Slow Hopping and Spin Dephasing of Coulombically Bound Polaron Pairs in an Organic Semiconductor at Room Temperature

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Polaron pairs are intermediate electronic states that are integral to the optoelectronic conversion process in organic semiconductors. Here, we report on electrically detected spin echoes arising from direct quantum control of polaron pair spins in an organic light-emitting diode at room temperature. This approach reveals phase coherence on a microsecond time scale, and offers a direct way to probe charge recombination and dissociation processes in organic devices, revealing temperature-independent intermolecular carrier hopping on slow time scales. In addition, the long spin phase coherence time at room temperature is of potential interest for developing quantum-enhanced sensors and information processing systems which operate at room temperature.

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Organic semiconductors are now widely used in a variety of optoelectronic devices, with major applications including organic light-emitting diode (OLED) displays and organic solar cells. The electronic transitions which mediate light-charge interconversion are common to both devices. In OLEDs, free charge carriers (polarons) are injected into the device, oppositely charged carriers become Coulombically bound to make up polaron pairs, which subsequently form strongly coupled excitons before they recombine, emitting light depending on the spin state of the intermediate polaron pair. Solar cells work in the opposite fashion, absorbing light to generate excitons, which then dissociate into polaron pairs, which again dissociate to form free charge carriers. These processes are shown in detail in Fig. 1(a).

It is reasonably easy to probe free polarons, as they directly contribute to conductivity, and excitons, as they emit light when they recombine. Polaron pairs, however, are neutrally charged, do not contribute to conductivity, and are optically inactive. As a result it is difficult to directly probe the state which lies at the heart of the process of optoelectronic conversion in organic semiconductors. In this Letter we show that we can use the spin properties of the polarons constituting these pairs to probe their dynamics, in particular, by measuring the spin phase coherence lifetimes with spin-echo techniques. By using the pair's internal quantum phase as a probe, the motion of polarons within a pair through the random magnetic environment arising from the Overhauser field of the polymer's nuclear spins can be determined. We show that after coherence has been encoded into the spin pairs the phase information can be recovered as long as the polaron remains on a particular segment of the polymer chain during the measurement. However, if there is a hopping or tunneling event to a nearby unit the phase coherence is nonrecoverable due to the changed orientation of the local Overhauser field [see Fig. 2(b)], since there is no long-range correlation of nuclear spins [1]. This migration of an individual charge carrier leads to a measurable decay in spin-echo amplitude of the ensemble.

Here we perform pulsed electrically detected magnetic resonance (EDMR) [2,3] on devices consisting of a an organic π-conjugated polymer poly[2-methoxy-5-(2'-ethylhexyloxy)–1,4-phenylene vinylene] (MEH-PPV), similar to devices previously studied [1,4]. The polymer was incorporated into an OLED with indium tin oxide (ITO) and calcium electrodes, as well as a hole injection layer of poly(3,4-ethylenedioxythiophene) (PEDOT) for balanced hole injection [5]. The use of pulsed EDMR is a particularly appropriate technique for investigation of coherent dynamics in organic materials, as the spin dynamics are set solely by the microwave pulses, whereas any variation in the RC time scales of the device only impact the readout time scale [2,6]. The correspondence between electrically and optically detected pulsed electron spin resonance experiments [7] on similar structures indicates that the polaron pairs seen in this work are oppositely charged. However, this method may also be of use for materials which contain bipolaron pairs [8] (pairs of like-charge polarons) or other more complex spin pairings [4].

