The effect of fringe fields from patterned magnetic domains on the electroluminescence of organic light-emitting diodes

Nicholas J. Harmon, Markus Wohlgenannt, and Michael E. Flatté

Department of Physics and Astronomy and Optical Science and Technology Center, University of Iowa, Iowa City, Iowa 52242, USA

ABSTRACT

Large magnetic field effects, either in conduction or luminescence, have been observed in organic light-emitting diodes (OLEDs) for over a decade now. The physical processes are largely understood when exciton formation and recombination lead to the magnetic field effects. Recently, magnetic field effects in some co-evaporated blends have shown that exciplexes deliver even larger responses. In either case, the magnetic field effects arise from some spin-mixing mechanism and spin-selective processes in either the exciton formation or the exciplex recombination. Precise control of light output is not possible when the spin mixing is either due to hyperfine fields or differences in the Lande g-factor. We theoretically examine the optical output when a patterned magnetic film is deposited near the OLED. The fringe fields from the magnetic layers supply an additionally source of spin mixing that can be easily controlled. In the absence of other spin mixing mechanisms, the luminescence from exciplexes can be modified by 300%. When other spin-mixing mechanisms are present, fringe fields from remanent magnetic states act as a means to either boost or reduce light emission from those mechanisms. Lastly, we examine the influence of spin decoherence on the optical output.

Keywords: magnetic field effects, organic semiconductors, organic light emitting diodes, magnetic patterning, thermally assisted delayed fluorescence, organic magnetoresistance

1. INTRODUCTION

Understanding large magnetic field effects (MFEs) in organic semiconductors, such as those comprising organic light emitting diodes (OLEDs),\(^1\) has progressed steadily over the last several years. In typical OLEDs, electron and hole polarons encounter one another in the bulk and temporarily form loosely bound states, known as polaron pairs, with a statistical ratio of 3:1 between triplet to singlets. These pairs may recombine into excitons [Figure 1(a)]; whether the loosely bound pairs are singlet or triplet may affect the rate of the exciton formation. Only singlet excitons lead to appreciable luminescence which makes most organic semiconductors fluorescent with internal electroluminescence quantum efficiency \(\leq 25\%\).\(^2\) The polaron pair stage is where MFEs play their role (since the exchange splitting is small) and interactions that cause singlet-triplet intersystem crossing, or spin mixing, lead to changes in exciton singlet/triplet formation ratios. Just in the last few years, MFEs in co-evaporated donor/acceptor organic blends have garnered enthusiasm. These systems work differently in that emission occurs via an exciplex (or intermolecular) route and not through an exciton (or intramolecular) pathway. Such blends are interesting for OLEDs since they allow a means to convert optically intet triplets to optically emissive singlets by means of the smaller singlet-triplet exchange splitting (< 100 meV) when compared to excitons. Triplet-to-singlet up-conversion and its concomitant output is known as thermally assisted delayed fluorescence (TADF) since the emission increases with temperature.\(^3,4\) The origin of magneto-electroluminescence (MEL) is commonly the hyperfine interaction (HF) between polaron carrier spins and hydrogen nuclear spins which are plentiful in most organic systems.\(^5,6\) Slight environmental discrepancies can also lead to differences in Lande g-factors (\(\delta g\)) between the positive and negative polarons which is another author of spin mixing.\(^7,9\) If manipulation of spin mixing and light emission is desired in either exciton or exciplex systems, neither the HF or \(\delta g\) mechanisms offer any feasible solution since these parameters are inherent for a given combination of materials.

Further author information: (Send correspondence to N. J. H.)
N. J. H.: E-mail: nicholas-harmon@uiowa.edu
In this Proceeding we make use of recent findings\textsuperscript{11–13} where spin mixing is controlled by a mechanism extrinsic to the organic semiconductor. By depositing electrically isolated thin magnetic films under the OLED, charge transport and light emission are dramatically altered when magnetic fringe fields permeate the OLED. We examine the case of patterned domain stripes which are amenable for theoretical study compared to the random domains.\textsuperscript{13, 14} By orienting the domains in a specified manner, spin mixing induced by fringe fields can be switched on and off which was not an option with either the HF or $\delta g$ mechanisms. Additionally, the form of the fringe field interaction grants unprecedented large values of a figure of merit $\Delta EL/EL = (EL(ON) - EL(OFF))/EL(OFF) = 300\%$. By adjusting the spacer width that separates the magnet from the organic layer, we suggest measurements that can distinguish the microscopic origins of exciplex spin dynamics.

