

# Challenges for organic spintronics

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In recent years, there has been a proliferation of models for spin-dependent electronic processes in organic semiconductors. Researchers aiming to utilize these processes for new organic spintronics devices should focus more on scrutinizing these models experimentally by embracing spectroscopy.

Organic electronics has grown into a vast research activity that has already achieved success in commercial applications with organic light-emitting diodes (OLEDs). The pursuit of future applications continues, and progress in device-driven phenomenology is swift. This cannot always be said of fundamental understanding. In particular, flurry has recently surrounded the study of magneto-optoelectronic properties, an emerging research area referred to as 'organic spintronics' that has produced a range of device concepts for magnetic-field sensors, spin valves and spin-OLEDs<sup>1–3</sup>. Organic spintronics not only defines a spin-based technology, it also describes research on fundamental microscopic spin-dependent electronic processes for which literature offers plenty of microscopic physical models. These models allow the formulation of hypotheses, to be tested in experiments. On occasion, however, the sequence between modelling, hypothesizing and experimenting has become undone: new observations are explained with new models, rather than serving to scrutinize existing ones.

We offer a brief critical perspective of the state of affairs of organic spintronics while pursuing two objectives: first, a call for the use of basic spectroscopy to untangle phenomena; and second, advocacy for a minimalistic approach to modelling, based on independently verified physical mechanisms. The challenge for the organic spintronics research community is to elucidate how phenomenology translates to physical insight.

## Spins in organic semiconductors

Organic semiconductors differ in many regards from inorganic or purely carbon-based materials such as graphene. They

are characterized by a higher degree of disorder in morphology, chemical purity, and molecular and electronic structure; and charge transport takes place mostly by hopping of injected carriers between localized states, which implies low mobility and uncertainty in carrier density. These materials also degrade easily, which can give rise to intriguing measurement artefacts. Spin coupling in organic semiconductors differs from that in inorganic semiconductors because the spin-orbit interaction is weak, and from that in purely carbon-based compounds because strong spin-hyperfine interactions can arise due to the omnipresent hydrogen.

Although these differences make organic spintronics interesting from the fundamental, and possibly technological, perspective, they are also the reason why experimental access to spin phenomena with conventional methods has been difficult. It is challenging to prove macroscopic spin polarization and transport within a molecular thin film. Techniques such as Kerr-effect microscopy are unsuitable because of electrode stray fields. The Hanle effect, a measure of spin precession in a spin current due to an external magnetic field, should lead to a precession angle-dependent resistivity change in spin-valve devices, which is not observed<sup>4</sup>. Circular dichroism, used in the first demonstration of spin-injecting light-emitting diodes, cannot be used owing to the lack of spin-orbit coupling; spin-OLEDs<sup>2</sup> could potentially reveal a modification of spin statistics through singlet/triplet fluorescence/phosphorescence ratio changes, but this remains to be shown. Until now, the most promising approach for microscopically tracking spin polarization has been muon spin rotation spectroscopy<sup>5</sup>. Yet this

technique, based on implanting high-energy muons in organic semiconductors, has revealed rather short (nanometre range) spin-diffusion lengths. Two-photon photoelectron emission spectroscopy offers compelling evidence for interfacial spin-transfer<sup>6,7</sup>, but cannot conclusively probe transition of spin-polarized carriers into the bulk device. Finally, electron magnetic resonance techniques are capable of probing spin states directly. In thin-film devices, these volume-sensitive methods are limited by the low dimensionality of the systems probed, the presence of electric contacts that can distort resonant excitation fields, and resonance artefacts due to paramagnetic or ferromagnetic (that is, electrode) resonances that are not related to the charge-carrier spin states under investigation.

## Spin relaxation times

The term organic spintronics has been used to describe either the purported exchange of spin for charge as the information carrier in devices or, more generally, for spin and thus magnetic field-dependent charge-transport processes. Both phenomena are related to spin relaxation. Spins may relax longitudinally or transversally. The first process, occurring over time  $T_1$ , describes loss of magnetization by spin-lattice relaxation or recombination. The second process denotes loss of spin phase occurring over time  $T_2$  ( $\leq 2T_1$ ).

