PBTTT by heavy metals and ferromagnetic metals. The sensitivity of detection was 50 - 100 ppm. The survey scan indicates that only light-atoms were present in the PBTTT film, i.e. carbon and sulfur are detected at high composition percentages, as shown in Fig. 2a and Table S1. The compositional ratio between carbon and sulfur is consistent with that expected from the chemical formula of PBTTT-C14. There are no heavy (or transition) metals contaminating the PBTTT film (Figure 2b shows high-resolution scans for selected atoms). Bromine and silicon are detected in high-resolution scans. The bromine present in the film most likely originates as one of the polymer endgroups, due to the nature of the synthesis\textsuperscript{S2}, and silicon can be introduced by siloxane contamination in the atmosphere, from plastic syringes, or from stirring the hot solution in a glass vial with a plastic lid, or perhaps present in the actual polymer itself as a contaminant during purification\textsuperscript{S3}. We consider it unlikely that such low atomic percentages of impurities would contribute to the spin relaxation and result in spurious effects.

Table S1: XPS analysis of the elemental composition of PBTTT.

<table>
<thead>
<tr>
<th>Element</th>
<th>Peak binding energy (eV)</th>
<th>Composition (Atom%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 1s</td>
<td>285.13</td>
<td>89.52</td>
</tr>
<tr>
<td>S 2p</td>
<td>164.08</td>
<td>9.05</td>
</tr>
<tr>
<td>O 1s</td>
<td>532.78</td>
<td>0.77</td>
</tr>
<tr>
<td>Si 2p</td>
<td>102.08</td>
<td>0.60</td>
</tr>
<tr>
<td>Br 3d</td>
<td>70.63</td>
<td>0.06</td>
</tr>
</tbody>
</table>
Figure 2: XPS analysis of the elemental composition of PBTTT. a, XPS survey scan of a 40 nm thick PBTTT film spin-coated on a SiO$_2$ (300 nm)/Si substrate. b, High-resolution scans of individual elements; O 1s, C 1s, S 2p, Si 2p, and Br 3d from left to right (top figures), Ni 2p, Co 2p, Fe 2p, Mn 2p, and Pd 3d from left to right (bottom figures).
D. Electrical property of Ni$_{80}$Fe$_{20}$/PBTTT/Pt trilayer

One of the main experimental discoveries of the presented work is that the spin diffusion length in PBTTT is almost independent of temperature. In order to link the spin diffusion length to spin relaxation time via a well established kinetic theory, $\lambda = \sqrt{D\tau}$, a determination of charge carrier mobility in PBTTT was essential. Charge transport in PBTTT is highly anisotropic with a lower mobility in the out-of-plane direction perpendicular to the polymer chain due to a larger distance between hopping sites. Current-voltage ($J$-$V$) characteristics of the Ni$_{80}$Fe$_{20}$ (30 nm)/PBTTT/Pt (7 nm) trilayer structure were investigated by using a cross-bar configuration, prepared under the same spin-coating and evaporation conditions (a photograph of the device is shown in the inset of Fig. 3c). Here, we confirmed that 99% of the input voltage was applied at the cross-bar junction using a quasi-four points probe method. The current density scales linearly with the applied voltage at small bias, which represents Ohmic conduction due to residual charge carriers present in the film, for example due to light, unintentional doping of the film by atmospheric exposure. When the applied voltage increases above a characteristic voltage, the current density varies as expected for a space-charge-limited-current (SCLC), indicating formation of a space charge in PBTTT. The SCLC regime is employed to determine the mobility in PBTTT using the Mott-Gurney law which relates SCLC current density, $J_{\text{SCLC}}$, to the voltage applied across the device, $V_{\text{eff}}$, as

$$J_{\text{SCLC}} = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu_0 \frac{V_{\text{eff}}^2}{d_S^3},$$

(S1)

