Optically detected magnetic resonance (ODMR) measurements on conjugated polymers and studies of poly-(n-Vinyl Carbazole) (PVK) based LEDs

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Optically Detected Magnetic Resonance (ODMR) measurements on conjugated polymers and studies of poly-(n-Vinyl Carbazole) (PVK) based LEDs

by

Moon-Ky Lee

A dissertation submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Major: Condensed Matter Physics

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For the Major Program
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1. GENERAL INTRODUCTION

Introduction to $\pi$-conjugated system

In 1977, the newly discovered electrically conducting organic polymers ushered in a new class of materials [1]. These new polymers are actually semiconductors, and possess several advantages over inorganic semiconductors such as improved electroluminescence (EL) properties, flexibility, solubility, and lower manufacturing cost. In the past 15 years these polymers and small molecules have been studied extensively and used to develop organic light emitting devices (OLEDs), thin panel displays, flexible displays, photovoltaic devices, and organic thin-film transistors.

The distinct feature of a $\pi$-conjugated polymer is its continuous delocalized $\pi$ orbitals along the chain. The defects in the structure, such as impurity atoms and twists, break these $\pi$ orbitals and shorten the conjugation length, which is the length of the uninterrupted $\pi$ orbitals. The energy gap between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) decreases with increasing conjugation length.

The $\pi$ orbitals result from hybridization of $s$ and $p$ carbon orbitals. For example, benzene (phenylene) consists of six carbon atoms and each has four $n = 2$ orbitals and three of them form planar $\sigma$ bonds with the neighboring two carbon atoms and a hydrogen atom; the remaining orbital forms a $\pi$ bond which is perpendicular to the $\sigma$ bond. The six electrons occupying the $\pi$ orbitals have two possible configurations with equal probability (see Fig. 1) and these orbitals form a "$\pi$ cloud" above and below the plane defined by the $\sigma$ orbitals.
Fig. 1. Benzene with two possible bonding configurations

When a ground state $\pi$ electron is photoexcited, it forms a thermalized electron ($e^-$)-hole ($h^+$) pair, which relax to a negative-positive polaron ($p^-p^+$) pair [2,3]. The singlet exciton (SE), which is generally responsible for the photoluminescence (PL), is formed either by photoexcitation from the ground state or by recombination of a ($p^-p^+$) pair: its radiative lifetime is $\sim1$ ns. The separated pair will become positive and negative free polarons and, in a polymer, move along the chain or hop to another chain, generally by a phonon-assisted process. These polarons will recombine to SEs or triplet excitons (TEs); like-charged polarons may relax to bound bipolaron ($bp^-\text{ or } bp^{++}$) states.

The polaron may be visualized as follows [3]: Each orbital can accommodate two electrons. In the $p^+$ state, the HOMO is half-filled and the LUMO is empty. In the $p^-$ state, the HOMO is filled and the LUMO is half-filled. In both cases, the HOMO and LUMO levels are pulled into the HOMO-LUMO gap by lattice relaxation (see Fig. 2).

In the $bp^-$ ($bp^{++}$) state, the HOMO and LUMO levels are both full (empty), and pulled more deeply into the gap by the stronger lattice relaxation (see Fig. 3). Equivalently, a bipolaron is formed by two equally charged polarons in the singlet spin configuration; the bipolaron state is more stable than the two-polaron state [4]. Bipolarons interact with other...
species like polarons and excitons and a \((bp^-, bp^{++})\) pair can decay non-radiatively by phonon emission or recombine into singlet exciton and decay radiatively.

\[ \begin{align*} 
&\text{positive polaron (p\textsuperscript{+})} \\
&\text{negative polaron (p\textsuperscript{-})} \\
&\text{positive bipolaron (bp\textsuperscript{++})} \\
&\text{negative bipolaron (bp\textsuperscript{-})} 
\end{align*} \]

\textbf{Fig. 2. Polaron levels in an organic semiconductor.}

\textbf{Fig. 3. Bipolaron levels in an organic semiconductor.}
Introduction to Photoluminescence Detected Magnetic Resonance (PLDMR)

PLDMR is an extension of electron-spin resonance (ESR) developed in the 60s [5]. It can detect very small microwave-induced changes in the PL induced by magnetic resonance conditions. These changes would clearly be due to spin dependent processes, so the technique can provide insight into optical process that are affected by spin-dependent processes.

