

Electrically Detected Magnetic Resonance in Ambipolar Polymer Field-Effect Transistors

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(Received 10 January 2025; accepted 26 August 2025; published 15 October 2025)

Electron spin resonance can provide unique insights into charge transport processes in organic semiconductors in a regime in which charge motion determines spin relaxation. In particular, electrically detected magnetic resonance (EDMR) probes directly the changes in charge transport properties that are sensitive to magnetic resonance excitation. Here, we present a systematic study of continuous-wave EDMR on conjugated polymer field-effect transistors (FETs) that can be operated in both unipolar as well as ambipolar regimes. We show that, in addition to a narrow, electron-hole recombination-induced EDMR signal that can only be detected in the ambipolar regime, there is also a broad EDMR signal when devices are operated in both unipolar and ambipolar regions. We attribute this signal to a spin blockade mechanism induced when mobile carriers encounter trapped charges along the charge transport percolation pathways and study its dependence on biasing conditions and temperature. The spin-blockade EDMR signature is also observed in conjugated polymer FETs that exhibit only unipolar operation. Our findings show that EDMR provides a powerful technique to study the role of spin blockade and bipolaron formation on the charge transport properties of a wide range of conjugated polymers.

DOI: [10.1103/7b3m-8zvz](https://doi.org/10.1103/7b3m-8zvz)

Organic semiconductors (OSCs) are being investigated for applications in flexible opto- and bioelectronics [1–4]. Electron paramagnetic resonance (EPR) provides a powerful experimental method for studying their exciton/charge transport processes [5,6] and associated spin relaxation processes in a molecular environment with weak spin-orbit coupling and hyperfine interactions [7–11]. Field-induced EPR uses field-effect transistor (FET) architectures to inject a well-defined number of spin-1/2 charge carriers controlled by the applied gate voltage, and allows extracting g factors, which hold information about the local molecular environment experienced by charges and excitons, or spin relaxation times, which give insight into coupling between charge, spin, and structural dynamics [7].

Electrically detected magnetic resonance (EDMR) involves a combination of spin-resonant excitation and electrical detection: In field-induced, continuous-wave (cw) EDMR, like in EPR, a dc magnetic field B_0 and a microwave field at a specific frequency are applied to resonantly excite the field-induced, spin-1/2 carriers between Zeeman-split energy levels. Rather than measuring

microwave absorption, changes in transistor source-drain current are monitored as B_0 is swept across resonance to study how charge transport processes in the FET accumulation layer depend on spin population.

EDMR has previously been applied to polymer light-emitting diodes, solar cells or metal-semiconductor interfaces, in which singlet or triplet excitons are formed from or split into oppositely charged electron and hole carriers; the EDMR response was attributed to magnetic resonance-induced changes in the population of singlet or triplet spin sublevels and associated changes in exciton formation and recombination rate. These can be detected through luminescence in optically detected magnetic resonance (ODMR) [12], or by EDMR through recombination-induced changes in charge concentration and current [13–17]. Here, we perform EDMR on ambipolar polymer FETs [Fig. 1(a)] by monitoring the current through the conduction channel (i.e., drain current I_D). Compared to light-emitting diodes/solar cells, these have the advantage that they can be operated not just in an ambipolar mode with both electrons AND holes present in the device, but also a unipolar mode with either electrons OR holes. We identify a second contribution to the EDMR signal, which arises from a spin-blockade effect [18] and show that EDMR provides a powerful experimental probe of charge trapping processes in conjugated polymers [19].

Results—

EDMR in ambipolar organic transistors: Poly[2,5-(2-octyldodecyl)-3,6-diketopyrrolopyrrole-alt-5, 5'-(2,5-di