![Energy in exciton picture](a) and Energy in exciplex picture](b) depict, respectively, the ON and OFF domain configurations. (e) In-plane magnetic configuration (c) with fringe fields directions (arrows only depict directions and not magnitudes) in the $x - z$ plane. Parameters used: $t = 20$ nm, $M_s = 8 \times 10^5$ A/m, and $a = 160$ nm. The calculation assumes $i_{\text{max}} \gg 1$.

### 2. EXCITONS AND EXCIPLEXES

We commence by comparing the charge/spin dynamics of exciton and exciplex recombination shown in Figure 1(a,b). The exciton picture has been well studied and is well known: polarons form singlet and triplet polaron pairs at rates $G_S$ and $G_T$; spin mixing occurs between the polaron pair states; meanwhile polaron pairs recombine into excitons at rates $k_S$ and $k_T$, respectively; spin evolution of excitons halts due to large exchange; singlet excitons luminesce. There is also a possibility for polaron pairs to dissociate at rate $k_D$.\textsuperscript{13,15} Early studies of exciplexes have assumed a very similar picture to the of excitons where exciplexes play the role of exciton.\textsuperscript{16–19} Spin may not evolve in the exciplex state since the exchange splitting, though smaller than in excitons, is still
comparable to room temperature. The MEL values achieved ∼10% are consistent with HF spin mixing and $k_S \ll k_T$. Contrarily, other workers modeled the situation as in Figure 1d where polaron pair formation is less important and spin mixing occurs primarily within exciplexes. Near room temperature an activated behavior is observed in the MEL which suggests that spin mixing occurs between singlets and some excited triplet states ($T^*$) that are near in energy to the singlets. The MEL measurements of Ref., placed among the highest recorded (>60 %), also rule out HF in favor of $\delta g$ spin mixing. The successes of the two models of exciplex MEL lead us to believe that different coevaporated blends may exhibit different roads to light emission. We contend that by incorporating a new type of spin mixing, coming from fringe fields, light can be shed on the microscopic processes that lead to radiative recombination for exciplexes.

3. CALCULATION OF MAGNETIC FRINGE FIELDS

Now we introduce a thin magnetic film with striped domains that emanate stray fields in the organic layer. Two options for striped patterns are shown in Figure 1(c,d); the repeats occur every $a$ along the $x$-axis while the film extends far out in the $y$-direction to $\pm \alpha$. The magnetic films have a thickness, $t$. Domains magnetized perpendicular to the plane are expected to be hardest to manufacture due to the magnetic anisotropy. Figure 1(c) is possible with sufficiently large $a$ and applied field to set the domains perpendicular to the striping pattern. As shown below, fringe fields appear in this orientation so this configuration (ON). Figure 1(d) is the most energetically favorable configuration but no fringe fields are produced if edge effects are negligible (OFF). We define a figure of merit to be $\Delta EL/EL$. Applied fields are not necessary when determining $\Delta EL/EL$ since the domains can be oriented with a ‘set’ applied field and remain in that state after the field is switched off. The external field is only needed to switch the domains between ON and OFF.

The magnetic scalar potential from a ferromagnet with magnetization, $M$, volume, $V$, and surface, $S$, is

$$\phi(R) = \frac{1}{4\pi} \left( -\int_V \nabla \cdot \frac{M(r)}{|R-r|} \, dr + \int_S \frac{n \cdot M(r)}{|R-r|} \, dA \right)$$

(1)

The magnetization is uniform within a specified domain so the first term vanishes, leaving

$$\phi(R) = \frac{1}{4\pi} M_s \int_S \frac{n \cdot M(r)}{|R-r|} \, dA.$$  

(2)

Using the principle of superposition, we treat an array of domains each denoted by an index $i$:

$$\Phi(R) = \sum_i \frac{1}{4\pi} M_{s,i} \int_{S_i} \frac{n_i \cdot M_i(r_i)}{|R-r_i|} \, dA_i.$$  

(3)

where each domain is uniformly magnetized and denoted by an index $i$. $R = (X,Y,Z)$ is the position outside the magnet, the indexed $r = (x,y,z)$ denote position within the magnet, and $A_i$ are area elements of the magnet’s surface. Since $H = B/\mu_0$ outside a magnetized volume, $B = -\mu_0 \nabla \Phi(R)$ where $\mu_0 = 4\pi \times 10^{-7}$ N/A$^2$. The fringe field then, evaluated at any point in $R$-space is

$$B_{FF}(R) = -\frac{\mu_0}{4\pi} \sum_i M_{s,i} \int_{S_i} \frac{n_i \cdot M_i(r_i)(r_i - R)}{|R-r_i|^3} \, dA_i.$$  

(4)

We make the following assumptions: $M_{s,i}$ and the length and width of $S_i$ are all constant for all $i$ in a given configuration of the magnet. Simple modifications to these assumptions such as alternating saturated magnetization, $M_s$, can be handled if needed.