In spin valves, spin-polarized current is directly injected into a material from electrodes with different coercive fields. As the electrodes change magnetization independently in an external field, they can act as spin filters for carriers, leading to hysteretic switching in device current that, in turn, provides a sensitive measure

of magnetic field<sup>2,8,9</sup>. Such spin transport between electrodes requires either high carrier mobilities or long spin-relaxation times. However, in contrast to materials such as silicon<sup>10</sup>, carbon nanotubes or graphene, where these conditions are routinely met, organic semiconductors exhibit low mobilities and impose large hyperfine fields, disorder and strong localization on carrier spins, which all promote spin randomization<sup>11–13</sup>, shortening  $T_1$  and  $T_2$ . In the absence of spin precession (due to externally applied perpendicular fields), spin polarization of propagating charge carriers decays within  $T_1$ . Yet, confusingly, the literature frequently refers to ‘spin coherence lengths’<sup>8</sup>, rather than longitudinal spin-relaxation.

There are prolific reports on ‘spin valves’ where models of spin transport have been taken from literature to arrive at astonishing conclusions. In one example<sup>14</sup>, spin lifetimes of  $\sim 1$  s were claimed, at variance with direct measurements of  $T_1$  using magnetic resonance<sup>15</sup>. Of course, models can be used to fit data, but they have to do so in the entire data space available. In this particular example<sup>14</sup>, it seems that the small hysteretic switching effect, observed over a large magnetoresistive background, can be explained by magnetoresistance originating from stray fields from electrodes<sup>16,17</sup>, and is not related to spin injection or extraordinarily slow spin-relaxation. In another extreme case<sup>18</sup>, steady-state electron paramagnetic resonance spectra of the commonly used organic semiconductor Alq<sub>3</sub> were fitted to extract  $T_2$ , disregarding dominant hyperfine spectral broadening mechanisms. The resulting subnanosecond relaxation times<sup>18</sup> are clearly incompatible with claims of long-lived spin coherence formulated elsewhere<sup>1</sup>.

Because there have only been limited observations of magnetization in organic spin valves, conclusions on spin polarization are drawn from device hysteresis. There are two caveats here. First, stray fields from the electrodes may lead to hysteretic behaviour<sup>16,17</sup> given the underlying magnetoresistive nature of charge transport in organic semiconductors. Second, interfacial organic magnetoresistance was recently demonstrated, based on changes in current due to coupling of long-lived (hydrocarbon) molecular radical spins with the ferromagnetic electrode<sup>19</sup>. In such devices, hysteretic resistivity switching is seen with just one magnetic contact. Characteristics of these devices are basically indiscernible from

purported spin valves with two contacts, posing the question whether hysteretic switching really can be viewed as proof of spin injection and transport in spin-valve structures.

### Spin-dependent transport

Further complexity arises because the very nature of charge transport is highly dependent on magnetic field, even if there is no net magnetization in the material. Organic magnetoresistance (OMR), dark magnetoconductivity in diode-like structures, dates back to 1967<sup>20</sup>. Various static magnetic-field effects, of the order of 1–10% at 10 mT, have been reported over the years<sup>21–25</sup>, notably by Frankevich. In recent years, differences in OMR magnitude between materials have been observed<sup>24</sup>, in particular in thin films of solution-processed polymers and vacuum-sublimed molecules. Variations in effect magnitude, sign changes and bias dependencies have been found. Notable OMR and magneto-electroluminescence phenomena on the sub-mT scale exist, with sign switching occurring between small, intermediate and large fields<sup>11,26,27</sup>. This research is particularly exciting because the underlying physical mechanisms of OMR bear analogies to those attributed to magnetophotosensory abilities of birds, which may involve macroscopic room-temperature quantum coherence and rephasing phenomena<sup>28</sup>.

Where should one start in developing a physical picture of OMR? Existing models include electron–hole pair mechanisms, doubly charged carrier species called bipolarons (optionally stabilized by counterions to give triions), triplet excitons, or magnetic field-dependent spin–orbit coupling known from inorganic and carbon-based materials. With rich phenomenology available experimentally, it is tempting to interpret OMR itself as a spectroscopic technique. Within the framework of a specific model, spin states can then be derived. It would be more preferable, however, to identify a specific spin species by robust independent spectroscopy (such as spin resonance, an inherently microscopic technique), formulate a corresponding model based on this species, and then test the model with custom-designed OMR experiments. As we exemplify below, this spectroscopy-based approach brings its own challenges, which can only be addressed by meticulous exploration.

