

Spin Engineering in Organic Light Emitting Devices

Michael Segal, Marc Baldo*

Dept. of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts, USA
Phone: 1-617-452-5132 , E-mail: baldo@mit.edu

Abstract

We review work performed by our group and collaborators in the area of exciton formation. There are three components: (i) measurement of singlet fractions, (ii) analysis of magnetic resonance measurements, and (iii) models of exciton formation. We find that the fraction of singlet excitons is a controllable quantity, pointing the way to a new generation of all-fluorescent organic light emitting devices.

1. Introduction

The formation of molecular excited states (excitons) in organic semiconductors determines the maximum achievable efficiency of organic light emitting devices (OLEDs). Excitons are generated in OLEDs from the combination of injected electrons and holes. Since its constituent electron and hole can each be spin-up or spin-down, an exciton can have four different spin states: three states, known as triplet states, have a total spin of one; and the remaining singlet state has a total spin of zero.¹ Many OLED materials, most notably many polymeric materials, can only emit light from the singlet state. Thus, in most polymeric OLEDs, the fraction of singlet states formed by charge injection determines the fundamental efficiency.

In the simplest model of exciton formation, it follows from counting states that singlets are expected to account for 25% of excitons. Several experimental and theoretical studies have recently suggested, however, that electrical excitation of polymers generates far more than 25% singlet excitons.^{2,3} Many of these studies have been based on electron spin resonance (ESR) measurements. Our research in this area can be divided into three broad categories: (1) formulating a robust method for measuring the spin statistics in an organic luminescent material and applying the method to an archetypal organic polymer in which a high

singlet ratio has been measured; (2) developing a model for the magnetic resonance in organic semiconductors and considering its implications for spin statistics; and (3) developing techniques to enhance the singlet fraction. We label devices in which the singlet fraction is artificially manipulated, 'extrafluorescent' OLEDs.

2.1. Measuring The Singlet Ratio

Fig. 1 shows the method we have developed for measuring the spin statistics in an organic luminescent material.¹ An OLED is fabricated with the material of interest serving as its luminescent layer, and two types of efficiencies are measured. First, the OLED is operated normally, with injected electrons and holes

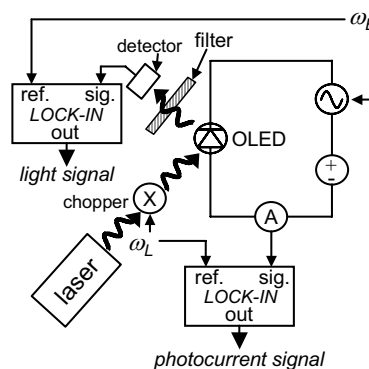


Figure 1 - The experimental setup of the spin statistics measurement. When the OLED is operated in forward bias, EL is collected by the detector. Spin statistics are determined by comparing the EL to the PL efficiency as determined by photoexciting the OLED under reverse bias. The photocurrent is detected synchronously with the optical chopping frequency, and the PL is locked to the modulation frequency of the reverse bias voltage. This scheme rejects leakage current and optical pump fluctuation. From Ref. [1].

combining to form both singlets and triplets in the ratio $\chi_s : (1-\chi_s)$. Only the singlets emit light. The ratio of the measured luminescence to the driving current gives the electroluminescent (EL) efficiency. Then, the OLED is operated in reverse bias while exposed to an optical pump, which generates only singlet excitons. The reverse bias electric field breaks some singlet excitons into electrons and holes, producing photocurrent and reducing the photoluminescence (PL) by an amount ΔPL . The ratio of ΔPL to the photocurrent then gives the PL efficiency. The singlet ratio χ_s is then simply the ratio of EL to PL efficiency.

This measurement technique has the advantage that it is a *relative* measurement: because the singlet ratio is derived from a ratio of efficiencies, not every photon must be captured, as in many other measurements. In addition, the shape of the ΔPL versus photocurrent characteristic reveals possible degradation of the luminescent material. A degraded material may otherwise yield artificially high singlet ratios.

Applying this technique to the archetypal small molecular weight luminescent material tris(8-hydroxyquinoline) aluminum (Alq_3) yielded a singlet ratio of $(20 \pm 1)\%$, in agreement with previous studies.⁴ The archetypal luminescent polymer poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) yielded a singlet ratio of $(20 \pm 4)\%$, in disagreement with other studies which have found it to be well above 25%.