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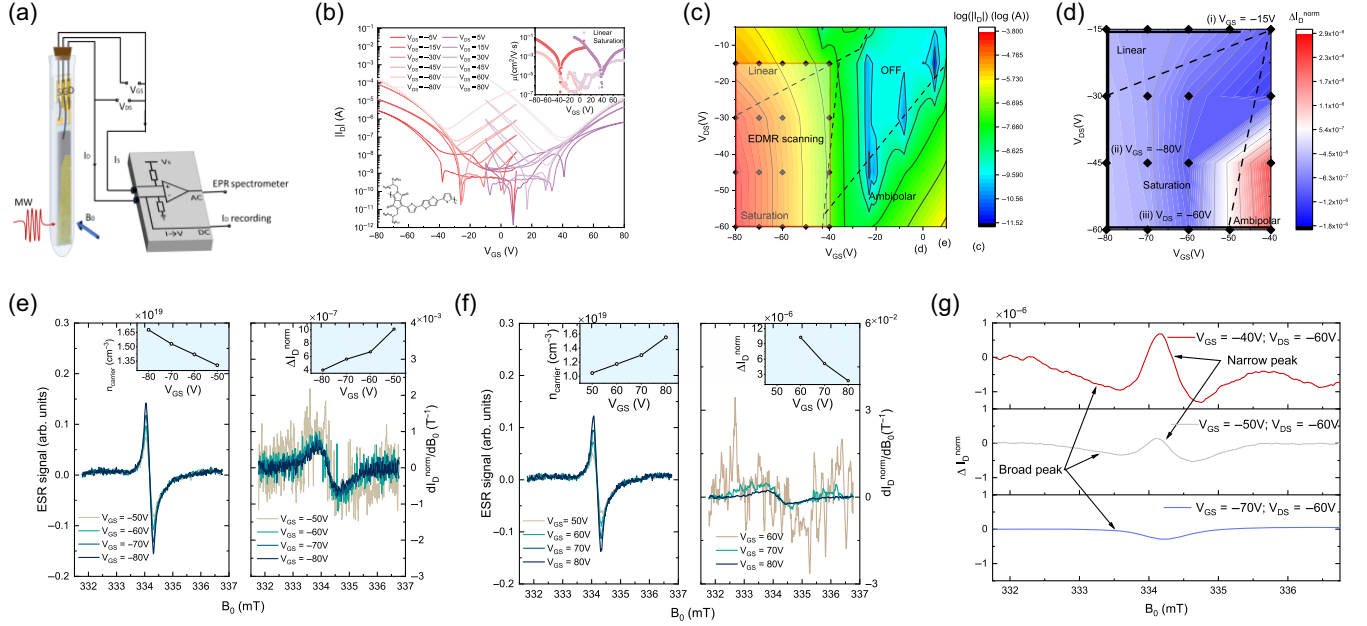


FIG. 1. Field-induced cw-EPR and cw-EDMR on ambipolar DPPDTT FETs at 200 K. (a) Schematic illustration of the experiment. (b) FET transfer curves (inset, calculated, gate-voltage dependent mobility values). (c) Map of channel current with varying V_{GS} and V_{DS} ; the dashed lines divide linear, saturation, and ambipolar regions, the diamonds indicate the points at which EDMR signals were measured. (d) Corresponding map of normalized EDMR signal ΔI_D^{norm} . (e),(f) EPR (left) and normalized EDMR (right) spectra in the p -type (e) and n -type linear regimes. The insets show the spin carrier concentrations estimated from the EPR peak amplitudes and peak ΔI_D^{norm} as a function of gate voltage. (g) Normalized EDMR spectra at different V_{GS} ($V_{DS} = -60$ V), the maximum (or minimum) values of the signal correspond to the ΔI_D^{norm} values in (d).

(thien-2-yl)thieno[3,2-b]thiophene)] (DPPDTT) [Fig. 1(b)] was selected as a model system from the widely studied family of DPP donor-acceptor copolymers [20] because it exhibits ambipolar charge transport with comparable field-effect mobilities for electrons and holes [21]. By selecting appropriate gate (V_{GS}) and source-drain voltages (V_{DS}), DPPDTT FETs can be operated either in a unipolar regime with either electrons or holes induced in the channel, or in an ambipolar regime, in which the current is carried by one type of carrier near the source and by the opposite carrier near the drain with a recombination zone in between. Figure 1(b) shows the transfer characteristics of a DPPDTT FET in unipolar p - and n -type and ambipolar regimes. In the latter, a minimum of the drain current I_D is observed at a defined V_{GS} , the value of which depends on V_{DS} ; I_D exhibits near-symmetric increases to both sides of the minimum. The gate-voltage dependent electron and hole mobilities are similar to each other within an order of magnitude (inset).

For EDMR we detect first-derivative changes of I_D upon modulating B_0 , $\Delta I(B_0)$, by a lock-in technique (Supplemental Material Secs. 1 and 2 [22]). A large offset due to Faraday voltages induced in the circuit loops between the device and the external connection wires is measured off-resonance and subtracted from the measured signal. Figure 1(a) shows a top-gate, bottom-contact (TGBC) FET in the EPR cavity. Because I_D varies with bias conditions

and temperature, normalization of the measured spectra as $dI_D^{\text{norm}}/dB_0 = d(I_D/I_D)/dB_0$ (in units of T^{-1}) provides a measure of the fraction of charge carriers that are affected by the magnetic resonance excitation. However, the normalization of the spectra also tends to reduce the signal-to-noise ratio when measuring under conditions with low dc current I_D .