Experimental setup

The PLDMR spectrometer used in this work consists of several parts, which are shown in Fig. 4. The sample is photoexcited by a laser, via mirrors, lenses, and filters. To improve the signal to noise ratio (S/N), the laser power is stabilized by a Cambridge Research LS100 laser stabilizer, which includes a Pockels cell-based optical negative-feedback circuit. The stabilizer reduces the fluctuations in the output power, whose spectrum is usually flat to ~300 kHz, from ~±0.5% to < ±0.03%. The PL is gathered through collecting lenses and detected by either a photomultiplier tube (PMT) or a silicon photodiode detector. The sample is vacuum sealed in a quartz tube to minimize degradation due to oxygen or water and placed in the quartz-finger dewar of the cryostat, which is inserted into the microwave resonance cavity. The microwave-induced change in the PL is monitored vs the DC magnetic field and detected by a lock-in amplifier that is referenced by the microwave chopping frequency. The relative change in the PL (ΔPL/PL) is typically 10⁻⁵ to 10⁻³.
The spins of the $e^-h^+$ pair that combine to form an exciton are “locked” to each other, to produce either a spin-0 singlet exciton (SE) or a spin-1 triplet exciton (TE). However, the spins of the $e^-h^+$ polaron pair interact with each other weakly, and their spin-spin coupling energy is usually negligible compared to the Zeeman splitting in the magnetic field $H_0$ applied for high-field magnetic resonance measurements. Because each $e^-h^+$, and polaron has spin 1/2 and aligns parallel or antiparallel to $H_0$, there are four possible energy levels:

$$E = (\pm g_e \pm g_h) \beta H_0/2$$  \hspace{1cm} (1)

where $g_e$ and $g_h$ are $e^-$ and $h^+$ g values, and $\beta$ is the Bohr magneton.

Fig. 4. *The experimental setup of PLDMR system*
Fig. 5 shows the energy levels of the different spin states of the polaron pairs vs $H_0$. The antisymmetric combination (i.e., the singlet configuration) of states $|2\rangle$ and $|3\rangle$ forms the excited state SEs ($S_1$) and can decay to the ground state ($S_0$) radiatively. States $|1\rangle$, $|4\rangle$, and the symmetric combination (i.e., the triplet configuration) of $|2\rangle$ and $|3\rangle$ form TEs; their radiative decay to the ground state is forbidden. Therefore, off-resonance the populations $n_2$ and $n_3$ will be lower than $n_1$ and $n_4$. In addition, we note that in any case, SEs may be quenched by polarons and TEs.

\[ S_1 + p^\pm \rightarrow S_0 + p^\pm^* \]  \hspace{1cm} (2)

or

\[ S_1 + p^\pm \rightarrow S_0 + p^+ + p^+ + p^- \]  \hspace{1cm} (3)

where $p^*$ is the excited state of a polaron, and where we can write similar equations for the quenching by TEs.

Under the magnetic resonance condition, the applied microwave field with photon energy $h\nu_{\mu\text{-wave}} = g_\mu\beta H_0$ will mix the states and equalize their populations so $n_1 = n_2 = n_3 = n_4$ [6]. Hence the signal-pair population will increase, and the overall population $\Sigma n_i$ will decrease. Consequently, the radiative decay rate (the PL) will increase, due both to the increased singlet pair population, and the decrease in the SE quenching rate. Since the PL will increase at the resonance field, a positive (PL-enhancing) spin $1/2$ resonance will be observed.
Fig. 7 shows a typical PL-enhancing spin 1/2 PLDMR. A negative (PL-quenching) resonance may also occur, e.g., when the overwhelmingly singlet configuration population of geminate polaron pairs is reduced due to spin mixing by the microwave field.