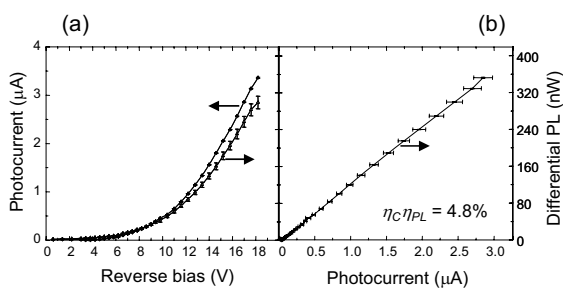


Figure 2 - (a) Synchronously-detected photocurrent and the corresponding decrease in PL for the polymer MEH-PPV as a function of reverse bias. (b) The relationship between the decrease in PL and photocurrent gives the synchronously-detected out-coupled PL efficiency. From Ref. [1].

More recent work, however, has raised questions concerning this MEH-PPV measurement. To control the location of exciton formation, MEH-PPV was employed as the hole transport layer (HTL) in a heterostructure. The electron transport layer (ETL) was the small molecular weight material bathocuproine (BCP). Since current in the device is limited by electron injection, holes pile up in MEH-PPV at its interface with BCP. Thus, excitons are formed from a precursor charge transfer (CT) state consisting of an electron in BCP and hole in MEH-PPV. Because the immediate precursor to the MEH-PPV exciton contains an electron on BCP, rather than MEH-PPV as in many all-polymer devices, the exciton formation process here is fundamentally different. In particular, spin mixing in the CT exciton precursor state will differ from spin mixing in an all MEH-PPV precursor state. We discuss the impact of CT state mixing further in section 2.3 below.

2.2. Magnetic Resonance and Spin-Dependent Exciton Formation

In ESR measurements, an organic semiconductor is cooled to low temperature and exposed to a continuous optical pump which generates singlet and triplet excitons. Some charges will also be formed by the dissociation of excitons. The charges may be solitary, or they may exist in closely spaced, oppositely charged pairs, so called polaron pairs, which are the precursors for excitons. A magnetic field is applied to split degenerate energy levels of the spin one triplet excitons and spin $1/2$ charges, and a microwave field tuned to this energy splitting causes an equalization of populations. It is experimentally observed that placing an organic semiconductor under resonance conditions increases its PL. The physical model for this behavior has a direct bearing on the question of the singlet ratio: one such model, based on spin dependent exciton formation, predicts high singlet ratios in polymers.²

We propose instead that the resonant phenomenon results from reduced quenching under resonance. It is well known that triplets and charges (more

precisely defined as polarons in these materials) can ‘quench’ singlets, preventing them from emitting light, and the populations of these

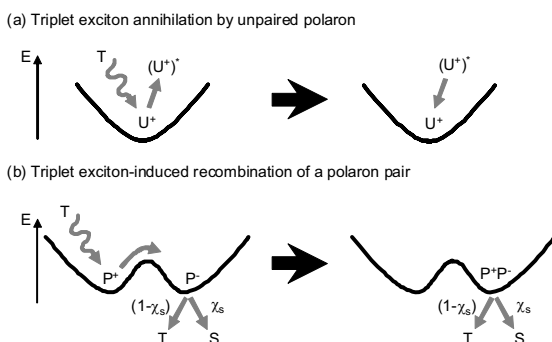


Figure 3 - Models for collision between a triplet exciton and (a) unpaired and (b) paired polarons at low temperature. In (a), a TE is annihilated by a solitary polaron. The polaron is excited by the collision but relaxes before it encounters an oppositely charged polaron, and is therefore unaffected by TE-polaron collisions or magnetic resonance. In (b), a pair of oppositely charged polarons is trapped in nearby energy wells. After collision with a triplet exciton, the triplet exciton is annihilated, and one of the polarons is excited, increasing its probability of crossing the energy barrier separating it from its oppositely charged partner. From Ref. [5].

quenchers are indeed observed to decrease under resonance. We further propose that the reason for this decrease is an enhanced rate of spin-dependent triplet-polaron collisions. In such a collision, shown schematically in Fig. 3, a triplet collides with a trapped polaron and is quenched. The excited polaron is then more likely to recombine with an oppositely charged polaron. This collision is allowed only 1/3 of the time out of resonance, but is effectively always allowed in resonance.