Fig. 1(e) shows the magnetized domains separated spatially by non-magnetic stripes. Magnetic surface charge densities form on each domain wall and alternate between + and -. These surfaces are located at each $x_i$ and have an area $2c(z_i - z_b) = 2ct$ where $z_i$ and $z_b$ are the top and bottom positions of the magnet. We define $x = 0$ to be halfway in between two such oppositely ‘charged’ plates (negative/positive plate lies at $x = \pm a/2$).
Each plate (or actually domain wall) is then indexed by $x_i = (i + \frac{1}{2})a$ with $-i_{\text{max}} < i < i_{\text{max}} - 1$. The $x$-edge length is $L_x = (2i_{\text{max}} - 1)a$. These adjustments can be implemented in Eq. (4) to ascertain

$$B_{\text{FF}}(R) = -\frac{\mu_0}{4\pi} M_s \sum_{i=-i_{\text{max}}}^{i_{\text{max}}-1} \int_c^{-c} \int_{-t}^{0} (-1)^i \frac{r_i - R}{|R - r_i|^3} \, dz \, dy.$$  

The integrations can be found in closed form solution though they are prohibitively expansive. After taking the limit $c \to \infty$, we obtain the vector

$$B_{\text{FF}}(R) = -\frac{2\mu_0}{4\pi} M_s \times \sum_{i=-i_{\text{max}}}^{i_{\text{max}}-1} (-1)^i \{ \arctan \left[ \frac{t + Z}{(i + \frac{1}{2})a - X} \right] - \arctan \left[ \frac{Z}{(i + \frac{1}{2})a - X} \right], 0, \frac{1}{2} \ln \left[ \frac{|(i + \frac{1}{2})a - X|^2 + Z^2}{|(i + \frac{1}{2})a - X|^2 + (t + Z)^2} \right] \}. $$

We are not aware whether this analytic solution to the magnetostatics problem has been determined previously. Our present description of $B_{\text{FF}}(R)$, though analytic, is unwieldy. This motivates us to find the simpler limiting functional form of our derived $B_{\text{FF}}(R)$ as a function of $Z$. An approximation for infinite stripes is that $t \ll a, Z$ which allows us to write reduced expressions for the fringe fields after expanding each term in small $t$:

$$B_{\text{FF}}(R) = -\frac{\mu_0}{4\pi} M_s a \times \frac{4\pi t}{a} \{ -\cos \left( \frac{\pi X}{a} \right) \cosh \left( \frac{\pi Z}{a} \right), 0, \sin \left( \frac{\pi X}{a} \right) \sinh \left( \frac{\pi Z}{a} \right) \}. $$

Figure 2 plots the ON fringe field magnitude (a) and gradient (b) as a function of height above magnetic layer. For finite sized magnets, one must be mindful of edge effects which cut-off the exponential fall-off predicted by Eq. (6). For distances much larger than the lateral dimensions of the magnetic film, the magnetic film appears as a magnetic dipole so the fall-off turns to a power law.

## 4. Calculation of Magnetic Field Effects

The Hamiltonian of the polaron pair or exciplex is $\mathcal{H} = \mathcal{H}_{\text{HF}} + \mathcal{H}_{\text{FF}} + \mathcal{H}_{\text{HF},\delta g} + \mathcal{H}_{\text{FF},\delta g}$ where

$$\mathcal{H}_{\text{FF}} = \frac{g_1 + g_2}{2} \mu_B \left( B_{\text{FF}}(r_1) \cdot S_1 + B_{\text{FF}}(r_2) \cdot S_2 \right),$$

$$\mathcal{H}_{\text{HF}} = \frac{g_1 + g_2}{2} \mu_B \left( B_{\text{HF}}(r_1) \cdot S_1 + B_{\text{HF}}(r_2) \cdot S_2 \right),$$

$$\mathcal{H}_{\text{HF},\delta g} = \frac{\delta g}{2} \mu_B \left( B_{\text{FF}}(r_1) \cdot S_1 - B_{\text{HF}}(r_2) \cdot S_2 \right),$$

$$\mathcal{H}_{\text{FF},\delta g} = \frac{\delta g}{2} \mu_B \left( B_{\text{FF}}(r_1) + B_{\text{FF}}(r_2) \right) \cdot (S_1 - S_2) + \frac{\delta g}{2} \mu_B \left( B_{\text{FF}}(r_1) - B_{\text{FF}}(r_2) \right) \cdot (S_1 + S_2);$$

where $B_{\text{HF}}$ is the hyperfine field, $r_{1,2}$ ($S_{1,2}$ ) are the positions (spins) of the two constituents, and $\delta g = g_1 - g_2$. The following calculations have been also conducted with typical values of $\delta g$ ($< 10^{-3}$) present but the fringe field mechanism swamps the $\delta g$ mechanism so we lose nothing by setting $\delta g = 0$.