where $\varepsilon_0$, $\varepsilon_r$, $d_S$ are the permittivity of free space, the relative permittivity and the thickness of the polymer film. $\mu_0$ is the zero-field mobility which is relevant for spin-pumping measurements for which there is no applied electric field. For the analysis, the voltage in eq. (S1) is an effective voltage across the polymer film since there is an expected built-in field due to the mismatch between the workfunctions of the electrodes, i.e. $V_{\text{eff}} = V - V_{\text{bi}}$. As shown in Fig. 3a, a good fit in the $V - V_{\text{bi}}$ range from 0.1 V to 1.0 V with eq. (S1) validates this method for calculating the mobility. The built-in voltage, $V_{\text{bi}}$, calculated from the fitting is also found to be less than 0.2 V. In other words, the measured current voltage characteristics represent the bulk conduction properties of the polymer, rather than injection-dominated conduction. The calculated $\mu_0$ and conductivity around zero bias voltage are both found to
be thermally activated with activation energy 185 meV, implying a nearest-neighbour hopping with the activation energy reflecting the energetic fluctuation between hopping sites\textsuperscript{84}. In addition, the current-voltage characteristic is approximately symmetric around $V = 0$ V which suggests that the injection barriers at both interfaces are small (Fig. 3c). A slightly smaller current at a positive bias represents a bigger injection barrier at the polymer/Pt interface, as shown in the inset of Fig. 3c. Potential contact resistance effects are investigated further by investigating the thickness scaling of the Ohmic conduction regime at low voltages for the three devices. From the extrapolation in Fig. 3d, the contact resistance is found to be low, ranging from 4% to 10% of the total resistance of the devices. At a voltage higher than 1.0 V, the eq. (S1) needs to be modified to include an electric field-assisted enhancement of current due to de-trapping of charges according to the Poole-Frenkel effect\textsuperscript{25}. From the conductivity in the Ohmic regime and the extracted mobility, the residual charge carrier concentration can be estimated to be $2 \times 10^{15}$ cm$^{-3}$ and is nearly independent of temperature (the inset of Fig. 3b).

To further confirm the existence of a residual charge concentration in the pristine PBTTT film, capacitance-voltage ($C$-$V$) characteristics were performed on a metal-insulator-semiconductor structure at room temperature. Figure 4a shows a $C$-$V$ curve measured for a Au(10 nm)/PBTTT (100 nm)/SiO$_2$ (200 nm)/n-Si (0.5 mm) structure, where the modulation frequency ($f_{\text{mod}}$) and voltage were 37 Hz and 200 mV. $C$ changes by accumulating and depleting charges in the semiconductor at the interface with a typical curvature. The saturation value at a negative bias corresponds to the capacitance of the insulator ($C_{\text{ins}} \sim 15.6$ nF cm$^{-2}$). The dopant charge concentration was estimated using a Mott-Schottky plot\textsuperscript{85}:

$$\frac{\partial}{\partial V}C^{-2} = \frac{2}{q\epsilon\epsilon_0N_A},$$

where $q$ and $N_A$ are the elemental charge and the residual charge concentration in the bulk of the PBTTT film, respectively. From the slope around a zero bias regime in Fig. 4b, $N_A$ is estimated to be $5 \times 10^{15}$ cm$^{-3}$. The obtained $N_A$ is of the same order of magnitude as the estimate from the $I$-$V$ characteristics above. Neither estimate of carrier concentration is entirely accurate, but the two methods provide consistent values of the same order of magnitude. We conclude from this that there is a significant concentration on the order of $10^{15} - 10^{16}$ cm$^{-3}$ of mobile polarons in the PBTTT film. These carriers may be the result of unintentional p-doping of the polymer due to exposure to the atmosphere or the result
of thermal injection of charge carriers from the contacts\textsuperscript{S6}. These are the spin carriers that transport the spin current through the PBTTT film.

The device was further tested for any magnetoresistance (MR) that could have been present and give rise to spurious effects in spin pumping measurements by measuring \( J-V \) characteristics under a magnetic field. Possible sources of MR can be from organic magnetoresistance (OMAR) of PBTTT and MR of Ni\textsubscript{80}Fe\textsubscript{20}. OMAR is one of a few bulk-magnetoresistance phenomena in non-magnetic materials at room temperature. Although its mechanism is still debated, one proposed mechanism is due to "spin-blocking" arising due to a magnetic field effect on the formation of singlet bipolarons from polarons\textsuperscript{S7}. The MR of Ni\textsubscript{80}Fe\textsubscript{20} is well established and its anisotropic magnetoresistance property has been made use in a wide range of sensors. The \( J-V \) characteristics are dominated by the PBTTT resistance and are measured to be the same under an applied in-plane magnetic field of \(-300\) mT and \(300\) mT showing a negligible MR (Fig. 5), defined by \( \text{MR} = \frac{[R(B) - R(0)]}{R(0)} \). More importantly, the device shows a negligible MR around the FMR field \((H_{\text{FMR}} \sim 120\) mT) as confirmed by measuring the resistance while sweeping the field in the range from \(-300\) mT to \(300\) mT. Therefore, spin pumping measurements are unlikely to have been contaminated by MR effects.
Figure 3: Electrical characteristics of a Ni_{80}Fe_{20}/PBTTT/Pt trilayer. a, Temperature (T) dependence of current-voltage (J-V) characteristics measured for a Ni_{80}Fe_{20} (30 nm)/PBTTT (120 nm)/Pt (7 nm) trilayer. The horizontal axis V - V_{bi} denotes an effective voltage at the SCLC regime, where a positive bias corresponds to the positive bias on the Pt contact with respect to the Ni_{80}Fe_{20} contact. The solid curves are fits obtained with eq. (S1). b, T dependences of conductivity obtained around the zero bias regime (top) and mobility calculated from the fits in a (bottom). The insets show the charge concentration (N) versus T (top) and the mobility versus T^{-1} (bottom). c, Current-voltage (I-V) characteristics for the Ni_{80}Fe_{20} (30 nm)/PBTTT (85 nm)/Pt (7 nm) trilayer measured at room temperature. The insets show a band diagram and a photograph of the crossbar structure. The active junction size amounts to 100 µm × 100 µm. d, I-V characteristics around the zero bias regime for the Ni_{80}Fe_{20} (30 nm)/PBTTT /Pt (7 nm) trilayer with the different PBTTT thickness (d_S = 45, 85, and 120 nm). The black solid lines represent results of linear fitting. The inset shows the resistances evaluated from the linear slope as a function of d_S. The error bars were made by taking the average of more than 10 devices for each thickness.
Figure 4: Charge carrier concentration from capacitance-voltage measurements. a, Capacitance-voltage (C-V) characteristics measured for a Au(10 nm)/PBT TT (100 nm)/SiO$_2$ (200 nm)/n-Si (0.5 mm) structure at room temperature. The modulation frequency and voltage are 37 Hz and 200 mV. b, Mott-Schottky ($C^{-2}$-V) plot. The circles and a solid line represent experimental data and linear fit around zero bias regime.