To test the triplet-polaron-mediated quenching theory, we have conducted a magnetic resonance experiment in which the optical pump was modulated at a rate too high for triplets or polarons to respond, but low enough for singlets to respond.⁵ The PL was then detected at the optical modulation frequency, and was found to be large and independent of modulation frequency. This data proves that magnetic resonance is a quenching phenomenon and is consistent with the triplet-polaron picture.

2.3 Models of Exciton Formation

To determine the significance of the ESR results we need a model of exciton formation. A general model is shown in Fig. 5. It considers electron

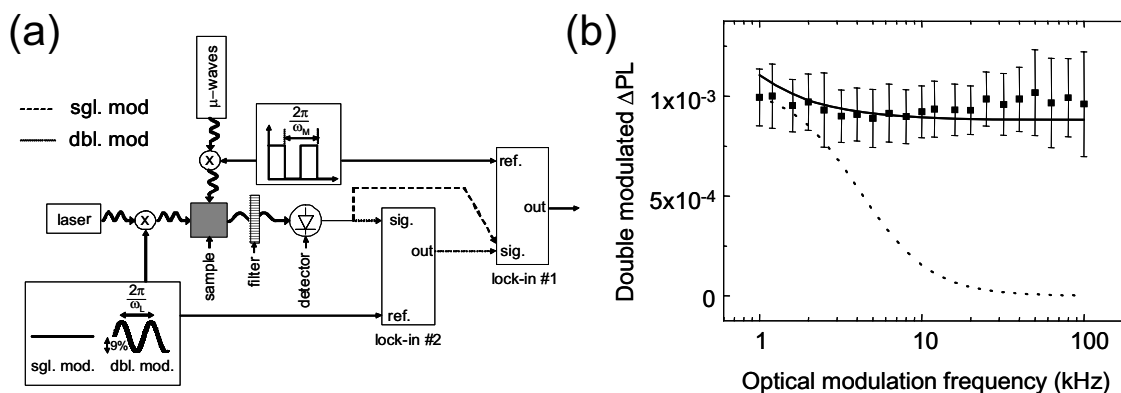


Figure 4 – (a) The experimental setup for measuring the frequency response of the photoluminescence-detected magnetic resonance. The single-modulation result is measured with a single lock-in amplifier and microwave power modulation only, using the dashed signal path. The double-modulation result is measured with two lock-in amplifiers and both laser power and microwave power modulation, using the dotted signal path. (b) Double modulation data for the polymer MEH-PPV as a function of laser modulation frequency with the microwave modulation frequency held constant at 200 Hz. The solid and dotted lines are the predictions of the triplet-polaron quenching and spin dependent recombination models respectively. From Ref. [5].

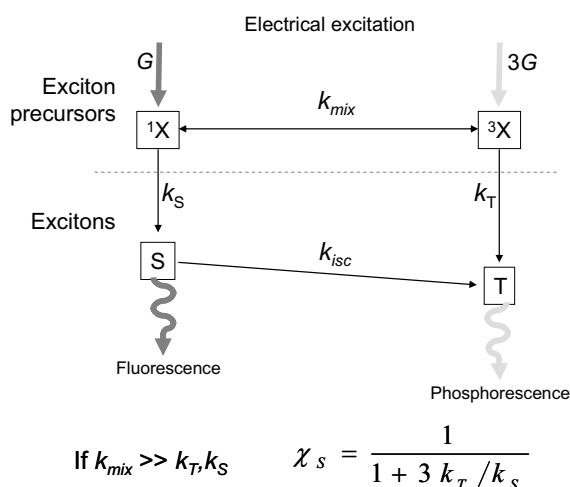


Figure 5 - Injected electrons and holes in organic semiconductors may form either singlet or triplet excitons. At large charge separations, singlet and triplet pair states are degenerate, and it is assumed that there is one singlet pair for every three triplet pairs. Once bound by Coulombic interactions, the formation of excitons is mediated by charge transfer states. If the mixing rate, $k_{mix} = 0$, then the singlet fraction is 25% or less.

hole pairs as a function of spin and separation. All electron hole pairs are in either the singlet or triplet spin configuration. Since charges injected into an OLED are uncorrelated, it is assumed that there is one singlet pair injected for every three triplet pairs. Thus, in the absence of mixing between the singlet and triplet channels, the singlet fraction will always be 25%.