Recently, we have shown that controllably perturbing the spin state of the polarons which comprise polaron pairs directly modifies both the conductivity [9] and the luminescence of an OLED [7]. Although conventional electron spin resonance is used to manipulate the spins, the change in optoelectronic properties is sensitive to singlet and triplet spin configuration within the pairs, and not to the ensemble magnetization, as is usually the case in electron spin resonance [9]. Because of this, the measurement is sensitive to the dynamics of the intermediate state, the

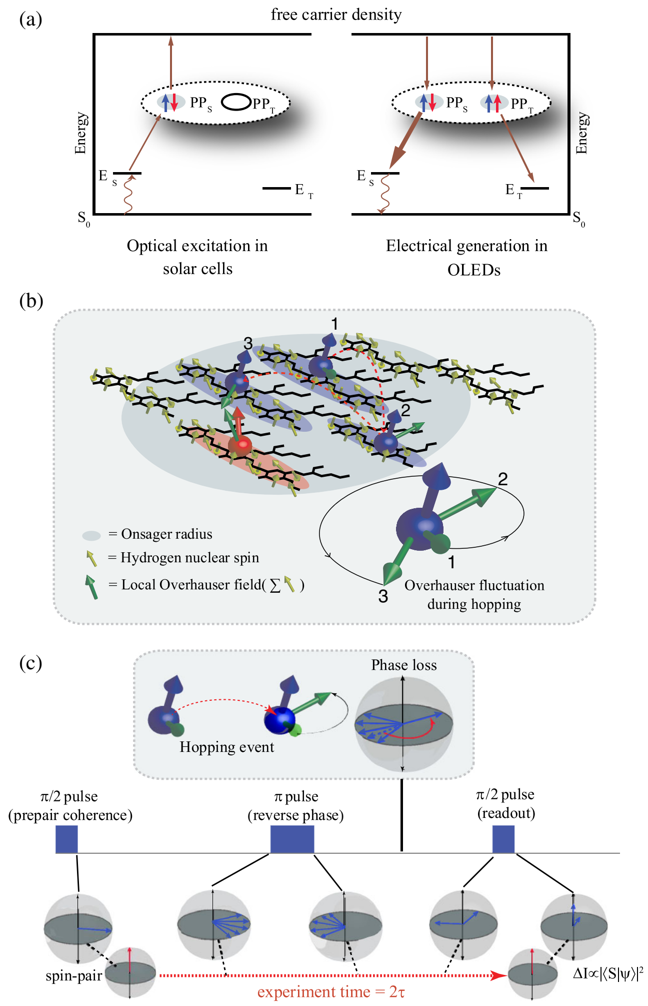

FIG. 1 (color online). (a) The important step in both the light-to-charge (solar cell) and charge-to-light conversion (OLED) is the polaron pair, a state that is accessible by the spectroscopic method discussed. Polaron pairs exist both in the singlet (S) and triplet (T) configuration and can couple to excitons at energies E_S, E_T. (b) An electron hopping through sites 1-2-3 (blue) and hole (red) form a carrier pair. As charges hop from site to site within the Onsager radius of the Coulombically bound pair, they experience an effective temporal fluctuation in the local magnetic field, even when the nuclear spin ensemble is quasistatic. The decoherence time therefore places an upper limit on the intersite hopping rate of charges within a pair. (c) The measured loss of phase coherence within a pair can be seen as a hopping event to a new Overhauser site during the spin-echo sequence, where the current change ΔI is proportional to the singlet content of the wave function.