Figure 5: Magnetoresistance of Ni$_{80}$Fe$_{20}$/PBT TT/Pt trilayer. a, I-V characteristics measured for a Ni$_{80}$Fe$_{20}$ (30 nm)/PBT TT (85 nm)/Pt (7 nm) trilayer under an external magnetic field ($B = -300$, 0, and 300 mT) at room temperature, where $B$ was applied in-plane as shown in the inset. b, $B$ dependences of $I$ at various applied voltages ($V = 1.0$, 0.1, and 0.01 V). The inset shows magnetoresistance MR around the FMR field, defined by MR = $[R(B) - R(0)]/R(0)$ at $V = 1.0$ V.
E. ISHE voltage at various nonmagnetic (NM) electrodes in Ni$_{80}$Fe$_{20}$/PBTTT/NM trilayer

Based on the spin pumping theory and the spin diffusion equation, a model for the ISHE voltage in a ferromagnetic/nonmagnetic/spin-sink trialyer film has been formulated$^{88}$. In the present system, the nonmagnetic layer is PBTTT, and the spin-sink layer corresponds to either Pt, Au or Cu. Since the spin Hall angle of PBTTT itself can be assumed to be much smaller than that of Pt and Au due to the comparatively weak SOC in the organic layer, the charge current density $I_C$ that is converted by ISHE at the spin-sink layer can be expressed as

$$I_C = \frac{2e w_F}{\hbar} j_p^{\text{pump}} \frac{\theta_{\text{SHE}}^{\text{NM}} \lambda^{\text{NM}} g_{s}^{\text{NM}} \tanh \left( \frac{d^{\text{NM}}}{2\lambda^{\text{NM}}} \right) \tanh \left( \frac{d^{\text{NM}}}{\lambda^{\text{NM}}} \right)}{\left[ g_{s}^{\text{NM}} \tanh \left( \frac{d^{\text{NM}}}{\lambda^{\text{NM}}} \right) + \frac{g_{s}^{\text{Pt}}}{2\pi} \cosh \left( \frac{d^{\text{S}}}{\lambda^{\text{S}}} \right) + \left[ g_{s}^{\text{S}} + \frac{g_{s}^{\uparrow \downarrow}}{2\pi} g_{s}^{\text{NM}} \tanh \left( \frac{d^{\text{NM}}}{\lambda^{\text{NM}}} \right) \right] \sinh \left( \frac{d^{\text{S}}}{\lambda^{\text{S}}} \right) \right]}$$

(S3)

where $e$, $\hbar$, and $w_F$ are the elementary charge, the reduced Plank’s constant, and the width of the ferromagnetic layer. $j_p^{\text{pump}}$ and $g_{s}^{\uparrow \downarrow}$ are the spin current density and interface mixing conductance determined only by the interface between the ferromagnetic and PBTTT layers. Note that both are independent of the spin-sink layer. $d^{\text{S}}$, $\lambda^{\text{S}}$, and $g_{s}^{\text{S}}$ are the thickness, the spin diffusion length, and the spin conductivity for the PBTTT layer. $d^{\text{NM}}$, $\lambda^{\text{NM}}$, $g_{s}^{\text{NM}}$, and $\theta_{\text{SHE}}^{\text{NM}}$ are the thickness, the spin diffusion length, the spin conductivity, and spin Hall angle for the nonmagnetic spin-sink layer. Here, the spin conductivity per unit area is defined as $g_{s} = \frac{\hbar}{2e^2 \sigma}$, where $\sigma$ and $\lambda$ are the conductivity and the spin diffusion length of the respective layer. By using experimental and literature values, the spin conductivities are calculated to be $g_{s}^{\text{Pt}} = 1.98 \times 10^{18}$ m$^{-2}$ and $g_{s}^{\text{Au}} = 1.55 \times 10^{18}$ m$^{-2}$. Since the spin conductivity of the spin-sink layers can be assumed to be significantly larger than both the interface mixing conductivity of the ferromagnetic/organic interface and the spin conductivity of PBTTT, equation (S3) can be simplified as follows:

