Trap-Filling Magnetoconductance as an Initialization and Readout Mechanism of Triplet Exciton Spins

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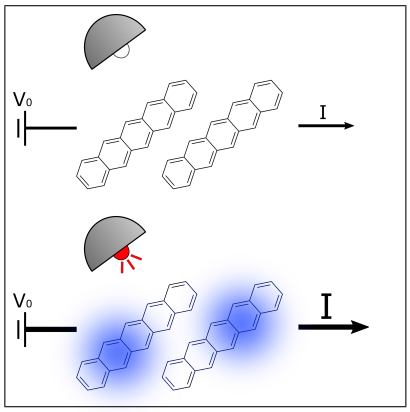
Abstract

Photoexcited triplet states are promising candidates for hybrid qubit systems, as they can be used as a controlling gate for nuclear spins. But microwave readout schemes do not generally offer the sensitivity needed to approach the single molecule limit or the scope to integrate such systems into devices. Here, we demonstrate the possibility of electrical readout of triplet spins at room temperature through a specific mechanism of magnetoconductance (MC) in polycrystalline pentacene. We show that hole-only pentacene devices exhibit a positive photoinduced MC response that is consistent with a trap-filling mechanism. Spin and magnetic-field dependent quenching of photogenerated triplets by holes quantitatively explains the MC response we observe. These results are distinct in both sign and proposed mechanism compared to previous reports on polyacene materials, and provide clear design rules for future spintronic devices based on this spin-sensing mechanism.

Graphical TOC Entry



Molecular electronics are an important class of emerging materials for spintronic, quantum sensing, and quantum computing applications due to the diverse and tunable spin physics that can be accessed through chemical synthesis. However, a key challenge is developing methods to address individual molecular spins via microelectronic circuits rather than bulk spectroscopies.[1–6] For instance, some very promising coherence times and gate operation types/speeds have been demonstrated for triplet excitons in organic molecules, including writing quantum information from the optically excited and polarized triplet state to attached nuclear spins, and back.[7–9] But the reliance on optical/microwave techniques in these experiments limits the potential scope for integrating such functionality into a device. In this work we show that the phenomenon of organic magnetoresistance (OMAR)[10–13] may be exploited to achieve sensitive *electrical* readout of triplet exciton spins via their interaction with charge carriers in polycrystalline pentacene.

OMAR, or its inverse magnetoconductance (MC), has been observed in many organic light emitting diodes and related structures, and has been explained via several mechanisms. The trion model is one of these; it has been invoked to explain the significant room-temperature MC seen especially in materials with high *electrically*-generated triplet density.[14–20] It describes the spin-dependent quenching interaction between a doublet charge and a triplet exciton. The term trion refers to a postulated bound quasi-particle consisting of three charges (usually an exciton and a radical) with a total spin of 3/2 and a net charge of ± 1. The six states within the total 3/2 spin system separate into doublet and quartet degeneracy, which then determine the outcome of exciton-charge collisions.

It was shown by Merrifield[21] that the rate constant for triplet-charge quenching depends on magnetic field in a manner predicted by the doublet character of the states within the quartet manifold: at low magnetic field, doublet character is spread more evenly over all six of the trion states and the quenching rate is maximized, while at high-field, doublet character is concentrated in just four of the states, causing a reduction in the quenching rate. As the ground state of this system is a doublet, spin-allowed internal conversion can only take place for those trion states with some doublet character.

The key attribute of this phenomenon that makes it potentially valuable for quantum information processing is its spin selectivity at high magnetic fields. Only a subset of the eigenstates result in quenching of the exciton, and these events produce distinguishable changes in device conductance. This suggests that if we fully understand the interaction and its impact on conductivity, spin-polarization controlled electrical currents could be used to: (1) Quench all excitons except those with a specific spin orientation, purifying a population, or iteratively preparing a single exciton with known polarization; (2) Non-destructively detect the spin-orientation of a triplet exciton or population thereof (for the non-quenching orientation(s)); (3) Deterministically quench triplet excitons via an unpolarized current pulse.

In this work we answer three scientific questions that lay the foundation for realizing such applications:

1. Does the exciton-charge interaction lead to a measurable magnetoconductance in polycrystalline pentacene? Other authors have assigned MC signals in polyacenes to different mechanisms.[22–24]

2. *If* (1) is affirmed, what is the kinetic mechanism? There are many possible interactions that could change the device current in response to spin-dependent triplet-charge reactions.