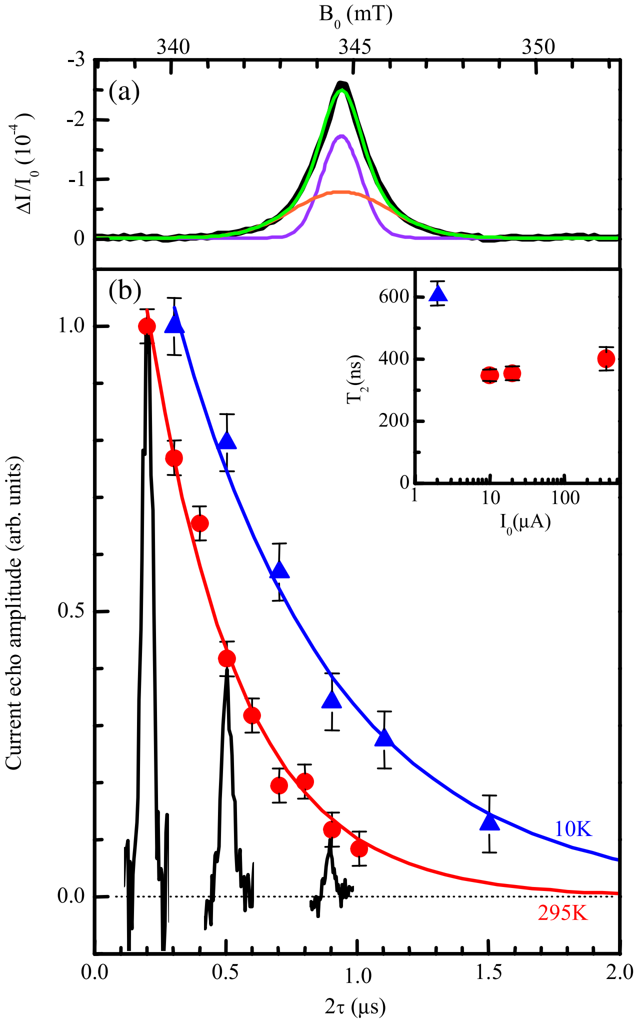

FIG. 2 (color online). Experimentally observed magnetic resonance spectrum and spin echoes. (a) The spectrum is described by two Gaussians [orange (wide) and purple (narrow) lines] representing the hyperfine field-broadened resonance of electron and hole [sum of Gaussians: green line (fit to data)]. (b) Using a Carr-Purcell (CP) spin-echo pulse sequence as described in Fig. 1(c), the effect of spin dephasing can be removed, providing a measure of the intrinsic phase coherence time T_2. The three black curves show CP echoes scaled to the time axis. The echo intensity follows an exponential decay with time and depends only weakly on temperature. All measurements were performed at 295 K unless otherwise marked. The inset shows T_2 values at different device currents to exclude the possibility of current-induced dephasing.

polaron pair. However, a number of challenges remain if we are to utilize this technique to understand the process which limits polaron pair coherence in devices. First, the simple Rabi oscillations shown in Ref. [9] provide only a lower limit on the spin phase coherence time (this point is explained below), and as a result do not allow us to determine the microscopic processes limiting spin phase coherence. Second, the measurements reported in Ref. [9] were undertaken at low temperatures. In this Letter, we utilize electrically detected Hahn echo sequences [10,11] to directly measure the phase coherence time at room temperature, under conditions much more similar to those in which devices operate. The echo sequence provides the basis for a computational model to simulate polaron pair spin decoherence, allowing us to extract an estimate of the hopping transport time scale of polarons bound in polaron pairs in the organic semiconductor MEH-PPV.

The first question we address here is how long the spin ensemble retains memory of its phase. In analogy to the terminology used in NMR spectroscopy, spin relaxation can be either longitudinal or transverse. In interpreting the transient response of the spin-dependent (electrically detected) resonance signal, it is important to distinguish pure decoherence (an irreversible loss in quantum phase information over time T_2) from simple dephasing (a situation where the phase relationship within an ensemble of spins becomes unknown due to either a reversible or an irreversible process over time T_2^*). Following a recent demonstration at low temperatures [9], coherent evolution of the carrier pair spins was measured at room temperature, yielding Rabi oscillations observed in the device current (not shown), much like what is discussed in Ref. [1]. The oscillations are exponentially damped with a time constant $T_2^* \sim 123$ ns. However, this damping arises due to phase variations within the pair resulting from the spatial inhomogeneity in the Overhauser field $B_H(x)$ as well as the limited homogeneity of the resonant driving field B_1, and not solely due to the intrinsic phase relaxation, providing only a lower limit to the true decoherence time.