We biased the device in different operating regimes [Fig. 1(c)] under conditions that minimized bias stress (Supplemental Material Sec. 3 [22]) and recorded the magnitude of the EDMR response [Fig. 1(d)]. In the linear regime with unipolar p - and n -type operation [Figs. 1(e) and 1(f)] the peak EPR signal (left panels) has a linear dependence on V_{GS} . The estimated spin concentrations on the order of 10^{19} cm^{-3} (assuming a 1 nm thickness of the FET accumulation layer) match with values expected from dielectric capacitance measurements (Supplemental Material Sec. 4 [22]). No difference in the peak position or g values is observed between electrons and holes, while EPR peak amplitudes for holes are slightly larger than for electrons. These observations are in good agreement with previous observations [23] and prove that the spins excited at resonance belong to the field-induced charge carriers that carry the FET current.

A key observation of this Letter is a clear EDMR signal in the linear operation regime with unipolar hole [Fig. 1(e)] or electron [Fig. 1(f)] conduction. We observe an EDMR

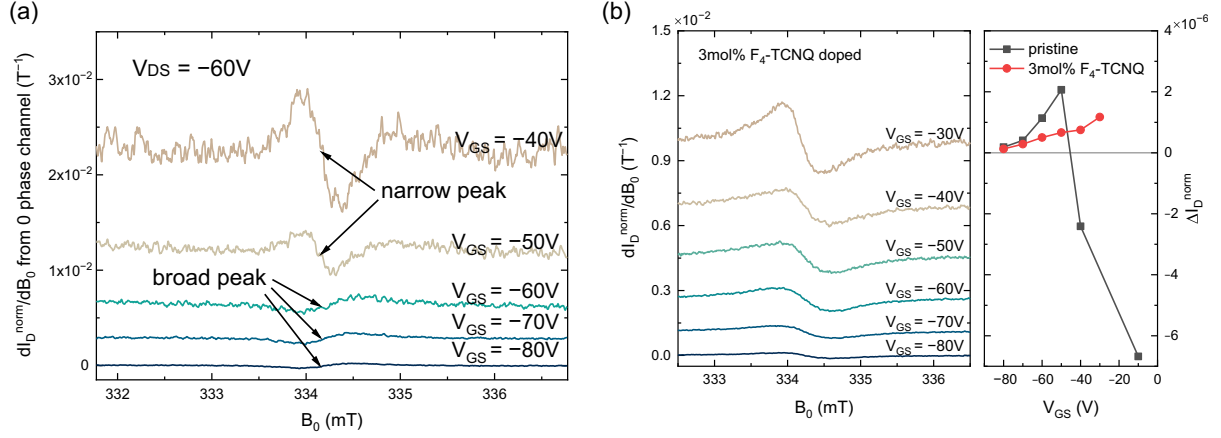


FIG. 2. Dependence of the double peak feature on biasing conditions. (a) Normalized EDMR spectra δI_{EDMR} in the ambipolar region at various V_{GS} ($V_{DS} = -60$ V). (b) EDMR spectra as a function of V_{GS} in F_4 -TCNQ doped, unipolar DPPDTT (left), the right panel compares the V_{GS} dependence of the EDMR peaks of pristine and F_4 -TCNQ doped devices in the saturation and ambipolar regions.

signal once a sufficient drain current passes through the channel; for $|V_{GS}| < 50$ V the signal is too noisy. The EDMR peak is significantly broadened to a full width at half maximum (FWHM) of 0.58 mT for both p and n regions compared to < 0.3 mT in EPR and can be fit by both Gaussian and Lorentzian models with comparable residuals (Supplemental Material Sec. 5 [22]). This broad EDMR linewidth could be due to either inhomogeneous broadening caused by different local environments experienced by the carriers causing the EDMR signal, or a short lifetime of the quantum states involved.