3. Are stable trions required in this mechanism, and do they exist in polycrystalline pentacene? While trion species are well known in certain systems such as carbon nanotubes and semiconductor nanocrystals, it is unclear whether they exist as stable particles in most organic semiconductors.[25–34]

Ultimately, we find that exciton-charge interactions *dominate* the photoinduced MC of polycrystalline pentacene devices when hole-only charge selective contacts are employed, and develop a quantum-classical model to explain the data in terms of a new trap-filling mechanism. However, we find that it is not necessary to invoke the existence of stable or metastable trion particles (exciton-charge complexes) to explain our experiments; transient exciton-charge encounters are sufficient. This clear understanding of the MC response in our devices allows us to propose specific design rules for future spintronic devices that exploit this phenomenon.

In order to observe an MC effect from triplet-charge interactions, devices were fabricated with the goal of generating a significant triplet density, but also only a single charge carrier type to limit the influence of polaron pairs.[35–40] It is also beneficial for the crystalline layer to be able to form trap sites, as these have been shown to be critical in triplet-charge MC experiments in other materials.[41–43] We chose polycrystalline pentacene as our model system, as it exhibits both the large charge carrier mobilities[44,45] that would be needed for responsive device structures and extremely efficient singlet fission, whereby 2 triplet excitons are produced for every absorbed photon.[46–50]

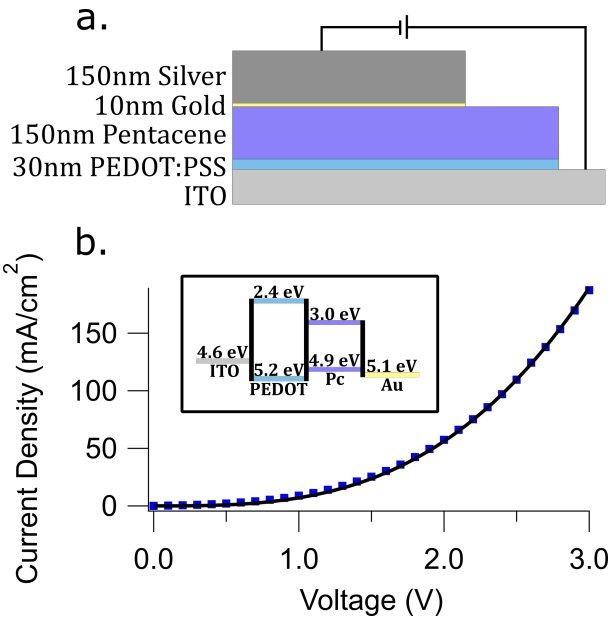


Figure 1: a. Polycrystalline pentacene device stack with layer thicknesses. **b.** J-V curve in the hole-only regime fit with equation (1). Inset: Flat band diagram of relevant transport and contact layers.

Figure 1 shows the device layers and characteristics under normal operating conditions. PEDOT:PSS was chosen as an efficient hole injection layer and a gold top contact was chosen, so that the Fermi level provides a small energetic barrier for hole transport, but a large barrier for electron transport, making it a commonly chosen electrode for hole extraction.[51–54] The additional 150 nm of silver provides contact stability and reduces the possibility of shunting without altering the device electrical properties as outlined in the SI. The positive bias regime of the J-V curve resembles ideal space-charge limited current models, but an increasing slope-voltage relationship with increasing bias suggests non-ideal behavior. We model these characteristics using the Mark-Helfrich equation, which describes non-ideal space-charge current through the interaction between mobile charges and a population of characteristic trap sites:

$$J = q^{1-l}\mu_n N_c \left\{\frac{\epsilon_0\epsilon_r l}{N_t(l+1)}\right\}^l \left\{\frac{2l+1}{l+1}\right\}^{l+1} \frac{V^{l+1}}{L^{2l+1}} \quad (1)$$

where J is the current density, q is the elementary charge, μ_n is the carrier mobility, N_c is the effective density of states at the relevant trans-

port band, ϵ_0 and ϵ_r are the vacuum and relative permittivity respectively, N_t is the effective trap density, V is the bias voltage, and L is the length of the active layer. The variable l represents the characteristic trap site energy with higher values representing deeper traps. This model accounts for exponential tail states in the band gap resulting in a higher power-law dependence of current to voltage.[55] Using typical energies of pentacene trap sites formed from both molecular sliding[56] and photo-oxidation[57,58] the Mark-Helfrich fit to our data (1b) reveals trap densities on the order of 10^{17} cm^{-3} for a mobility of 0.1 $cm^2V^{-1}s^{-1}$. However, it should be noted that these fits are not unique: adequate fits can be obtained for a range of different mobilities, each corresponding to a different trap density, where higher mobilities correspond to lower trap densities.