![Energy vs Magnetic Field Diagram](image)

**Fig. 5.** Energy of a polaron pair vs magnetic field, \( n_i \) is the population of the state \( |i\rangle \), \( R_s \) is the singlet radiative recombination rate, and \( R_t \) is slower nonradiative triplet recombination rate.

**Spin 1 resonance signal**

Spin 1 resonances are due to TEs, with typical lifetimes of ~10 \( \mu \)s up to many ms. These resonances can be observed at two different regions of \( H_0 \) (see Fig. 7). At field \( A \), the so
called "half-field spin 1 resonance" will occur, due to the forbidden transitions between the \( |+1> \) and the \( |-1> \) states. At field B and C, the "full-field resonance," the transitions between the \( |+1> \) and the \( |0> \) states and the \( |0> \) and the \( |-1> \) states will occur. Since the locations of A, B, and C depend on the orientation of \( H_0 \) relative to the principal axes of the TE state, an amorphous or powder sample will yield a half-field and full-field "powder pattern" such as those shown in Fig. 7 and 8. Fig. 6 is obtained by combining the Zeeman splitting and the spin-spin dipole interaction [7]. The hyperfine interaction between the electronic and nuclear dipole moments is neglected because of the amorphous structure of the sample and the rapid diffusion of the excitons which will simply result in line broadening due to this term [8].

![Energy vs magnetic field for spin-1 resonance](image)

**Fig. 6.** *Energy vs magnetic field for spin-1 resonance*
Fig. 7. Typical spin 1/2 (top) and full-field spin-1 powder pattern (bottom) PLDMRs.
Fig. 8. *Half-field spin 1 PLDMR.*
Origin of the positive (PL-enhancing) spin 1/2 resonance

As discussed above, the positive spin-1/2 resonance may be due, among other mechanisms, either to enhanced recombination of singlet pairs to SEs (at the expense of recombination of triplet pairs to TEs), or to reduced quenching of SEs by a lower polaron and TE population. This latter “reduced quenching mechanism” is supported by various results, including ODMR [9-12]. We now examine the decay pathways in greater detail.

In a π conjugated system, there are several decay pathways. The nonradiative channels include the following:

\[ p^+ + p^- \rightarrow T \]  \hspace{1cm} (4)

\[ p^+ + p^- \rightarrow S_0 + \text{phonons} \]  \hspace{1cm} (5)

\[ S_1 + p^\pm \rightarrow S_0 + p^{\star\pm} \]  \hspace{1cm} (6)

\[ S_1 + p^\pm \rightarrow S_0 + p^{\pm} + p^+ + p^- \]  \hspace{1cm} (7)

\[ p^+ + p^+ \rightarrow bp^{\pm\pm} \]  \hspace{1cm} (8)

\[ bp^{++} + p^- \rightarrow p^+ \]  \hspace{1cm} (9)

\[ bp^{++} + p^- \rightarrow p^- \]  \hspace{1cm} (10)
\[ T_1 + S_1 \rightarrow T_1 + S_0 + \text{phonons}. \] (11)

The radiative decay channel

\[ p^+ + p^- \rightarrow S_1 \rightarrow S_0 + h\nu + \text{phonons} \] (12)

\[ T_1 + T_1 \rightarrow S_1 \rightarrow S_0 + h\nu + \text{phonons}, \] (13)

where \( T_1 \) is a TE state.

Eqs. (6) and (7) are the quenching channels. However, Eq. (13) provides another luminescent channel and leads to another mechanism which might explain the positive 1/2 resonance, namely triplet–triplet annihilation [13, 14]. Indeed, Fig. 9, reported by Partee et al., shows the delayed fluorescence (DF) of a typical conjugated polymer as an evidence for triplet–triplet annihilation to SEs [14]. Yet the figure only provides the contribution of all bimolecular processes to the PL. Since nongeminate polaron recombination is also bimolecular, the DF may be due to that recombination rather than triplet-triplet annihilation.