A complete set of scans covering both unipolar and ambipolar operation regimes was performed [Figs. 1(c) and 1(d)]. In the linear regime, V_{DS} starts at -15 V so that the transistor has sufficient I_D even at low V_{GS} (near -40 V) [23]. In the unipolar, linear regime only a single, broad peak is observed [blue spectrum in Fig. 1(g)]. However, in the ambipolar region the signal becomes dominated by a second, significantly narrower peak (red) with similar g value, that is superimposed on the broad EDMR feature. In the transition region (gray), a double-peak feature arises from a superposition with opposite sign or phase of the narrow and broad peaks, that results in a partial cancellation of the signal at resonance, suggesting that there are multiple physical processes contributing. We also noticed some asymmetric behavior in the EDMR line shapes. One contributing factor to this comes from the slow current degradation with the continuously applied bias voltage while the spectra are recorded. Such asymmetric behavior becomes significant when the recorded dI_D^{norm}/dB_0 spectra are integrated to obtain the $I_D^{\text{norm}}(B_0)$ waveforms. Other features like the bump in the integrated spectrum above 336 mT in Fig. 1(g) were not observed reproducibly, but do not affect the analysis of the main EDMR feature around 334 mT (Supplemental Material Sec. 5 [22]).

Origin of narrow EDMR peak in ambipolar regime: Using pulsed EDMR measurements we established that both the broad and the narrow EDMR signals in Fig. 2(a) correspond to an increase of the channel current (see the End Matter). To understand whether the narrow peak in the ambipolar region requires both carriers, or is induced merely by a certain electric potential distribution in FET devices, we used p -doped DPPDTT films by adding 3 mol % F_4 -TCNQ [24] to the solution. The p doping suppresses ambipolar conduction with little impact on material structure [25] (Supplemental Material Sec. 8 [22]). Upon doping, no signature of the narrow peak occurs within $30 \text{ V} < |V_{GS}| < 80 \text{ V}$, only the broad peak is observable [Fig. 2(b)], confirming that the narrow peak observed in the ambipolar regime requires both electrons and holes and arises from a recombination process. Magnetic resonance changes the balance of forming excitons in the different singlet or triplet spin states from oppositely charged carriers, as they enter the recombination zone in the channel. This leads to a change charge carrier concentration profile in the recombination zone, which affects the device current. The origin of the narrow peak is similar to the EDMR/ODMR response previously reported in polymer diodes [12,13].

Origin of broad EDMR peak: Returning now to the broad peak, which is present not just in the ambipolar region, but also in the unipolar linear and saturation regions, we investigated its magnitude along the path indicated by the solid black line in Fig. 1(d): Segment (i) is in the linear regime, segment (ii) transitions from linear to saturation regime. Segment (iii) is in the saturation regime and enters the ambipolar regime near its end point, this manifests itself in the appearance of the narrow peak at $V_{GS} = -50$ V. Along segments (i) and (iii) the magnitude of the EDMR signal, ΔI_D^{norm} , decreases monotonically with increasing $|V_{GS}|$, i.e., higher hole concentration