MC measurements were carried out on pristine devices by measuring the electrically modulated change in current via a lock-in amplifier under increasing magnetic field. The magnetoconductance is defined by:

$$MC = \frac{I(B) - I(0)}{I(0)} 100\% \qquad (2)$$

Figure 2 shows results of a device tested in the dark and under illumination. These results are mostly in agreement with thin film acene-based OMAR literature, which finds negligible dark MC and an illuminated MC on the order of 1%.[59–64] However, the sign of the response is in stark contrast to the negative MC effects seen in some acene-based field effect transistors (FETs).[22–24] Of the most commonly cited mechanisms responsible for OMAR, the bipolaron mechanism typically only causes a negative MC response and can be observed in dark MC measurements.[65–68] Additionally, dark injection of electron-hole pairs provides a significant contribution in ambipolar devices, but would be observable in the dark, and should be suppressed by our hole-only device structure.[35–40] Nevertheless, MC in polyacene materials has been most commonly explained through the magnetic field-dependent production or recombination of photogenerated electron-hole pairs. For instance, the negative MC effect observed in FETs was attributed to a reduction in the photogenerated triplets (and subsequent electron-hole pairs) caused by splitting of the triplet energy levels due to the Zeeman effect.[22] Others have explained positive MC in a similar way, arguing that polaron-pair *recombination* is inhibited at high magnetic field due to the splitting of the singlet and triplet configurations of the electron-hole pair.[23] These mechanisms may be operative in other materials and device structures, but they do not appear to contribute to our results.

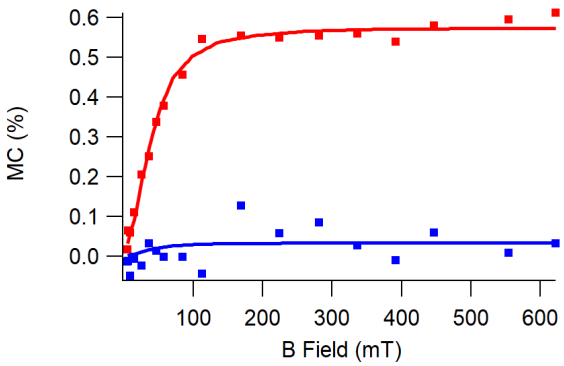


Figure 2: MC of pentacene-based devices. Solid lines represent fits to the kinetic model. Top curve: 1690 μW/mm^2 light intensity, Bottom curve: No illumination.

Figure 3 shows the effects of increasing light intensity while holding DC bias constant and vice versa. A larger applied bias voltage provides an increase in carrier density through direct hole injection. Increasing illumination intensity provides an increase in triplet density through singlet fission, but also possible photogenerated current through electron-hole dissociation. The large error associated with MC measurements at low bias or illumination is an expected inherent effect as the low current density during these measurements produces a smaller signal-to-noise ratio. The trends counter-intuitively show MC actually decreasing slowly as the triplet and/or polaron density increases.

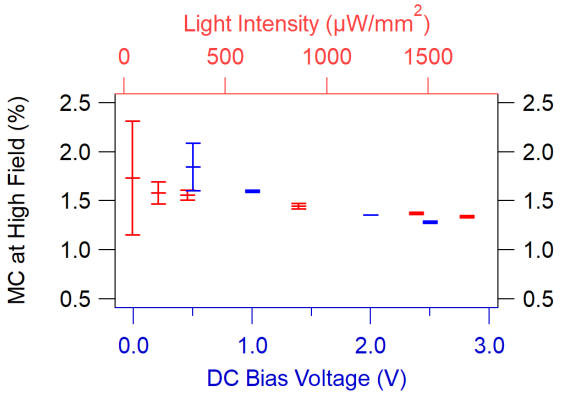


Figure 3: Effects of light intensity at a constant DC bias (red) and DC bias at a constant light intensity (blue) on MC. Data points represent MC measured at 500mT field strength and include standard error. The trends show that the MC is not a photocurrent based phenomenon and is already maximized at low triplet and current density. The points with larger error highlight the inherent noise associated with low current measurements.