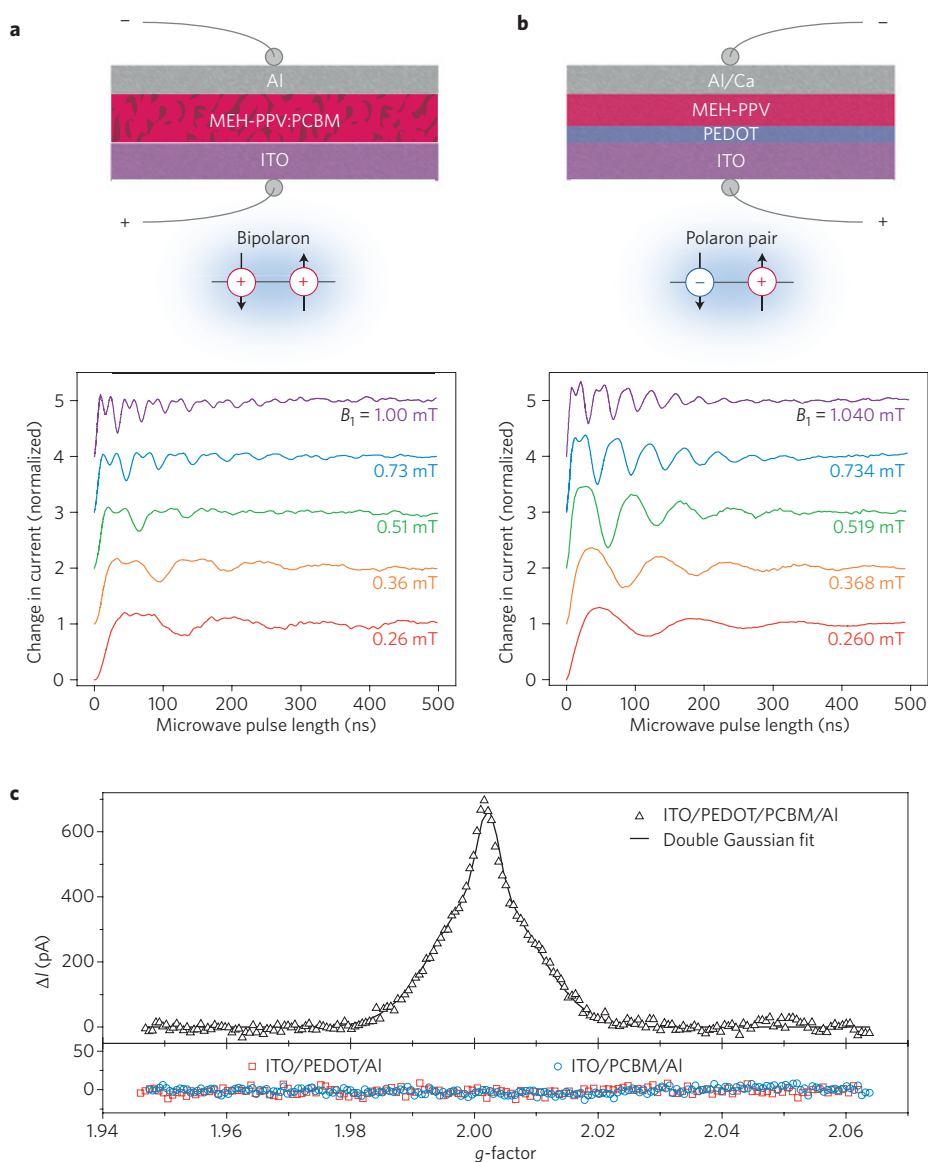
### Models of magnetic-field effects

One model explaining magnetic-field effects is the carrier-pair mechanism,

which describes field-induced changes of spin permutation symmetry, affecting dissociation and recombination by residual exchange interactions. This model has surfaced in different guises, as the radical-pair mechanism in spin chemistry<sup>29</sup>, the polaron-pair (PP) process<sup>21</sup> in organic electronics and the carrier-pair effect in semiconductors<sup>30</sup>. An obvious criticism is that different rates of pair recombination and dissociation are involved, which appear as free parameters when applying the model to static magnetic-field observables such as OMR. However, all rates can be quantified spectroscopically by coherent pulsed magnetic-resonance techniques<sup>31</sup>, where changes in current (or luminescence) are measured under a static magnetic field and a pulsed microwave field.