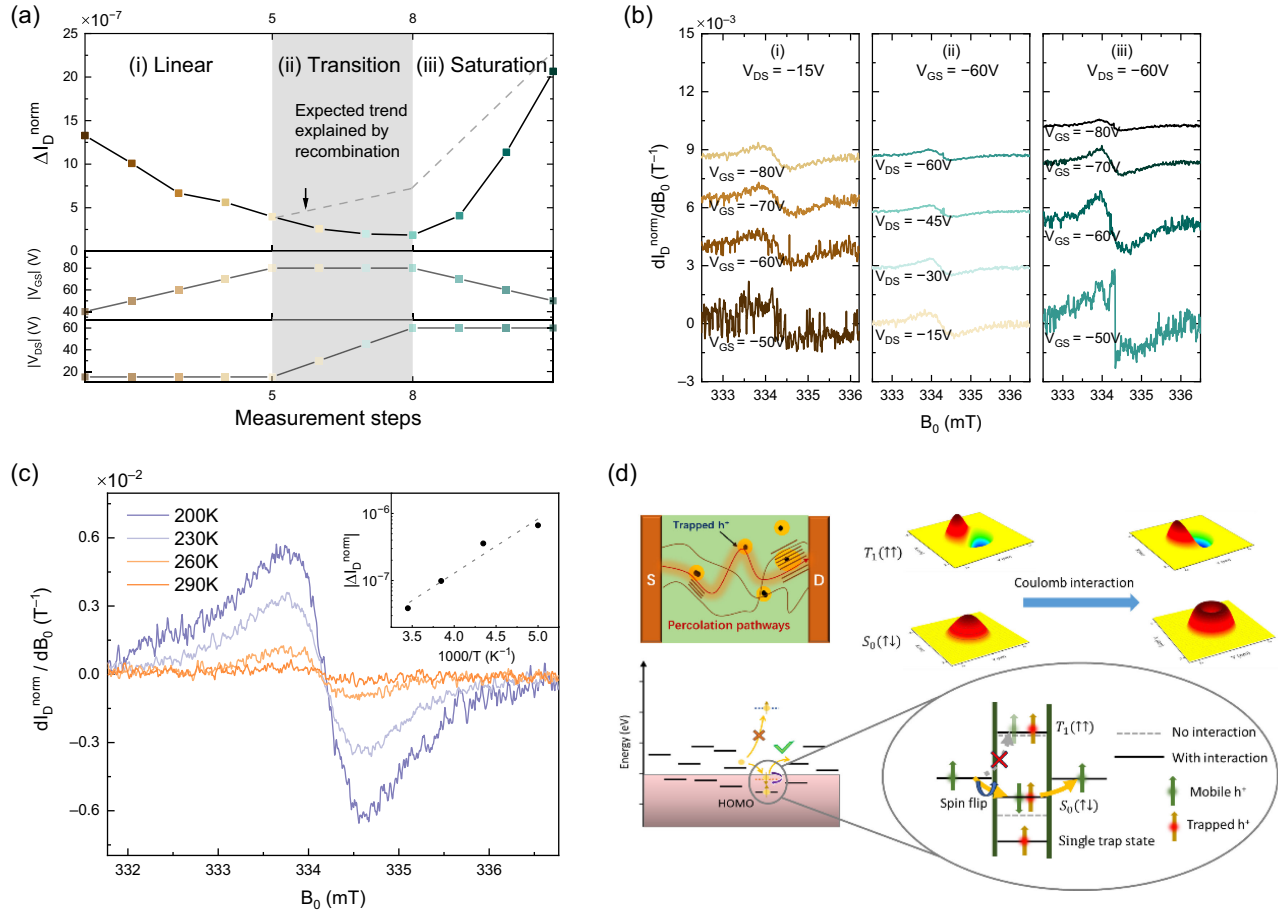


FIG. 3. EDMR response as a function of biasing conditions and temperature. (a) Normalized EDMR ΔI_D^{norm} with various V_{GS} and V_{DS} following paths (i), (ii), and (iii) outlined in Fig. 1(d). (b) Normalized EDMR spectra of the data points in (a). (c) Normalized EDMR spectra as a function of temperature in the linear region ($V_{GS} = -80$ V, $V_{DS} = -15$ V), inset: exponential fit of relative peak magnitude as a function of $1000/T$. (d) Schematic diagram illustrating the spin blockade mechanism. The percolation pathways in the polymer film are shown (top left) with a diagram of single-particle site energies encountered along the percolation pathways (bottom left) and a two-electron energy diagram at a trap site. Solid and dashed lines show the energy level with and without Coulomb interactions. The two-electron wave functions of singlet and triplet states are plotted in the top-right with and without Coulomb repulsion by fixing one of the two holes in the centre of the quantum dot.

[Figs. 3(a) and 3(b)]. Along segment (ii) the signal amplitude exhibits a decrease with increasing $|V_{DS}|$. This dependence was reproducibly observed in two other devices (Supplemental Material Sec. 9 [22]).

To explain the broad EDMR peak, we first considered an electron-hole recombination mechanism between mobile majority carriers and trapped minority carriers. Electron-hole recombination is the main source of EDMR signals in organic light-emitting diodes (OLEDs) with bipolar injection, though a weak EDMR signal, that is potentially of similar origin as our broad EDMR peak observed here, can also be observed in hole-only diode devices [26]. The electron-hole mechanism was found to be inconsistent with the observed $|V_{GS}|$ and $|V_{DS}|$ dependence (Supplemental Material Sec. 10 [22]). To explain the variation of ΔI_D^{norm} with $|V_{GS}|$ and $|V_{DS}|$ consistently, a spin blockade explanation is proposed instead, that involves bipolaron formation

at trap states in the polymer and was previously invoked to explain the magnetoresistance of organic semiconductors [27]. When a carrier is trapped in a state close to the percolation pathway, it may block the transport of mobile carriers, if the mobile carrier attempting to cross through the occupied trap state has the same spin orientation as the trapped charge [Fig. 3(d)]. Such spin blockade due to the Pauli exclusion principle requires additional energy for the mobile carrier to temporarily dwell in a higher energy state on the trap site before moving on along the pathway. Under magnetic resonance conditions, the spin of either charge can be flipped, so that even if both carriers have the same spin orientation, a lower energy, singlet bipolaron state is accessible for the passing carrier enhancing the current. Within this model, the reduction of the EDMR signal with increasing $|V_{GS}|$ can be explained by additional percolation pathways becoming available at high