The weak dependence of the MC signal on illumination intensity noted in Figure 3 shows that photocurrent is not a major contributor to our results. Moreover no MC response was observed in the absence of an applied bias using photo-modulation as the detection mechanism, as would be expected if photocurrent dominated the MC response. This is despite the fact that a significant and measurable magnetic field-*independent* photocurrent is present in these experiments. Finally, we do not anticipate an influence from magnetic field-dependent singlet fission rates in our pentacene devices due to the exothermic nature of singlet fission in this system,[69] as distinct from the isothermic nature of singlet fission in tetracene.[22]

Thus, we conclude that the trion mechanism is most likely dominant in our hole-only pentacene devices, where we only observe MC under illumination, *and* with an applied bias. In what follows we proceed to model the results on this basis.

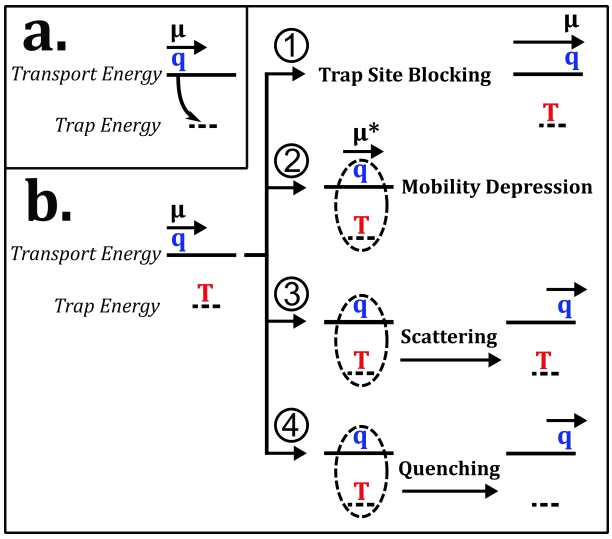


Figure 4: a. A mobile charge q can become trapped in a lower energy trap site, reducing the effective mobility μ **b.** Triplet states can instead occupy these trap sites resulting in several possible interactions: **1.** Triplet states can fill trap sites increasing the effective charge mobility **2.** A triplet and charge can interact to form a meta-stable heavy trion, reducing the effective mobility. Lastly, the triplet-charge complex can either **3.** scatter apart or **4.** quench to the ground state, depending on the total spin of the species involved.

As visualized in Figure 4, there are several ways exciton-charge (trion) interactions could influence the effective charge mobility: (1) Triplets may block what would otherwise be trap sites for charges, leading to an increase in conductivity when triplet density is high; (2) the trion may be stable or meta stable, and because it possesses a higher effective mass than a free charge, it leads to a reduction in conductivity when the triplet and charge densities are high; (3) triplet excitons produce more charge-carrier scattering events when they are present, leading to a reduction in conductivity at high triplet concentrations; (4) the exciton-charge quenching interaction may liberate charges from deep traps, as the energy of the exciton transfers to the charge upon quenching, leading to an increase in conductivity when the triplet density is high.

Since we observe only positive magnetoconductance, which indicates an increase in conductivity when quenching is *minimized*, the only mechanism we include in our proposed ki-

netic model is mechanism (1). Processes (3) and (4) occur, but quenching is not assumed to lead to de-trapping effects, and scattering does not reduce the mobility in the model. Mechanism (2) is similarly discounted, because we do not need to assume a finite trion lifetime to model the data. Moreover, there is insufficient literature evidence of the stability and lifetime of the trion complex. These simplifications are necessary because the contributions from each mechanism simply lead to differing signs of the MC effect, and are thus not readily distinguishable. It is not an assertion that mechanisms 2-4 are invalid, only that they do not dominate our results.

The complete kinetic model is shown in Figure 5, wherein a DC bias applied to the device is represented as an initial concentration of mobile holes determined via the M-H fitting of the J-V curve. Illumination is represented as a generation term of free triplets G_T determined via the excitation wavelength and fraction of light absorbed at an illumination intensity of 1690 μW/mm^2. Triplet species are also allowed to relax with a triplet relaxation rate constant k_{Tr}.