In the PP model, spin relaxation controls singlet-to-triplet and triplet-to-singlet mixing, and the resulting singlet and triplet densities within the PP ensemble determine conductivity. A static magnetic field modifies the influence of hyperfine fields on spin relaxation, inducing the magnetoresistive effect. Depending on the ratio of singlet and triplet recombination and dissociation rates, mixing either decreases or increases conductivity. A common preconception is that the model only describes either positive or negative OMR, not both. This understanding arises if only one of two mixing channels, the singlet recombination channel, is taken into account. The triplet recombination channel is considered to be small and, therefore, negligible. However, we know from spin spectroscopy that each current ‘quenching’ of one of the permutation symmetries (that is, a positive resistance change due to resonantly induced spin mixing) occurs together with an ‘enhancement’ caused by the orthogonal spin permutation symmetry<sup>31</sup>. The observed net current change is the sum of both enhancement and quenching, which usually have different magnitudes. Polaron-pairs therefore describe negative and positive differential currents for resonant spin mixing and, in the same way, for OMR, where hyperfine fields mix spins.

Another criticism is that both positive and negative carrier species are required, yet OMR occurs in devices presumed to support only single carrier species<sup>32</sup>. It is very difficult to establish sufficiently small minority-carrier densities such that a device is truly unipolar. The magnetoresistive effects observed in ‘unipolar’ devices are small enough to be produced by majority-carrier recombination with residual minority-



**Figure 1** | Scrutinizing bipolaron and PP models. Using electrically detected spin-Rabi oscillations induced by magnetic resonance allows the evaluation of magneto-transport processes involving weakly coupled pairs of spins with  $s = 1/2$ . All measurements were performed at room temperature, under vacuum, in X-band ( $\sim 9.3$  GHz,  $B_0 \sim 347$  mT) Bruker Elexsys 580 pulsed electron paramagnetic resonance spectrometers. At low driving fields,  $B_1$  (that is, at low microwave intensities), harmonic Rabi flopping is observed in the current, indicative of a single spin-1/2 species. The Rabi frequency increases linearly with driving field amplitude. At stronger driving fields, spin beating occurs, doubling the precession frequency, which implies the presence of pairs of two spins with  $s = 1/2$  each. **a**, A photovoltaic device consisting of 80% PCBM ( $C_{60}$ ) and 20% conjugated polymer (MEH-PPV) (data taken from ref. 36), interpreted in support of the bipolaron model. Curves are offset from the baseline for clarity. **b**, A pure MEH-PPV polymer device with a hole-injecting (ITO/PEDOT) and an electron-injecting (Ca/Al) contact (4 V bias, 10  $\mu$ A current). The two spin beating experiments shown in **a** and **b** reveal qualitatively identical behaviour that confirms the presence of pairs of two spins, each with  $s = 1/2$ . However, they do not allow discrimination between unipolar bipolarons or bipolar PPs. **c**, The electrically detected magnetic resonance spectrum of a neat PCBM film with suitably matched contacts allowing for bipolar injection (ITO/PEDOT for holes, Al for electrons). Spin-dependent processes are observed (3 V bias, 10  $\mu$ A current, measured four days after device processing). Identically contacted PEDOT control samples without PCBM revealed no signal (0.55 V bias, 8  $\mu$ A current). Control measurements on PCBM without the PEDOT hole-injecting layer also did not reveal any signal at any time within three weeks of device fabrication (0.53 V bias, 10  $\mu$ A current).

carriers<sup>32</sup>. One popular material to make the case of unipolar OMR has been electron-transporting  $C_{60}$ . However, as shown below, although  $C_{60}$  is a poor hole conductor, it can support bipolar injection and therefore, in principle, the PP process.

Bobbert *et al.* proposed that most observed features of OMR can be elegantly explained by the introduction of new quasiparticles — bipolarons<sup>33</sup>. These would have the charge of two electrons (or holes) and give rise to spin-dependent conductivity through Pauli blocking. Substantial, and possibly unrealistic, structural relaxation of the molecular framework, of the order of 10 kT at room temperature, would be required to stabilize bipolarons against Coulombic repulsion and dissociation<sup>33</sup>. Although impressive agreement can exist between modelling and experiment<sup>26,27,33</sup>, notably the recent demonstration of extraordinary OMR in excess of 2,000% in apparently unipolar templated one-dimensional transport channels accurately described by the bipolaron model<sup>34</sup>, it seems crucial to carry out spectroscopy that can actually provide independent support for the existence of such a new particle. This, however, has proven stubbornly tricky. Doubly charged states identified in electrochemistry, where counterions are present, may not relate directly to transient quasiparticles in bulk films where Coulombic repulsion dominates. Photoinduced absorption also cannot offer unambiguous proof of the existence of such a species. Shinar *et al.* have asserted that the explanation of continuous-wave spin-resonance signals requires the existence of bipolarons<sup>15</sup>, but this argument does not take into account the fact that current and luminescence quenching and enhancement can both arise under resonance within the PP mechanism<sup>13,31,35</sup>. The challenge is to identify a bipolaron directly by its resonance signature, and to exclude other mechanisms at the same time.