$$I_C = \frac{2e w_F}{\hbar} j_p^{\text{pump}} \frac{\theta_{\text{SHE}}^{\text{NM}} \lambda^{\text{NM}} \tanh \left( \frac{d^{\text{NM}}}{2\lambda^{\text{NM}}} \right)}{\cosh \left( \frac{d^{\text{S}}}{\lambda^{\text{S}}} \right) + \frac{1}{2\pi} \frac{g_{s}^{\uparrow \downarrow}}{g_{s}^{\text{S}}} \sinh \left( \frac{d^{\text{S}}}{\lambda^{\text{S}}} \right)}$$

(S4)

Since $j_p^{\text{pump}}$, $g_{s}^{\text{S}}$ and $g_{s}^{\uparrow \downarrow}$ are independent of the spin-sink layer, the total charge current density generated by the ISHE in the spin-sink layer scales with the spin Hall angle, spin diffusion length, and $\tanh(d^{\text{NM}}/2\lambda^{\text{NM}})$ of the spin-sink layer. We finally obtain the general
expression of $V_{\text{ISHE}}$ for the ferromagnetic/PBTTT/spin-sink trilayer, as follows:

$$V_{\text{ISHE}} = \frac{2eW}{h} j_s' \theta_{\text{SHE}}^{NM} \lambda^{NM} \tanh \left( \frac{d^{NM}}{2\lambda^{NM}} \right),$$

(S5)

where $j_s'$ is defined as $j_s' = j_{\text{pump}}^{NM} \frac{\cosh(\frac{d^{NM}}{2\lambda^{NM}})}{\cosh(\frac{d^{NM}}{2\lambda^{NM}}) + \frac{1}{2\pi} g_{\uparrow\downarrow}^s \sinh(\frac{d^{NM}}{2\lambda^{NM}})}$. Given the fact that the thickness dependence of voltage follows exponential decay, it is considered reasonable that $j_s'$ itself decays exponentially. In fact, when a spacer layer separated by the ferromagnetic and spin-sink layers is thick enough and has much longer spin lifetime compared to the ferromagnetic layer the mixing conductance is limited simply by the spin conductivity of spacer layer (the PBTTT layer)$^{S9}$: $\frac{1}{2\pi} g_{\uparrow\downarrow}^s \sim 1$. Hence, we can assume $j_s' \sim j_{\text{pump}}^{NM} \frac{\cosh(\frac{d^{NM}}{2\lambda^{NM}})}{\cosh(\frac{d^{NM}}{2\lambda^{NM}}) + \frac{1}{2\pi} g_{\uparrow\downarrow}^s \sinh(\frac{d^{NM}}{2\lambda^{NM}})} = j_{\text{pump}}^{NM} \exp(-\frac{d^{NM}}{\lambda^{NM}})$. This indicates that $j_s'$ is independent of the spin-sink layer and indeed follows exponential decay, which is well consistent with our experimental results. We emphasize that based on this model the characteristic length determined from the measured $V_{\text{ISHE}}$ decay as a function of the PBTTT thickness can be approximated to the spin diffusion length of the PBTTT layer. Since we selected the thicknesses of the spin-sink layers ($d^{NM}$) to scale with the literature values of the spin diffusion lengths in Pt, Au, and Cu (referred to as $d^{NM}/\lambda^{NM}$ and $\tanh(d^{NM}/2\lambda^{NM})$ in Table S2), the measured voltage ratio of the devices with various spin sink layers should scale simply with both the spin Hall angle ($\theta_{\text{SHE}}^{NM}$) and conductivity ($\sigma^{NM}$) of the spin-sink layer. It is noted that the measured $V_{\text{ISHE}}$ ratio of the Pt to Au devices,

Table S2: Parameters for calculation of $V_{\text{ISHE}}$ in various spin-sink layers.