Next we consider mixing processes. Charge pairs are subject to both Coulombic interactions, which are independent of spin, and shorter range exchange interactions, which are spin dependent. For large charge separations, exchange interactions are negligible, and singlet and triplet pair states are degenerate. Spin-orbit, spin-lattice and spin-spin interactions can mix separated charge pairs. However, with no preference for either spin, mixed separated states are expected to maintain 25% singlets.

In an exciton, the electron-hole separation approaches zero and exchange interactions become strong, typically stabilizing the triplet exciton by approximately 0.7 eV. Thus, mixing predominately encourages intersystem crossing from the singlet to the lower energy triplet exciton. Mixing may be employed to increase the singlet character of the triplet state, and so enhance phosphorescence. But exciton mixing cannot increase the singlet fraction or fluorescence.

Thus, mixing excitons or widely separated charge pairs cannot enhance the singlet fraction. Rather we must focus on the immediate precursors to excitons. The exact identity of these precursors is unclear, but in small-molecular weight devices, they likely take the form of a charge transfer state with the electron and the hole localized on neighboring molecules. Mixing the precursor states is the aim of the ESR experiments. Thus,

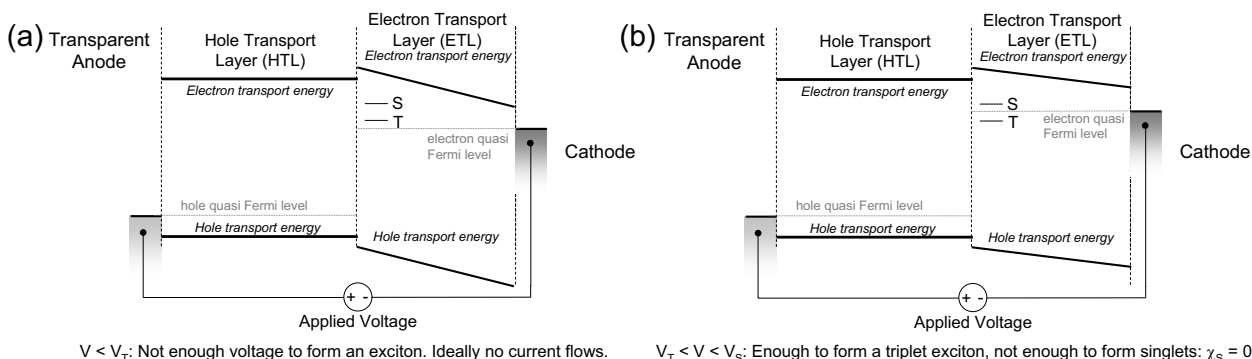


Figure 6 - Ideally, the limiting step for current flow in a heterostructure is electron-hole recombination. In (a) there is insufficient voltage to form excitons. In (b) there is sufficient voltage to form triplet excitons but not singlet excitons. Note that the electron quasi Fermi level is significantly below the LUMO. Current flow at such low biases requires transport through deep states within the organic semiconductor.

the absence of significant spin-dependent polaron-polaron interactions in PLDMR and ELDMR has important ramifications for the singlet fraction. Either the precursor states are already maximally mixed (hence resonance causes no change), or the precursor states are not degenerate and cannot be mixed. The recent report by Lupton, *et al.*⁶ which analyzed the interchange between singlet and triplet polaron pairs in polymers, suggests the latter.

The model of Fig. 5 suggests that ‘extrafluorescent’ OLEDs with $\chi_S > 25\%$ are possible if exciton precursors can be mixed independently of excitons. In Fig. 6 we show that this is possible in a heterostructure because electrons and holes can be confined on opposite sides on the heterostructure. *Ideally, the limiting step in current flow in a heterostructure OLED is electron-hole recombination.* If the OLED is indeed recombination-limited, the voltage applied to the OLED determines the difference between the quasi Fermi level for electrons in the ETL and the quasi Fermi level for holes in the HTL. Thus, the applied bias forms charge separated states at the interface with energy, $E < qV$.