### Bipolaron or polaron-pair model?

Differentiating between bipolaron and PP models is crucial for understanding OMR, but not at all trivial, as the same spectroscopic data set can be used to argue in support of either model<sup>36,37</sup>. Behrends *et al.* provided a detailed study of electrically detected spin-Rabi beating of two spin-1/2 carriers in a polymer/PCBM (a  $C_{60}$  derivative) film<sup>36</sup>. The film consisted mostly of PCBM, which forms percolation pathways in the blend. The blend configuration was chosen to estimate majority-carrier populations in either constituent of the film: holes are expected

to reside on the polymer, electrons on the PCBM<sup>36</sup>. Figure 1a shows representative current transients: at weak driving fields, only one spin precesses under application of a resonant microwave excitation pulse, leading to characteristic Rabi flopping as a function of pulse length. At high intensities, two spins lock into the driving field, resulting in a doubling in Rabi-oscillation frequency characteristic of spin-1 species. This species was attributed to two correlated holes (a hole bipolaron) as the resonance seems to correspond to the polymer *g*-factor and, under the given operating conditions, electrons and holes are not expected to be present in the polymer simultaneously<sup>36</sup>. However, spin beating also occurs in neat polymer films, where it most likely originates from correlated precession of PPs, electrons and holes<sup>38,39</sup>. Corresponding traces are shown in Fig. 1b: they are qualitatively identical to the blend results. The same effect, along with quenching–enhancement transients, is also found in photoluminescence-detected magnetic resonance<sup>13</sup>, which should be dominated by recombining bipolar PPs, not unipolar bipolarons, which cannot recombine.

A central assumption in attributing spin beating to bipolaron formation is that pair processes (unipolar or bipolar) are absent in PCBM<sup>36</sup>. So what about neat PCBM films? Figure 1c shows electrically detected magnetic resonance of an indium tin oxide (ITO)/hole-injecting layer (PEDOT)/PCBM/Al device. The resonance lineshape and dynamics display PP characteristics<sup>38</sup>. Spin beating is also observed, with signal intensity increasing with oxidation (doping). The spectrum overlaps the features reported for the polymer/PCBM blend<sup>36</sup>. As controls, we performed electrically detected magnetic resonance on ITO/PEDOT/Al and ITO/PCBM/Al devices. Owing to the low-lying PCBM cation, no hole injection is detected in the absence of PEDOT, making transport unipolar, as for sole PEDOT structures. Behrends' spectra<sup>36</sup> appear to arise from superpositions of spectral signatures of the polymer PP<sup>38,39</sup> and the PCBM PP resonances.

In essence, Behrends *et al.* assert that the observed spin-dependent processes cannot be due to recombination because

this would be energetically unfavourable. However, recombination losses in organic solar cells are known to be substantial; even thermally activated recombination could give rise to strong minority-carrier spin-resonance signals. We therefore conclude that the data do not definitively exclude PP involvement and are thus not unambiguous proof of the involvement of bipolarons in charge transport. As this example illustrates, spectroscopy need not be conclusive: even with state-of-the-art techniques, open questions can remain, necessitating further experimentation. The research community should not shy away from such fundamental challenges in favour of pursuing solely device-oriented exploration.

### Call for spectroscopic studies

Although the formulation of hypotheses constitutes an important part of the scientific process, researchers in organic spintronics should be encouraged to put more emphasis on scrutiny and refutation of existing models. This means developing and applying detailed spectroscopies, rather than solely pursuing new effects and devices. In-depth spectroscopy can come with its own challenges: it can provide evidence, but not necessarily definitive conclusions. Experiments must serve alone to test models, but do not constitute predictive models on their own: there is no such thing as an 'experimental prediction'<sup>40</sup> of observations. It must be accepted that models cannot be proven experimentally, for example, there is no definitive proof of the PP versus the bipolaron model. Consolidation of knowledge in reductionist axiomatic formulations rather than creation of new models will advance our fundamental understanding. It is therefore crucial to distinguish observational phenomenology from deterministic spectroscopy. We make the general case here for an increased use of spectroscopy to achieve this goal, highlighting as an example the array of coherent spin techniques available that allow microscopic spin physics to be linked with macroscopic magnetic properties. □

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