Both holes and triplets undergo trapping with rate constants γ_{pnx} and γ_{Tnx} and detrapping with rate constants k_{pdt} and k_{Tdt} respectively. Triplet-hole interactions occur with a bi-molecular encounter rate coefficient of γ_{TCA}, allowed when either species is not trapped. It is this quenching rate constant, γ_{TCA}, that forms the link between the quantum and classical components of the model. Upon interaction, the particles form a trion encounter complex with total spin character of either 1/2 (Doublet) or 3/2 (Quartet) and immediately quench or scatter respectively. In the model, this spin character is represented as the doublet or quartet character of the density matrix ρ_D or ρ_Q, which will be explicitly solved for in the following analysis. The ratio of triplet-polaron pairs that take on doublet or quartet character thus describes the probability of quenching at each encounter; it is fundamentally magnetic field dependent, and we calculate it by solving for the steady-state density matrix of a model Hamiltonian that describes this spin system.

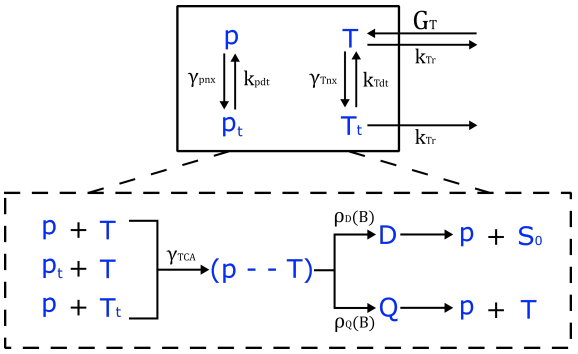


Figure 5: Proposed kinetic model including initial hole density, generation and relaxation of triplets, trapping and detrapping processes, and the quenching or scattering interaction based on the doublet/quartet character of the complex.

We adopt the density matrix approach employed by Schellekens et al. for this purpose,[70] which models the particles and subsequent reactions with the stochastic Liouville equation in the steady-state limit, given by:

$$0 = -\frac{i}{\hbar}[H,\rho] - \frac{1}{2}(k_{-1}+k_2)\{\Lambda_D,\rho\} - \frac{1}{2}k_{-1}\{\Lambda_Q,\rho\} + \frac{1}{6}k_1\Gamma \tag{3}$$

The first commutator term represents the evolution of the density matrix governed by the Hamiltonian of the triplet-polaron system. The second two terms represent the removal of particles from the system and incorporate the anti-commutator of the doublet and quartet projection operators Λ_D and Λ_Q with the density matrix. The final term represents addition of particles to the system with a constant Γ. The reaction rate constants k_1, k_2, and k_{-1} correspond to the triplet-polaron interaction and the forward and reverse trion reactions, respectively. These reaction rate constants are not explicitly included in the kinetic scheme where triplet-polaron encounters are allowed to resolve immediately. The Hamiltonian of the triplet-charge system is approximated by the un-coupled Hamiltonians of the component particles given by:

$$H = H_{Z,T} + H_{Z,D} + H_{hf,T} + H_{hf,D} + H_{zfs,T}$$
$$H_{Z,i} = \frac{g\mu_B}{\hbar} B_{app} \cdot S_i$$
$$H_{hf,i} = \frac{g\mu_B}{\hbar} B_{hf,i} \cdot S_i$$
$$H_{zfs,T} = \frac{D_{zfs}}{\hbar^2} S_{T,z}^2 + \frac{E_{zfs}}{\hbar^2}(S_{T,x}^2 - S_{T,y}^2) \quad (4)$$

Where $H_{Z,i}$ and $H_{hf,i}$ represent the contributions from the Zeeman splitting and hyperfine interactions of the individual particles. $H_{zfs,T}$ represents the zero-field splitting of the triplet state with commonly used D_{zfs} and E_{zfs} energetic parameters.[71]

The lack of a coupling term between the triplet and doublet states in the Hamiltonian is notable in this context: there is no mathematical representation of an inter-particle *distance*, implying that the coherent evolution of the density matrix occurs independent of triplet-charge encounters. The steady-state solution merely calculates the average spin configuration at each encounter. Thus the interpretation of k_1, k_2, and k_{-1} should not be used to infer an encounter-complex (trion) lifetime, but merely needs to be representative of the residence time of charges and excitons within the device.