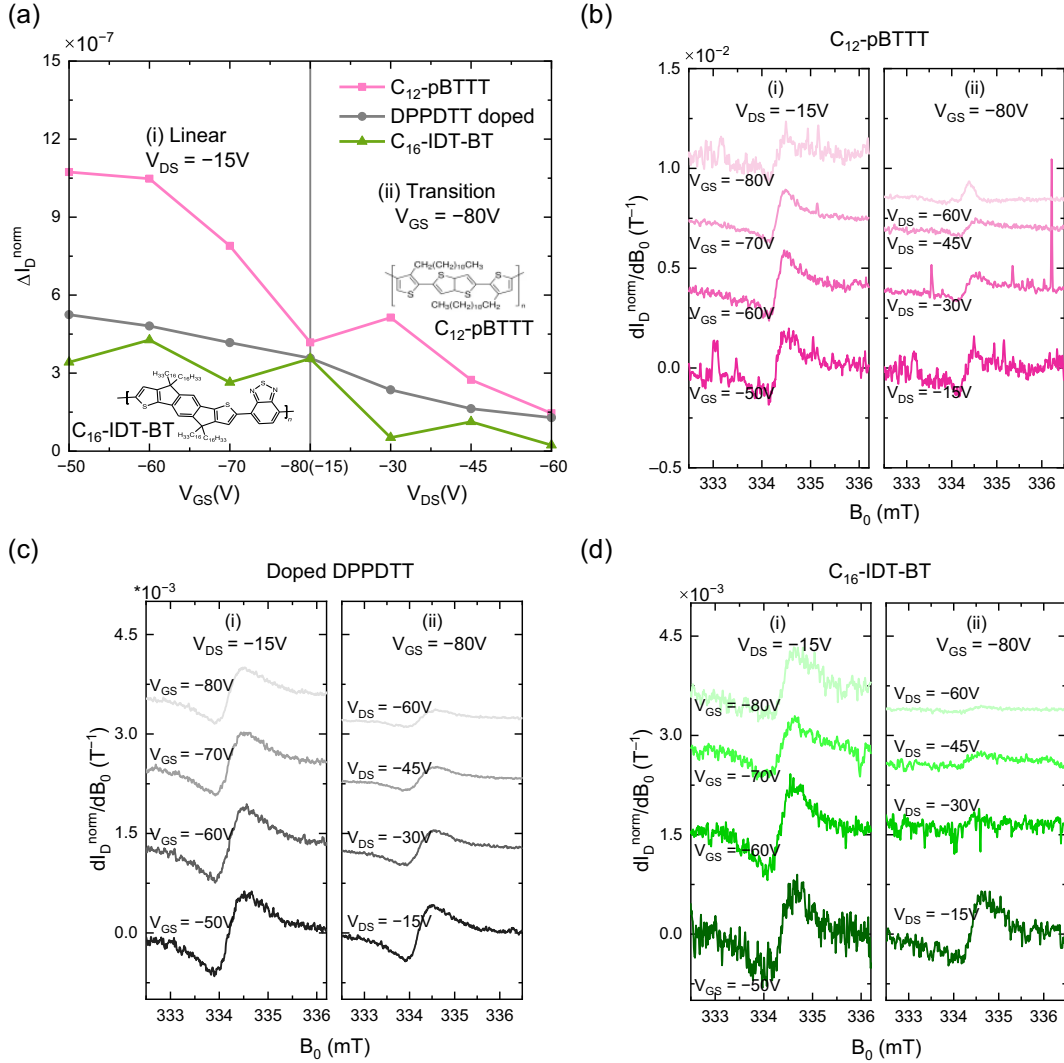


FIG. 4. Generality of observed EDMR response in other polymer systems. (a) ΔI_D^{norm} peak values at different biasing conditions in regime (i) and (ii) for C_{12} -pBTTT, F_4 -TCNQ doped DPPDTT, C_{16} -IDT-BT at 200 K. (b)–(d) Corresponding EDMR spectra.

gate voltage making spin blockade less prevalent. The reduction of the EDMR signal with increasing $|V_{DS}|$ could be explained by the source-drain electric field making more percolation paths available and assisting the transport along them, such that trap sites are less effective in blocking the current flow.