<table>
<thead>
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<th>NM</th>
<th>$V_{\text{ISHE}}^{NM}$ ($\mu$V)</th>
<th>$\sigma^{NM}$ (S cm$^{-1}$)</th>
<th>$d^{NM}$ (nm)</th>
<th>$\lambda^{NM}$ (nm)</th>
<th>$d^{NM}/\lambda^{NM}$</th>
<th>$\tanh(d^{NM}/2\lambda^{NM})$</th>
<th>$\theta_{\text{SHE}}^{NM}$</th>
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</thead>
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<tr>
<td>Pt</td>
<td>0.956</td>
<td>$6.17 \times 10^6$</td>
<td>7</td>
<td>10 (ref. 20)</td>
<td>0.70</td>
<td>0.34</td>
<td>0.04 (ref. 20)</td>
</tr>
<tr>
<td>Au</td>
<td>0.026</td>
<td>$1.23 \times 10^7$</td>
<td>40</td>
<td>60 (ref. S10)</td>
<td>0.67</td>
<td>0.32</td>
<td>0.0035 (ref. 32)</td>
</tr>
<tr>
<td>Cu</td>
<td>0</td>
<td>$2.98 \times 10^7$</td>
<td>300</td>
<td>500 (ref. 11)</td>
<td>0.60</td>
<td>0.33</td>
<td>$\sim 0$ (ref. 23)</td>
</tr>
</tbody>
</table>

$V_{\text{ISHE}}^{Pt}/V_{\text{ISHE}}^{Au} = 36.8$ does indeed scale in the expected manner with the corresponding ratios of the spin Hall angles and conductivities, $\frac{\theta_{\text{SHE}}^{Pt}}{\theta_{\text{SHE}}^{Au}}/\frac{\sigma^{Pt}}{\sigma^{Au}} = 33.5$. This strongly suggests that the spin Hall angle of the spin sink layer is responsible for the measured voltages as predicted by the trilayer spin pumping model (eq. (S5)). Although there is some uncertainty
Figure 6: $J$-$V$ characteristics for various nonmagnetic (NM) electrodes in Ni$_{80}$Fe$_{20}$/PBT(TT)/NM trilayer. Current-Voltage ($J$-$V$) characteristics for a Ni$_{80}$Fe$_{20}$ (30 nm)/PBT(TT) (100 nm)/NM trilayer, where a, NM = Pt (20 nm), b, NM = Au (20 nm), and c, NM = Cu (20 nm), respectively. Band diagrams are shown in each inset. Device preparations and measurements were carried out with the equivalent condition in Fig. 3.

In the literature about the spin Hall angle of Pt with values ranging from 0.0067 to 0.08\textsuperscript{11}, the measured voltage ratio is certainly much larger than that one expected from a simple resistance ratio, $R_{Pt}/R_{Au} \approx 6.98$. We have further carried out similar spin pumping measurements on Cu devices, in which the absolute resistance of the Cu layer is adjusted to that of the Pt device ($\sim 10$ Ω) by reducing the thickness of the Cu layer from 300 to 10 nm. Even in this sample, no voltage was observed at a resolution of 5 nV. This provides further compelling evidence that the ISHE in the spin-sink layer is indeed the origin of the voltage signal measured in our trilayers.

We emphasize that all the experimental results including the thickness and spin-sink layer dependences can be consistently explained by the model presented above, in which we simply assumed the spin diffusion equation: $j_s = -\frac{\hbar}{2e}\sigma \nabla \mu_s$ and a spin-dependent electrochemical potential $\mu_s$ is built up that drives the spin current.