We approach Equation 3 by first constructing the triplet spin Hamiltonian in the low-field basis ($T_xT_yT_z$), which includes the Zeeman and hyperfine interactions with chosen parameters given in Table 1. The low-field basis Hamiltonian is then transformed into the high-field basis ($T_+T_0T_-$) and diagonalized at each applied magnetic field value to provide a Hamiltonian represented in an eigenbasis valid for any given field strength. Creating the tensor product of the doublet and triplet Hamiltonians and applying a second unitary transformation produces the full doublet/quartet Hamiltonian.[72,73] The stochastic Liouville equation can then be solved to produce a magnetic field dependent density matrix, yielding the doublet and quartet character of all 6 mixed states. The classical kinetic model then generates relevant species, tracks their populations, and resolves triplet-polaron interactions as quenching or scattering based on the doublet/quartet ratio provided by the density matrix. The change in conductance is calculated from the change in the free hole concentration, solved to steady state.

D_{zfs}	1395 MHz
E_{zfs}	54 MHz
σ_{hf}	20mT
k_1	$1x10^6\ s^{-1}$
k_2	$3x10^6\ s^{-1}$
k_{-1}	$2x10^6\ s^{-1}$

Table 1: Model parameters

The density matrix one obtains by solving the stochastic Liouville equation depends on the relative orientation of the molecular and Zeeman reference frames (see SI). Similarly the local hyperfine field strength has a significant impact for low applied magnetic fields. Thus, we averaged the doublet/quartet probabilities over an isotropic distribution of molecular orientations, consistent with the polycrystalline nature of our films. A similar averaging was incorporated using 50,000 random hyperfine field strengths drawn from a Gaussian distribution with standard deviation σ_{hf}. Estimating the average hyperfine field strength observed by the triplet state at any given time is difficult, as literature reports vary widely.[70,74] The value for σ_{hf} chosen in Table 1 was derived from a fit of the kinetic model to the illuminated MC curve in Figure 2. The large value required to fit our data (20 mT / 560 MHz) is consistent with that reported by Schellekens,[70] and suggests either splitting of the triplet and/or doublet states by many protons (typical hyper-fine coupling constants are 10-20 MHz), or another yet to be defined broadening mechanism.

The model described above provides excellent fits to the data in Figure 2 at an illumination intensity of 1690 μW/mm^2, but employs a trap density different to that found from the Mark-Helfrich fits of the device characteristics (10^{15}cm^{-3} vs 10^{17}cm^{-3}). It also qualitatively reproduces the counter-intuitive decline in MC magnitude with both increasing voltage and increasing light intensity (see Figure 3 and S9), but can't fully explain how weak this trend is

in the experimental data. As we discuss in the SI, this suggests that the traps driving the MC response may be associated with interfaces or filamentary current pathways, allowing a small density of trap sites to dominate the MC behavior. Such spatially heterogeneous phenomena cannot be fully captured by our 1-dimensional model, and any future more quantitative work in this area will most likely require a full kinetic Monte Carlo treatment of both transport and MC effects. Nevertheless, the model also predicts substantial sensitivity of the MC magnitude to changes in trap density, as the experiments take place in a regime where the MC response is limited by the availability of traps, not the concentration of triplets or charges (see figure 3). A higher trap density is expected to substantially increase the MC magnitude. To test this behavior we sought to increase the trap-density in our devices through photooxidative stress.

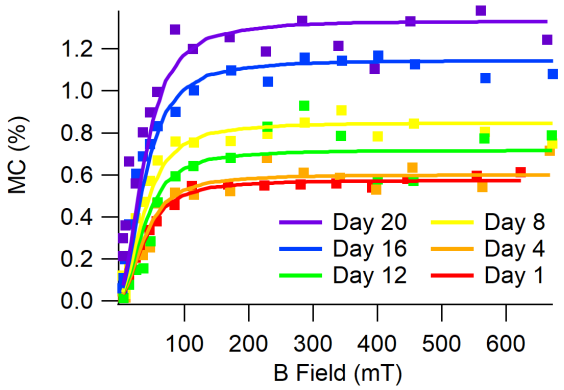


Figure 6: Trap density dependence on MC via extended photo-oxidation under ambient light. Solid lines represent fits to the kinetic model.