This coherent phase loss due to the $B_H(x)$ and B_1 inhomogeneities can be undone with a first-order decoupling scheme, in this case a modified version of the Carr-Purcell echo sequence [12], leaving only the dephasing effects due to irreversible processes. The experiment is implemented as follows [11] [Fig. 1(c)]: with the external static magnetic field B_0 defining the z axis and after approach of the steady state, which is dominated by triplet pairs due to the much longer triplet lifetime, an on-resonance microwave $\frac{\pi}{2}$ pulse [13] is applied. This pulse rotates one (or both) of the spins of the pair into the transverse plane. Once in the x-y plane, the spins precess around a transverse field $B_T(x) = B_0 + B_H(x)$. The spatial inhomogeneity of the hyperfine field $B_H(x)$ leads to a coherent dephasing of the ensemble, with those spins experiencing the larger $B_T(x)$ precessing faster. After a delay time τ, a π pulse is applied, equal in magnitude and frequency to the first, but of twice its duration. Those spins experiencing a larger $B_T(x)$ now lag spins with a smaller $B_T(x)$ in their precession, such that at a time τ after the second pulse all the spins regain the same relative phase. If the observable were the polarization, as in standard ESR, one would simply see an increase in magnetization in the form of an echo (a Hahn echo) at a time τ after the π pulse. However, since we detect changes in current due to variations in the spin-singlet content of the ensemble, a magnetization rephasing will not lead to current changes unless we add an additional $\frac{\pi}{2}$ pulse, a readout pulse, to project the rephased state back onto the z axis [10]. As we increase the time between pulses, τ, a corresponding decrease in the observed echo current signal is seen due to irreversible loss of phase information during the time 2τ (Fig. 2). A single exponential describes this dephasing with a true phase coherence time [12,14], $T_2 = 348(18)$ ns at room temperature. Upon cooling to 10 K, T_2 increases to 611(44) ns, a mere factor of 2 difference from the room-temperature value.

Loss of spin phase coherence due to recombination or dissociation of spins in the ensemble, or irreversible spin flips due to spin-orbit interactions, can be discounted as the source of decoherence, since the spin lifetime T_1 should also be limited by such a process [6]. However, we observe a lower limit for the spin lifetime of $T_1 > 36\ \mu\text{s} \gg T_2$ from the transient current response to an on-resonance pulse [6], allowing us to exclude this mechanism of rapid spin flips. Decoherence could arise due to spin-dipolar interactions between charge carriers, but would have to display a significant dependence on current density due to an increase in the local magnetic field fluctuations caused by elastic and inelastic scattering events [15]. However, we find that after a large change in device current there is no effect on the measured spin-echo coherence time (Fig. 2 inset), indicating that spin-spin interactions are not likely responsible for decoherence. Decoherence resulting from a temperature-activated Orbach process, a two-phonon event involving an excited state [16], is also unlikely given the small change in coherence time with temperature (blue triangle in the inset of Fig. 2). Therefore, we conclude that decoherence arises due to hopping of the carrier pairs or of one of the pair partners in the inhomogeneous distribution of nuclear Overhauser fields, $B_H(x)$.

To investigate the influence of hopping on the measured phase coherence time, we numerically simulate the evolution of an ensemble of polaron pairs during application of an echo sequence. As a measure of coherence, we find the probability of the polaron pair returning to the initial state (either $T^+ = |\uparrow\uparrow\rangle$ or $T^- = |\downarrow\downarrow\rangle$) after an echo sequence is applied. To include the influence of hopping, we generate for each spin pair a simplified Overhauser field environment, consisting of a $5 \times 5 \times 5$ grid of sites. This approach is motivated by the recent work by Kersten *et al.* [17] where each molecular site is assigned the magnitude of random Overhauser field contribution, $B_H(x)$, and a specific site energy, drawn from random Gaussian distributions (the FWHM for the electron is 0.96 mT and for the hole is 2.15 mT) taken from the literature [18,19]. The spins may hop independently to nearest-neighbor sites in a stochastic manner. The characteristic hopping time in transport may be varied by modifying the hopping attempt frequency. The characteristic hopping time t_{hop} denotes the time between hops of either spin in the pair. In this work, we have set these two hopping rates to be equal, such that the characteristic hopping time of a single spin is $2t_{\text{hop}}$. The spatially varying Overhauser field obtained is then incorporated into the echo simulation.