We have also considered the workfunction difference of the present Ni$_{80}$Fe$_{20}$/PBT(TT)/NM trilayer structure since the Schottky barrier due to the workfunction difference may affect not only on an estimation of mobility, but also on a charge current drifting due to a built-in potential. Figure 6 shows $J$-$V$ characteristics for present trilayers with various NM layers, where a NM = Pt, b NM = Au, and c NM = Cu, respectively. Regardless of the fact that the workfunction changes by $\sim 1.0$ eV from Pt to Cu (see band diagrams in insets of Fig. 6), $J$-$V$ characteristics are found to be symmetric around $V = 0$ V, which indicates that the
Ohmic contacts are established at both interfaces, in other words, a built-in potential across a classical Schottky barrier is less significant. It has been explained that the theoretical model on the spin pumping is insensitive to the impedance mismatching problem due to the Schottky barriers. In the ref. 18 in the main manuscript, for example, even if the external electric voltage (\(\sim 0.6\) V) applies to a junction between ferromagnetic metal and adjacent non-magnetic layer during spin pumping, the observed \(V_{\text{ISHE}}\) changes only by a factor of 3. It is because that the spin pumping theory relies mostly on the exchange interaction. Furthermore, since superlinear behaviours with the almost same current density are also confirmed for present trilayers with different workfunctions we are able to conclude that mobilities determined from the SCLC equation (S1) are independent of the magnitude of workfunctions difference: \(\mu_{0}^{\text{Pt}} = 3.1 \times 10^{-5}\) cm\(^2\) V\(^{-1}\) s\(^{-1}\), \(\mu_{0}^{\text{Au}} = 3.9 \times 10^{-5}\) cm\(^2\) V\(^{-1}\) s\(^{-1}\), and \(\mu_{0}^{\text{Cu}} = 3.0 \times 10^{-5}\) cm\(^2\) V\(^{-1}\) s\(^{-1}\). From the demonstrated electrical characteristics above, we are able to further validate that the NM layer dependence of the measured \(V_{\text{ISHE}}\) originates not from ambiguities related to workfunction differences, does scale simply with both the spin Hall angle and conductivity of the spin-sink layer.
Organic semiconductors are highly resistive and this is an important requirement for the present measurements to minimize potential artefacts from signals generated in the Ni$_{80}$Fe$_{20}$ layer. Although as investigated above there was some unintentional doping PBTTT films, the electrical resistivity around the zero bias region was measured to be high, $\rho = 1.79 \times 10^9 \Omega \text{ cm}$ from the $I - V$ characteristics using a cross-bar structure (Fig. 3d). Such a highly insulating nature (resistivity $\sim 10^9 \Omega \text{ cm}$) was also confirmed for an actual trilayer device used for the spin pumping measurements, which had a relatively large junction area (2.0 $\times$ 2.5 mm$^2$). From this the vertical electrical resistance of a film having the thickness of 20 nm is estimated to be 7.16 $\times$ 10$^4 \Omega$. Although the estimated resistance of the PBTTT layer is much higher than that of the Pt layer (40 $\Omega$), it should be confirmed that any spurious voltage or current that are generated in the Ni$_{80}$Fe$_{20}$ layer cannot contaminate significantly the ISHE generated voltage in the Pt layer. To estimate how efficiently a spurious voltage generated in the Ni$_{80}$Fe$_{20}$ layer could be transmitted through the PBTTT film and contribute to the voltage signal across the Pt film we have considered the following equivalent circuit model of the trilayer device as shown in Fig. 7.

**Figure 7: Equivalent circuit of Ni$_{80}$Fe$_{20}$/PBTTT/Pt trilayer.** a, Detailed and b, simplified equivalent circuits. Output Voltages at the Pt ($V_{\text{Pt}}$) and Ni$_{80}$Fe$_{20}$ ($V_{\text{Py}}$) layers calculated with c, $I_F = 0.25 \mu A$ and d, 150 $\mu A$. Red circles and curves display the experimentally obtained $V_{\text{ISHE}}$ and its exponential decay.

An equivalent circuit is designed by combining three layers (Ni$_{80}$Fe$_{20}$, PBTTT, and Pt),
as shown in Fig. 7a, where $I_F$, $R_F$, and $R_N$ are the charge current assumed to be generated in the Ni$_{80}$Fe$_{20}$ layer due to spurious effects, the electrical resistance of the Ni$_{80}$Fe$_{20}$ and Pt layers. $V_{Pt}^{out}$ and $V_{Py}^{out}$ are output voltages in the Pt and Ni$_{80}$Fe$_{20}$ layers, obtained from the equivalent circuit. There should also be a current source at the Pt layer corresponding to a charge current converted from a spin current transmitted to the Pt layer by inverse spin Hall effect. However, this is not considered here to focus on estimating the contribution from any spurious effects in the Ni$_{80}$Fe$_{20}$ layer to the measured $V_{out}$. The PBTTT layer is divided into $n$ layers, with the $i$th PBTTT layer having both parallel ($R_i^y$) and perpendicular ($R_i^x$) resistances, where parallel and perpendicular directions are referenced with respect to the plane of the device. Since $R_i^y$ is much higher than $R_i^x$, expected from the dimension of the actual device, the parallel connections are considered as an open circuit. Consequently, the integrated equivalent circuit is simplified to that shown in Fig. 7b, where $R_{tot} = \sum_{i=1}^{n} R_i^x$ is estimated from the experimentally obtained resistivity, above. $R_N$ and $R_F$ are also measured to be 40 and 283 Ω, respectively. From the equivalent circuit, the output voltages can be expressed as $V_{Pt}^{out} = \frac{R_N R_F}{2R_{tot} + R_N + R_F} I_F$, and $V_{Py}^{out} = \frac{(2R_{tot} + R_N)R_F}{2R_{tot} + R_N + R_F} I_F$. Figure 7c,d displays the output voltages calculated with $I_F = 0.25 \mu$A and 150 μA together with the experimentally obtained $V_{ISHE}$ as a function of $R_{tot}$. It is clearly seen that $V_{Pt}^{out}$ calculated by the equivalent circuit model steeply decreases as $1/R_{tot}$, which is in contrast to the decay of $V_{ISHE}$; $V_{ISHE}$ decays exponentially shown as the red curve. Furthermore, for a source current of 0.25 μA the voltage signal $V_{Pt}^{out}$ is much smaller than the experimental signal level due to the ISHE. Only if the source current is increased to a large value of 150 μA, would the magnitude of the spurious signal approach that of the experimental one. Therefore, we can conclude that any spurious effects that potentially generates the charge current are irrelevant to the obtained $V_{ISHE}$. It should be noted that the magnitude of $V_{out}$ could be reproduced using a higher charge current, for example $I_F = 150 \mu$A in Fig. 7d. However, $I_F = 150 \mu$A is far from a realistic value since the magnitude of $V_{out}$ in the zero resistance limit would then reach large values up to 10 mV and spurious effects would have manifested themselves strongly in spin pumping/ISHE experiments on Ni$_{80}$Fe$_{20}$/Pt. By applying the same equivalent circuit to a Ni$_{80}$Fe$_{20}$/PBTTT/Cu trilayer, where no voltage has been observed, the upper limit of $I_F$ is roughly estimated to be 10 nA. This is small enough for us to conclude that spurious signals generated in the Ni$_{80}$Fe$_{20}$ layer do not contribute significantly to the measured output.
signal in the Pt. To validate the equivalent circuit model that we proposed above, we have further conducted another control experiment. An Al (30 nm)/Ni$_{80}$Fe$_{20}$ (10 nm)/PBTTT (60 nm)/Pt (7 nm) trilayer device was fabricated, where the Al layer having much lower resistance ($\sim 2$ $\Omega$) is used for a shunt circuit: any spurious voltages/current in the Ni$_{80}$Fe$_{20}$ layer can be short-circuited in the Al layer, and the original ISHE voltage in the Pt layer should be protected. Regardless of attaching the Al layer or not, the exact same magnitude of output voltages is observed in the Pt layer. This clearly validates that the resistance of PBTTT is high enough for establishing the electrical isolation from any spurious voltages in the Ni$_{80}$Fe$_{20}$ layer.
G. Contribution of hyperfine interaction