Figure 6 shows experimental data collected from a polycrystalline pentacene device subjected to photo-oxidation across several weeks. Each fit uses the kinetic model with trap density as the only free parameter. Typical trap sites formed via the vapor deposition of pentacene tend to be shallow, no more than 100 meV into the band gap,[56] whereas photo-oxidation has been shown to induce the formation of deeper characteristic oxidative trap sites around 280 meV.[58] Therefore, extended photo-oxidation should not only increase the total trap density but also the energetic depth of trap sites, both increasing the effective trap-filling and thus the MC response. The results reveal roughly a doubling of the MC response with extended photo-oxidation, in good agreement with the kinetic model. Fitting parameters from the model reveal that if the energetic trap depth were kept constant, this increase in MC would correspond to a trap density increase from $2.2\text{x}10^{15}\text{cm}^{-3}$ to $4.9\text{x}10^{15}\text{cm}^{-3}$ across the 20 day period.

In conclusion, we have measured the photoinduced magnetoconductance of pentacene-based hole-only devices deliberately designed to facilitate triplet-charge interactions, whilst suppressing other mechanisms of MC.[22–24] The positive MC response of our devices is largely independent of photogenerated current, unlike that observed in most polyacene-based FETs. They show negligible dark MC and minimal applied bias dependence, but a high sensitivity toward trap density. These data are successfully described using a novel trap-filling quantum-kinetic model, where triplets prevent charges from falling into trap sites when the spin configuration forbids quenching. A key finding is that stable or meta-stable trions are not a prerequisite for triplet-charge interactions to dominate the MC response; collisions are adequate to explain the data.

These insights provide design rules for fabricating devices that can harness electrical detection and manipulation of triplet spins for high temperature initialization and readout. Organic devices constructed with narrow channels and energetically deep trap sites will offer a higher sensitivity measurement through maximization of triplet-polaron encounters and more consequential outcomes, respectively. In particular, traps formed from deliberately introduced guest molecules could both serve as specifically designed triplet hosts and as transport traps. These results shed more light onto the disputed mechanisms behind organic magnetic field effects and highlight the importance of harnessing trap sites to the benefit of spintronic, quantum sensing, and molecular electronic applications.

Experimental Methods

General Information. Pentacene 99.9% sublimed grade was used as received from Millipore Sigma. AI 4083 grade PEDOT:PSS was used as received from Ossila. Devices were fabricated on cleaned SiO_2 passivated indium-tin-oxide (ITO) coated glass with 8-12 Ohm sheet resistance. ITO was etched using a 10% Hydrochloric acid solution mixed with a Zn metal powder. Adhesive tape serves to mask the unetched area(s). Substrates were sonicated in acetone and isopropyl alcohol and UV-Ozone cleaned. PEDOT:PSS was passed through a 0.45 μm cellulose filter, spin-coated at 4000 rpm for 30 seconds, gently wiped from one substrate end and annealed at 160°C for 30 minutes. 150nm of pentacene was vacuum deposited between 220-240°C from a ceramic crucible at a rate of 1.5Å/s and a system base pressure of 10^{-8} kPa. The top electrode was fabricated by vacuum depositing 10nm Au followed by 150 nm of Ag at a rate of 0.35Å/s and 2 Å/s respectively. Ag paint in toluene was applied to the top and bottom contact points, and devices were stored in an oxygen and moisture free environment (Nitrogen glovebox, 0.1 ppm O_2 / H_2O before testing).

Current-Voltage measurements were taken on a Keithley 237 Source Measure Unit under nitrogen flow. MC measurements were taken inside a magnet with 600 mT maximum field strength, and measured via a Pyramid HP-1 Hall Probe. A Stanford DS335m function generator supplies the device with a 1V root mean square DC and 0.5V peak-to-peak AC. A Femto HSA-100 current pre-amplifier is connected between the device and ground, and its output measured by a Stanford SR830 DSP Lock-In Amplifier. The sample is illuminated through an optical window via a 660 nm red LED with a listed maximum irradiance of 20.9 $\mu W/mm^2$ and bandwidth of 20 nm. Devices were photo-oxidized via bright white fluorescent light.

Hazards

Hydrochloric acid and Zn metal solution may evolve hydrogen gas and should only be used in small quantities away from possible ignition sources. The reaction must run to completion before deposition in a capped waste bottle, or dangerous pressure may develop!

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Supporting Information Available:

Additional instrument diagram and relevant experimental spectra. Full solution to the stochastic Liouville equation, including explicit matrix representation and influence of applied field orientation and strength of hyperfine interaction. Kinetic model implementation and parameter list.

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