Estimation of the energy scale for spin blockade and the associated wave function extent: The broad EDMR signal decreases by more than an order of magnitude from 200 to 290 K [Fig. 3(c)]. The temperature dependence can be well-fitted by an exponential [inset of Fig. 3(c)]

$$\Delta I_D^{\text{norm}} = \tilde{I}_0 \exp\left(\frac{\Delta E_c}{k_B T}\right), \quad (1)$$

with activation energy $\Delta E_c = 175$ meV (for a discussion of this simple model see Supplemental Material Sec. 11 [22]). We assume that ΔE_c reflects the energetic barrier

associated with overcoming spin blockade, i.e., the energy difference between the lowest energy singlet state $S_0(\uparrow\downarrow)$ and the first excited triplet state $T_1(\uparrow\uparrow)$ [Fig. 3(d)] [18]. We compared ΔE_c to the activation energy E_A of the field-effect mobility and found E_A to be significantly smaller ($E_A = 112 \pm 3$ meV, Supplemental Material Sec. 11 [22]). From the small magnitude of the EDMR signal ($|\Delta I/I_D| < 10^{-6}$) it is evident that the number of carriers affected by spin blockade is small, i.e., not all percolation paths are blocked by a trapped charge. E_A reflects the distribution of site energies encountered by mobile carriers moving along percolation pathways that are not blocked.

To extract, as a sanity check, an order-of-magnitude estimate of the size of the wave functions involved in spin blockade we used a simple two-electron, two-dimensional particle-in-a-box model to calculate the S_0 and T_1 states as a function of box size. The Coulomb interaction results in a central dip in the S_0 state wave function [Fig. 3(d)].

The characteristic size of the trap state L_0 was estimated to be $\sim 1 - 2$ nm (Supplemental Material Sec. 12 [22]), which is consistent with the trap residing on conjugated units of the polymer.

Generality of EDMR response in other polymer systems: Similar EDMR response with similar dependence on V_{GS} and V_{DS} was also observed in other conjugated polymers, suggesting that the observed bipolaron spin-blockade phenomenon in the unipolar charge transport regime is general [Fig. 4]: Unlike DPPDTT, C_{16} -IDT-BT, and C_{12} -pBTTT FETs do not exhibit ambipolarity but operate in unipolar p type, linear, and saturation regimes only. Therefore, we compared their EDMR response with that of F_4 -TCNQ doped DPPDTT FETs. C_{16} -IDT-BT showed the lowest ΔI_D^{norm} , which may reflect its near-amorphous and nanocrystalline microstructure with a low degree of energetic disorder and relatively shallow traps [28,29]. C_{12} -pBTTT exhibited the highest ΔI_D^{norm} , which may be consistent with a higher degree of crystallinity, a wider distribution of trap state energies [30,31] and its low field-effect mobility at room temperature and high E_A value (Supplemental Material Sec. 13, Table S1 [22]).

Discussion and conclusions—We have demonstrated that a characteristic EDMR signature due to a spin blockade mechanism can be generally observed in the unipolar charge transport regime of conjugated polymers. Our approach based on gate-voltage tunable, ambipolar FETs provides an elegant way to distinguish this spin blockade EDMR signal from a narrow, recombination-induced EDMR signal that can be observed only under ambipolar conditions. This is not possible for two-terminal diodes, for which identification of the spin-dependent process causing the EDMR response can be plagued with ambiguity [32,33]. Our findings provide an experimental validation of theoretical predictions, that spin-blockade processes should affect the charge transport and the organic magnetoresistance (OMAR) effect in conjugated polymers [28]. OMAR is an important physical phenomenon that gives rise to exceptionally strong magnetoresistance effects at room temperature, which have been proposed for magnetic field sensing applications; however, its underpinning mechanism has remained controversial [34,35]. Our approach also provides an experimental method for studying interactions between mobile and trapped charge carriers in a percolation transport regime and for identifying the microscopic nature of the trap states involved, which is an important problem affecting the device physics of organic FETs, to which only few experimental methods are applicable. One of the directions we will be pursuing in the future is whether the EDMR method can be applied to better understand bias-stress instabilities, for which the nature of the trapped charge species is not well understood. Our technique of using ambipolar FETs to distinguish between different EDMR mechanisms is potentially applicable beyond organic

semiconductors to other functional materials, in which ambipolar devices can be realized.