The spin dynamics of either the polaron pair or exciplex are described by a two-spin density matrix $\rho$ which evolves according to the stochastic Liouville equation:

$$\frac{\partial \rho}{\partial t} = -i \hbar [\mathcal{H}, \rho] - \frac{1}{2} \{ k_S P_S + k_T P_T, \rho \} - k_D \rho + \frac{1}{4} \hat{G},$$

where $P_S$ and $P_T$ are the singlet and triplet projection operators, $\text{Tr} \rho \ll 1$, and $\hat{G}$ is the exciplex generation matrix:

$$\hat{G} = \begin{pmatrix} G_S & 0 & 0 & 0 \\ 0 & G_T & 0 & 0 \\ 0 & 0 & G_T & 0 \\ 0 & 0 & 0 & G_T \end{pmatrix}.$$
If the assumption $Tr \rho \ll 1$ is violated, interesting phenomena like sign changes and a doubling of the MEL amplitude are expected for the hyperfine and $\Delta g$ interactions (and has not been studied at all for fringe field interactions) with $G_S \neq G_T$. Study of this regime is an interesting route for further research. For the exciton model, it is assumed that $G_S = G_T$ while $G_T$ in the exciplex model considers only those exciplexes that are activated near the singlet level so $G_T \leq G_S$. The exciplex effects are maximal for $G_T = G_S$ ($k_B T \gg \Delta ST$) which for simplicity we assume throughout our calculations here.

To calculate the figure of merit, Eq. (11) is solved with steady state conditions where $B_{FF}(r_1)$ is calculated in the organic layer from the approximative Eq. (6) where $r_1$ is determined randomly within a box of height 30 nm (unless otherwise states), positioned at $Z = Z_{min}$ above the magnet, and lateral size of the box is equal to the magnetic film's lateral size. Since the current path is in $\hat{z}$, the average carrier hop occurs in the $z$-direction so $B_{FF}(r_2) = B_{FF}([x_1,y_1,z_1 + d])$ where $d = 1$ nm is the hopping length. If transport occurred laterally (in $x - y$ plane), the fringe field influence would be smaller since fringe fields do not change exponentially in $X$ but sinusoidally as Eq. (6) demonstrates. The EL is finally determined from $EL \propto k_S Tr P_{S\rho}$.

5. DISCUSSION

Figure 3 shows $\Delta EL/EL$ under the operation of only the fringe field ($\mathcal{H}_{HF} = 0$) for both the exciton and exciplex pictures. Starting on the right side of the graph, if there is no fringe field gradient there is no spin mixing or change in EL. As the height above the magnets, $Z_{min}$, is reduced (and gradient increased), the figure of merit plateaus at 100%. The reason for this plateau is similar to that of the $\delta g$ mechanism for which all $T_0$ states may upconvert to $S$ states, doubling the EL.$^{10}$ It indicates that spin mixing between $T_{\pm}$ and $S$ states are
Figure 3. Change in EL versus average fringe field gradient for exciplexes: $k_D = 10^{-12}$ ns$^{-1}$ (black), $k_D = 10^{-9}$ ns$^{-1}$ (red), $k_D = 10^{-6}$ ns$^{-1}$ (blue), and $k_S = 3 \times 10^{-10}$ ns$^{-1}$, $k_T = 0$ for all and excitons: black: $k_S = 3 \times 10^{-2}$ ns$^{-1}$, $k_T = 6 \times 10^{-2}$ ns$^{-1}$; red: $k_S = 3 \times 10^{-1}$ ns$^{-1}$, $k_T = 6 \times 10^{-1}$ ns$^{-1}$, and $k_D = 0$ for both. The patterned FM is permalloy with $M_s = 8 \times 10^5$ A/m, $t = 20$ nm, and $a = 160$ nm. The hyperfine field is zero.

slower compared to $T_0$ and $S$ states. $k_D$ is large enough to inhibit further mixing which explains why the curves shift left as $k_D$ increases. As the gradient increases further and dissociation is sufficiently small, the figure of merit rises to 300% which is indicative of all triplet exciplexes upconverting and recombining as singlets. Since the spin-selective rates for excitons are similar to one another, contrary to that of exciplexes, the figure of merit for the exciton parameters takes on less extreme values. We assume $k_S \lesssim k_T$.