As the applied voltage increases, the interfacial charge separated states recombine into different final states:

Non-radiative recombination: $0 < V < V_T$:

The voltage is insufficient to form any excitons. Charge separated states recombine directly to the ground state. Direct recombination current is typically very small and is often masked by leakage current due to imperfections in the heterostructure.

Triplet excitons: $V_T < V < V_S$:

In this region, there is sufficient voltage to form triplet excitons ($V=V_T$), but insufficient voltage to form singlet excitons ($V=V_S$). Electrical excitation in this bias range should generate 100% triplet excitons.

Enhanced singlet formation: $V_S < V$:

In this region, there is just enough voltage to form the singlet exciton, and Marcus inversion should inhibit the formation of triplets. Thus, this bias should enhance the formation of singlet excitons.

To achieve enhanced singlet fractions, it is necessary, however, to mix the CT state at the heterostructure. At sufficiently large biases exciton formation rates increase and charge transport becomes limited by injection or bulk mobilities rather than exciton formation. This transition is observed in Fig. 7.

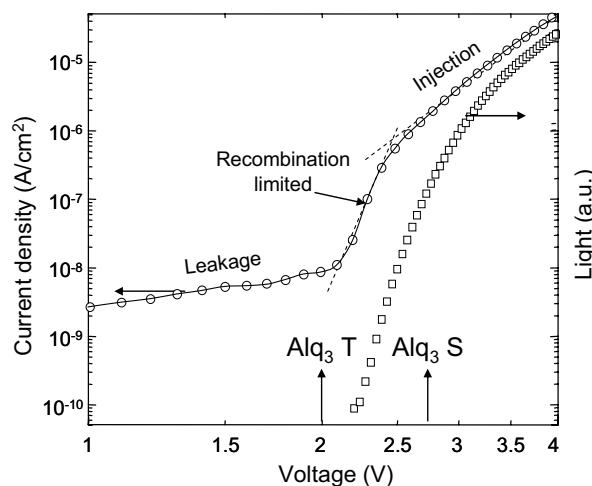


Figure 7 - A comparison of the current-voltage characteristics of an Alq₃-based OLED and its fluorescence, with the Alq₃ singlet and triplet exciton energies.

3. Conclusion

High efficiency OLEDs should harvest all excitons for luminescence regardless of spin. Our conclusion is that mixing is essential. Phosphorescence results from excitonic mixing, and potentially ‘extrafluorescence’ from mixing of precursor states. The realization of successful extrafluorescence promises to enhance the efficiency of materials currently used in fluorescent OLEDs - potentially by as much as a factor of four.

4. Acknowledgements

This work was supported by 3M and the National Science Foundation.

5. References

- [1] M. Segal, M.A. Baldo, R.J. Holmes, S.R. Forrest, and Z.G. Soos, *Physical Review B* **68** (7), 075211 (2003).

- [2] M. Wohlgenannt, K. Tandon, S. Mazumdar, S. Ramasesha, and Z.V. Vardeny, *Nature* **409**, 494 (2001).
- [3] Y. Cao, I. Parker, G. Yu, C. Zhang, and A. Heeger, *Nature* **397**, 414 (1999); J.S. Wilson, A.S. Dhoot, A.J.A.B. Seeley, M.S. Khan, A. Köhler, and R.H. Friend, *Nature* **413**, 828 (2001).
- [4] M.A. Baldo, D.F. O'Brien, M.E. Thompson, and S.R. Forrest, *Physical Review B* **60**, 14422 (1999).
- [5] M.K. Lee, M. Segal, Z.G. Soos, J. Shinar, and M.A. Baldo, *Physical Review Letters* **94**, 137403 (2005); M. Segal, M.A. Baldo, M.K. Lee, J. Shinar, and Z.G. Soos, *Physical Review B* **71**, 245201 (2005).
- [6] M. Reufer, M.J. Walter, P.G. Lagoudakis, A.B. Hummel, J.S. Kolb, H.G. Roskos, U. Scherf, and J.M. Lupton, *Nature Materials* **4** (4), 340 (2005).