Acknowledgments—Z. W. acknowledges financial support from Trinity College in Cambridge for his Ph.D. study. We are grateful for the financial support from the European Research Council (Advanced Grant 101020872) and the Engineering and Physical Sciences Research Council (Programme Grant EP/W017091/1). H. S. acknowledges the support from a Royal Society Research Professorship (RP/R1/201082).

Z. W. fabricated the transistor devices, conducted the cw-EDMR experiments, analyzed the data, and led the project coordination. I. K. and J. B. assisted in building the experimental setup and helped in data analysis and interpretation of data. T. M. provided expertise in the cw-EPR spectrometer. GIWAXS measurements were carried out by Z. W. at Diamond light source (I07 beamline). Z. W. contributed to the writing and editing of the final manuscript, with the intellectual input from all authors. H. S. supervised the project.

Data availability—The data that support the findings of this article are openly available [36], embargo periods may apply.

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End Matter

Pulsed EDMR measurements—In our lock-in measurements it is not straightforward to interpret the observed phase, which is not just determined by whether the current is increased or decreased at resonance, but

also by the relative phase delay between current response and magnetic field modulation, which is affected by other experimental factors that could differ for the two peaks (Supplemental Material Secs. 6 and 7 [22]).

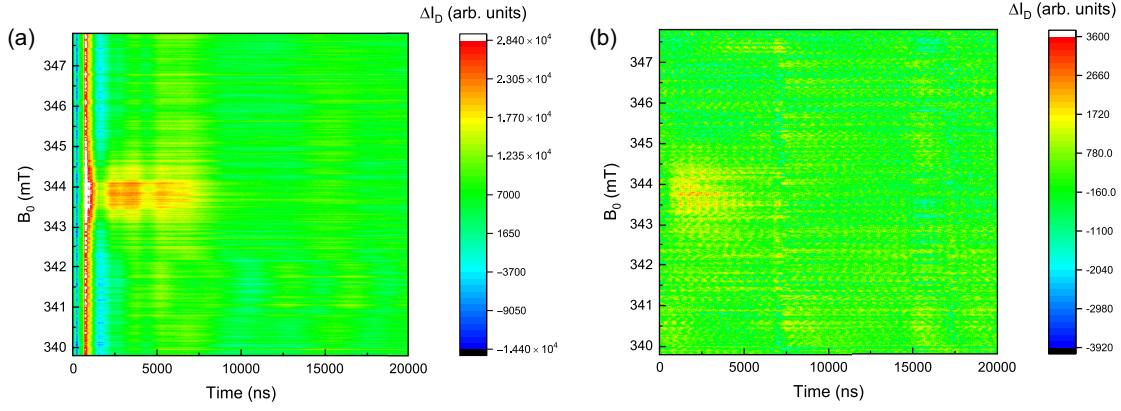


FIG. 5. Pulsed-EDMR measurement of the time-dependent ΔI_D change after a short microwave pulse excitation in the saturation [$V_{GS} = -80$ V, $V_{DS} = -60$ V, (b)] and ambipolar region [$V_{GS} = -30$ V, $V_{DS} = -60$ V, (c)]. The pulsed-EDMR was measured at a frequency of 9.69 GHz, while the cw-EDMR measurements were acquired at 9.37 GHz. Together with a small error in the magnetic field, which is less accurately calibrated in our pulsed-EDMR measurements, this explains the small difference in resonance position (343.9 mT in pulsed-EDMR vs 334.2 mT in cw-EDMR due to the differences in MW frequencies and field calibration between different EPR setup).

To identify whether the two EDMR peaks correspond to a current increase or decrease, we conducted pulsed-EDMR measurements. By applying a short (320 ns) microwave pulse to the device (biased in ambipolar and saturation region) and recording the changes in current with time, we determined unambiguously that both the broad peak in the unipolar regime [Fig. 5(a)] and the narrow peak in the ambipolar regime [Fig. 5(b)] correspond to a current *increase*. At resonance, the current response reaches a maximum value at ~ 2500 ns

(influenced by the bandwidth of the current amplifier) before decaying gradually. The current oscillations are due to the pulse side bands filtered by the amplifier. This response time is much faster than the 25 μ s period of the B -field modulation in cw measurements. However, the small difference in response time on the order of 1 μ s scale between saturation and ambipolar regimes [Figs. 5(a) and 5(b)] may explain the phase difference in the double-peak feature in cw measurements.