Alternatively, if $k_S \gtrsim k_T$ (not shown), the excitonic $\Delta EL/EL$ changes sign but still does not reach the magnitude seen for exciplexes.

Figure 4. Exciplexes (red): $k_S = 3 \times 10^{-3}$ ns$^{-1}$, $k_T = 0$, $k_D = 10^{-6}$ ns$^{-1}$. Excitons (blue): $k_S = 6 \times 10^{-1}$ ns$^{-1}$, $k_T = 12 \times 10^{-1}$ ns$^{-1}$, $k_D = 0$. The thickness of the organic layer is taken to be 10 nm. Shorter heights are less valid since the condition $t < < Z_{min}$ is not met for Eq. 6.

Figure 4 displays the figure of merit when HF is included too. Given our definition of the figure of merit, at
small fringe field (high above the magnets), it is zero because the ON and OFF do not differ in any significant
way. The fringe field acts much like an external field for the usual (HF-based) MEL for spin pairs which is
indicated by the sign of the figure of merits which is opposite those in Fig. 3.10,15 Even though HF mixing is
dominating the response (< 100% or 300%), we find that the fringe fields still act as an ON/OFF switch to the
optical output intensity.

6. THE ROLE OF SPIN DECOHERENCE

Thus far we have not taken into account any spin relaxation or decoherence for the two pertinent spins. Spin
relaxation (with rate 1/T1) is typically very weak in organic semiconductors which warrants neglect. Spin
decoherence times (T2) are on the order of microseconds which is much slower than the operative rates in the
excitonic model but comparable to kS in the exciplex model. Therefore the theory thus set forth should be
adjusted to account for T2 of the two spins.

Spin decoherence enters into our calculation by defining decoherence Lindblad operators for each of the two
spins, L3(1) and L3(2):

\[ L_3(1) = 1 \otimes L_3, \quad L_3(2) = L_3 \otimes 1 \]  

(12)

where

\[ \hat{L}_3 = \sqrt{\frac{1}{2T_2}} \sigma_z, \]

are written in the Zeeman basis. If T1 was important additional operators L1 and L2 would be included. To
express in the S – T basis (which is what we have done throughout this Proceeding), the following transformation
matrix must be applied:

\[ \hat{T} = \begin{pmatrix}
0 & 0 & 1 & 0 \\
-\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 & 0 \\
\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 & 0 \\
0 & 0 & 0 & 1
\end{pmatrix} \]  

(13)

and the new operators in the preferred basis are \( \hat{T}^T L_i(j) \hat{T} \). The Lindblad operators then add to the stochastic
Liouville equation in the following way:

\[ \frac{\partial \rho}{\partial t} = -\frac{i}{\hbar} [\hat{\mathcal{H}}, \rho] - \frac{1}{2} \{ k_S P_S + k_T P_T, \rho \} - k_D \rho + \frac{1}{4} \hat{G} + L_3(1) \rho L_3(1)^T + L_3(2) \rho L_3(2)^T - \frac{1}{2} \{ L_3(1)^T L_3(1) + L_3(2)^T L_3(2), \rho \}. \]  

(14)

A full account of spin decoherence’s role in modifying the figure or merit or MEL for the different spin mixing
mechanisms will be examined in a future publication.

7. CONCLUSIONS

In these Proceedings we determine the influence of patterned magnetic fringe fields on light emission in two
types of OLEDs. The disparate responses between excitons and exciplexes give a means of deciding between
two exciplex models that have been promulgated. The form of the fringe field is similar to that of the so-
called isotropic \( g \) mechanism but since the fringe field gradient is not constrained to be aligned with the fringe
field, this mechanism is more efficient in converting triplet to singlets thereby dramatically increasing radiative
recombination (to 300% instead of 100%). Another mechanism that we expect to yield MFEs up to 300 % is
anisotropic \( g \)-factor spin mixing. Up to this point, the \( g \) tensor has been assumed to be isotropic which leads
to only \( S \leftrightarrow T_0 \) spin mixing. If the two sites involved in recombination are not aligned and their \( g \) tensors are
anisotropic, then mixing of all four states may occur when a field is applied.

We have shown that fringe fields offer a way to control magnetic field effects which was not possible with
other mechanisms. In our theory we have assumed that the organic layer is of the same lateral dimensions
as the magnetic film and only examined the average responses. A future route for this research is to consider
laterally small organic layers with the aim to optically detect individual domain orientations which would yield
a conversion of magnetic bit information to an optical output.
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