For a fixed t_{hop}, the echo simulation is performed for a large number of echo times, 2τ. An example is shown in the inset of Fig. 3(a). The decoherence data generated follow an exponential decay yielding a characteristic

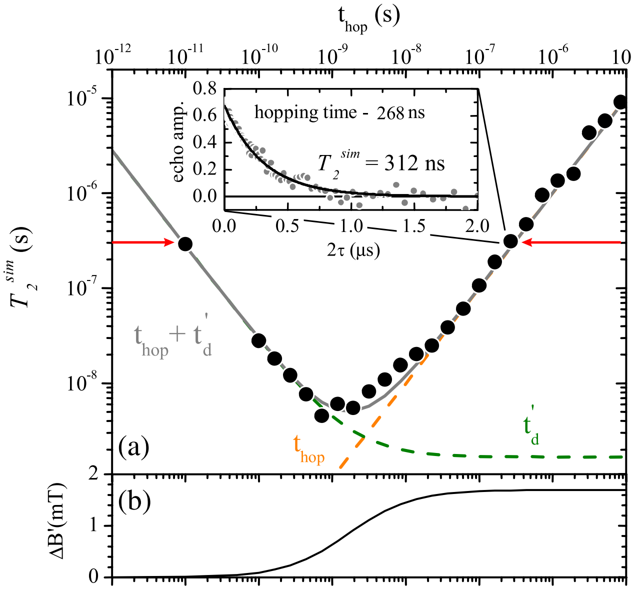

FIG. 3 (color online). Computational modeling of the expected echo decay time $T_2^{\rm sim}$ as a function of polaron hopping time for an ensemble of polaron pairs. The inset shows the computed decay for a single hopping time, simulated for a number of different echo wait times 2τ. The echo is described by an exponential decay. (a) The simulated decoherence time $T_2^{\rm sim}$ is plotted in the main panel as a function of hopping time. For very short hopping times, $T_2^{\rm sim}$ increases with decreasing hopping time due to motional narrowing. The simulated data are well described by the relation $T_2^{\rm sim} = t_{\rm hop} + t_d'$, where t_d' describes on-site dephasing due to the local Overhauser fields estimated from the resonance line width. The modeled decay time coincides with the experimentally measured time of 320 ns for two hopping times (red arrows). (b) The expected resonance line width depends on hopping time due to motional narrowing, providing a measure to differentiate between the two possible hopping times.

coherence time $T_2^{\rm sim}$. Figure 3(a) shows the decay time obtained for a range of different hopping times. As the figure reveals, at slow hopping times $T_2^{\rm sim}$ is equal to the hopping time plus the dephasing time expected due to the change in magnetic environment after a hopping event; $T_2^{\rm sim} = t_{\rm hop} + t_d^0$, where $t_d^0 = 1/g\mu_B B_H^{1/2}(x)$ is determined by the FWHM, $B_H^{1/2}(x)$, of the Gaussian distribution of hyperfine fields $B_H(x)$. However, when the hopping time becomes shorter than the time required for dephasing due to the randomization of the environment after every hop, the decay time $T_2^{\rm sim}$ is found to increase rapidly. This counterintuitive effect is a process known as motional narrowing [20,21], whereby the rapid change in random Overhauser fields due to fast hopping leads to a time-averaged *reduction* in the effective disorder. This phenomenon can be accounted for by equating $T_2^{\rm sim} = t_{\rm hop} + t_d'$, with $t_d' = t_d^0(1 + t_d^0/t_{\rm hop})$. The simulated data in Fig. 3(a) are accurately described by this analytical result (gray line).