The hyperfine interaction, in particular, the interaction between the magnetic moment of polarons and the nuclear moment of protons, has been found to play a significant role for modulating the magnetoresistance\(^\text{17}\) even though it creates a small, random perturbation to an effective magnetic field. However, in our measurements the external magnetic field is much higher than the hyperfine field. Thus the hyperfine coupling gives rise to a small random perturbation on the applied field and can be neglected. Furthermore, if hyperfine coupling was dominant one would expect charge carriers to be particularly susceptible to spin dephasing when they reside in a trap state, as spins are expected to precess around the local direction of the hyperfine field while residing in the localized trap states. While charges are moving they experience locally fluctuating hyperfine fields, which are less effective in spin dephasing. In a hyperfine model one would therefore expect a decrease of \(\tau_s\) in the trap dominated transport regime at low temperatures.

These conclusions are fully consistent with recent temperature-dependent electron spin resonance (ESR) measurements on gate-induced polarons in PBT TT films\(^\text{28}\). From the analysis of an averaged motion frequency the trap resident time was found to become longer as temperature decreased. At low temperatures below 100 K, where the charge carrier motion is completely inhibited, the ESR linewidth saturated, reflecting the averaged inhomogeneous hyperfine field. At intermediate temperatures from 100 to 200 K, where the charge carriers become mobile, the ESR linewidth drastically sharpens because of a motional narrowing effect. The presence of the motional narrowing indicates that inhomogeneous hyperfine fields which spins experience get more effectively averaged as the charges move faster. Therefore, the motional narrowing should indeed enhance the spin relaxation time at higher temperature due to an effectively weaker hyperfine interaction, as argued above. However, in a high temperature regime above 200 K, the ESR motional narrowing was found to be suppressed and the observed ESR linewidth clearly broadened, which was assigned to the spin-lattice relaxation due to SOC becoming dominant. These ESR results are fully consistent with both our experimental results in the temperature range of 200 to 300 K and the hopping mediated EY mechanism that we proposed in the main text.
H. Frequency dependence of electric voltage of Ni₈₀Fe₂₀/PBTTT/Pt trilayer