As a result of the motional narrowing, there are two hopping times that are compatible with the experimentally observed decoherence time at room temperature—$t_{\rm hop} \sim T_2 = 320$ ns and $t_{\rm hop} \sim 10^{-11}$ s $\ll T_2$. However, we are able to distinguish between these two cases by considering the line width of the resonance shown in Fig. 2(a), which provides a measure of the local Overhauser field. Figure 3(b) plots the calculated line width, $\Delta B' = \frac{1}{2}(\frac{1}{2\pi g \mu_B t_d'})$, as a function of the hopping rate. For slow hopping, the line width is set by the hyperfine disorder field, $B_H^{1/2}(x)$. For fast hopping, the line shape is motionally narrowed and becomes increasingly small. If the faster of the two hopping times compatible with the experimental T_2 value is considered, we would expect a line width of approximately 0.01 mT. However, this is substantially smaller than the $\sim$2 mT line width seen experimentally [Fig. 2(a)], and as such, we can exclude fast hopping as the source of the observed coherence decay. We thus conclude that the hopping time in the MEH-PPV OLED measured here is approximately 320 ns at room temperature, increasing only to 610 ns at low temperature.

The ability to observe this rich phase coherence behavior demonstrates the potential of using organic semiconductors for room-temperature electronics based on quantum coherence effects. More importantly, however, the method reveals surprising insight into elementary charge transport processes in these materials, which are hard to access by other means [22,23]. Whereas transient electroluminescence and pump-probe spectroscopy [24] are nonequilibrium techniques probing the final step in carrier recombination and the first step in exciton dissociation, respectively, the experiments presented here are sensitive to the first step in recombination and the final step in dissociation, and thus report on equilibrium conditions.

These processes occur remarkably slowly (on the time scale of microseconds at room temperature) and must originate from correlated carrier pairs, since spin memory exists. In contrast, in transient absorption experiments, correlated pair recombination is often interpreted to occur swiftly, within tens of nanoseconds [24]. Seeing that such recombination poses a major loss channel in organic photovoltaic devices, it is helpful to be able to identify this process spectroscopically.

We note that during the phase coherence time T_2, the local spin bath is treated as quasistatic due to the much longer nuclear spin-flip times. This approximation allows limits to be placed on the time scale for conformational changes in the hydrogenated side chains, as well as the lifetime of nuclear spins, as both would lead to variations of the Overhauser field felt by the carriers. In addition, the T_2 times pose a limit for intrapair charge hopping rates, since hopping of a carrier within a pair from one molecular site to another would lead to dephasing due to the randomly varying Overhauser fields. As the temperature is lowered, the size of the Coulombically bound carrier pair increases. This Onsager radius is given by the balance of Coulomb and thermal energy. Since T_2 decreases only by a factor of 2 over a 30-fold increase in temperature, we conclude that intrapair charge carrier hops are rare and only weakly thermally activated under equilibrium conditions. This surprising conclusion contrasts with the strong Arrhenius-type activation seen in (nonequilibrium) time-of-flight experiments [25]. On the other hand, if charge hopping occurs solely by tunneling and is not phonon assisted, no thermal activation should be observed. Such an absence of thermal activation is generally seen in photoconductivity [26] and has posed a long-standing puzzle to a quantitative description of charge transport in organic electronics. We conclude that equilibrium carrier dynamics in organic semiconductors are inherently slow and very weakly thermally activated, pointing to a tunneling-type form of intersite coupling.

In summary, organic semiconductors exhibit surprisingly long pure spin coherence times at room temperature. Electrical access to spin coherence phenomena promises facile integration and scalability in quantum information architectures. In addition, spin coherence spectroscopy offers a new perspective on carrier migration in organic semiconductors, revealing the absence of thermally activated hopping under equilibrium transport conditions in disordered materials.

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