A series of further control experiments allows us to exclude any contributions to the measured electric voltage from thermoelectric effects from the observed \( V_{ISHE} \) signals. Firstly, the sign reversal of \( V_{ISHE} \) by reversing \( \mathbf{H} \) observed in Fig. 2 of the main text clearly indicates that field-independent thermoelectric effects, such as the Seebeck effect, cannot be attributed to the observed \( V_{ISHE} \) signal. Furthermore, the magnetic field angle \( \theta \) dependence of the electric voltage \( V_{ISHE} \) shown in Fig. 3 of the main text provides an evidence that field-dependent thermoelectric effects, such as the Nernst effect, are also irrelevant to the observed \( V_{ISHE} \) signals. We also tested the microwave frequency dependence of \( V_{ISHE} \) to further confirm the absence of the Nernst effect. The electric voltage due to the Nernst effect at FMR would be proportional to \(|\nabla T \times \mathbf{H}_{\text{FMR}}|\), where \( \nabla T \) is a temperature gradient perpendicular to the film plane induced by the microwave absorption at FMR. With the assumption that the magnitude of \( \nabla T \), \( |\nabla T| \), is proportional to the microwave absorption intensity \( I \) at FMR, \( |\nabla T| \) is almost constant for different magnetic field angles \( \theta^{S12} \). Therefore, the magnitude of the thermoelectric voltage \( |\nabla T \times \mathbf{H}_{\text{FMR}}| = |\nabla T|\mathbf{H}_{\text{FMR}} \cos \theta \) is expected to be almost constant for different \( \theta \) except around \( \theta = 90^\circ \), since \( \mathbf{H}_{\text{FMR}} \) is almost proportional to \( 1/\cos \theta \) for \( \theta < 80^\circ \). This behavior is in stark contrast to the observed \( \theta \) dependence of \( V_{ISHE} \). We also found that the magnitude of the electric voltage \( V_{ISHE} \) is almost constant for different external magnetic field strength, as shown in Fig. 8.

Microwave frequency \( f \) dependence of the electric voltage provides further evidence that the observed electric voltage is induced by spin pumping and ISHE. Figure 8 shows the \( f \) dependence of \( V_{ISHE} \) measured for the Ni₈₀Fe₂₀ (10 nm)/PBTTT (40 nm)/Pt (7 nm) trilayer using a coplanar waveguide. The \( V_{ISHE} \) signals are almost independent of \( f \), which is a feature of the spin pumping. The \( f \) dependence of the spin pumping is obtained as\(^{S13}\)

\[
\bar{V}_{ISHE} = \frac{V_{ISHE}}{P_{\text{abs}}} = \frac{e}{\pi} \frac{w_F \lambda^{\text{NM}} \tanh(d^{\text{NM}}/2\lambda^{\text{NM}})}{v_F \sigma^{\text{NM}} d^{\text{NM}} \sigma^{\text{NM}} \alpha M_s \sqrt{(4\pi M_s \gamma)^2 + (4\pi f)^2}},
\]

where \( P_{\text{abs}} \) is the absorbed microwave power at the FMR, which is obtained from Landau-Lifshitz-Gilbert equation. \( w_F \) and \( v_F \) are the width and the volume of the Ni₈₀Fe₂₀ layer. \( d^{\text{NM}} \), \( \sigma^{\text{NM}} \), \( \lambda^{\text{NM}} \), and \( \theta^{\text{NM}}_{\text{SHE}} \) are the thickness, the conductivity, the spin diffusion length, and the spin Hall angle of the nonmagnetic layer (Pt). \( g^{\uparrow \downarrow}_{\text{eff}} \), \( \alpha \), and \( \gamma \) are the the mixing conductance, the Gilbert damping constant, and the gyromagnetic ratio. The saturation magnetization...
Figure 8: Frequency dependence of the electric voltage. Microwave frequency \( f \) dependence of \( \bar{V}_{\text{ISHE}} = V_{\text{ISHE}}/P_{\text{abs}} \) for the Ni\textsubscript{80}Fe\textsubscript{20} (10 nm)/PBTTT (40 nm)/Pt (7 nm) trilayer, where \( P_{\text{abs}} \) is the absorbed microwave intensity. The solid circles are the experimental data and the solid curve is the theoretical value. The inset shows the relation between \( f \) and \( H_{\text{FMR}} \). The solid curve is the theoretical curve obtained using the Kittel formula with \( 4\pi M_s = 0.805 \) T.

\( 4\pi M_s = 0.805 \) T is obtained from the relation between the microwave frequency \( f \) and the FMR field \( H_{\text{FMR}} \) with the Kittel formula: \( f = (\gamma/2\pi)\sqrt{H_{\text{FMR}}(H_{\text{FMR}} + 4\pi M_s)} \) (see the inset to Fig. 8). Equation (S6) shows that \( V_{\text{ISHE}} \) is expected to vary with frequency as \( \bar{V}_{\text{ISHE}} \propto \left[\sqrt{(4\pi M_s\gamma)^2 + (4\pi f)^2}\right]^{-1} \), which is not sensitive to the microwave frequency \( f \). This is fully consistent with the experimental observations, as shown in Fig. 8 (see the solid line). The presented \( H_{\text{FMR}} \)-independent \( V_{\text{ISHE}} \) is in contrast to the prediction from Nernst effect. Therefore these results further support that the measured electric voltage is not due to magnetic field dependent thermoelectric effects.