Indeed, the reports by List et al. on methyl-bridged ladder-type poly(p-phenylene) (LPPP) show that the triplet-triplet annihilation model is inconsistent with the PLDMR [15]. Rather, they show that SE quenching by TEs (Eq. (11)) is the source of the half-field PLDMR and SE quenching by TEs and polarons is the source of the full-field PLDMR, as photoinduced absorption-detected magnetic resonance (PADMR), which is a variation of PLDMR, shows unambiguously that the polarons and TEs population decrease at resonance.
Fig. 9. The delayed fluorescence (DF) $R'_{PL}$ of 2,5-dibutoxy poly(p-phenylene ethylene) DBO-PPE powder (squares) and 0.025 mg/ml frozen DBO-PPE/toluene solution (circles) at 20 K vs the laser modulation frequency $v$. The lines are the least-squares Lorentzian fits with $\tau = 210$ $\mu$s for the powder and $\tau = 520$ $\mu$s for the frozen solution. Inset: The ratio of the cw DF to the prompt fluorescence (PF) vs laser power.
From their PADMR and PLDMR work on polymers, Wohlgenann et al. [16] suggest another model. They assume the cross section of a singlet polaron pair to form a SE ($\sigma_{SE}$) is higher than the cross section of a triplet polaron pair to form a TE ($\sigma_{TE}$). Hence, off-resonance the singlet-pair population is lower than the triplet-pair population due to its faster decay rate to SEs. Therefore, at resonance there is a net conversion of pairs from the triplet to the singlet configuration, and the total PL increases due to the enhanced “delayed PL” from the enhanced population of nongeminate singlet polaron pairs. Fitting their delayed PL model to the observed PADMR intensity, they predict the ratio $\sigma_{SE}/\sigma_{TE}$, in a variety of polymers, and consequently the yield of SEs in the corresponding polymer LEDs (PLEDs). The predicted values range from 25% in small molecules and polymers with a short conjugation length, which should not yield a PADMR or PLDMR, to 60% in polymers with a long conjugation length. Since the yield of SEs determines the internal quantum efficiency of the OLED, it is a central issue in the science and technology of OLEDs.

Recapping the forgoing discussion, it is clear that two models of the positive spin 1/2 PLDMR, the quenching model and delayed PL model, appear to be consistent with the behavior of the resonance. Yet the central issue of the yield of SEs in OLEDs demands that the nature of this resonance be resolved. To discriminate between the quenching and delayed PL model, we developed a novel variation of PLDMR, which we dub “double modulation PLDMR” (DM-PLDMR). In the typical PLDMR experiments, one quantity, typically the microwave power, is modulated and the resonance is detected by a lock-in amplifier that is referenced by the microwave modulation frequency. The existing laser power is then constant during the measurement. In the DM-PLDMR measurement, both the laser and microwave power are modulated, and two lock-in amplifiers are used to monitor the
resonance. Using a laser stabilizer, we modulated the laser intensity sinusoidally by up to 9% relative to the DC intensity. The laser power modulation rate varied from 1 kHz to 100 kHz. The first lock-in was referenced by the laser power modulation and its time constant was 1 ms. Thus, the delayed PL was filtered out of the output of that lock-in at a high laser modulation frequency. This enabled us to determine the contribution of the prompt and delayed PL to the resonance. If the resonance is due to the delayed PL, the DM-PLDMR intensity will decrease as the laser modulation frequency increases; if the resonance is due to the quenching mechanism, it will be independent of the laser power modulation frequency. The results of the DM-PLDMR are discussed in detail in Chapter 2.

Introduction to OLEDs

The first organic electroluminescence (EL) device was reported in 1953 [17]. However, the initial studies met with limited success. It was a thin-film OLED, reported by Tang and Van Slyke in 1987 [18], which opened a new door and launched a rapidly growing intense effort to develop OLED science and technology. By using tris-(8-hydroxyquinoline) aluminum (Alq\textsubscript{3}), Tang and Van Slyke demonstrated a new approach to overcome problems presented by thick single-crystal devices, such as high operating voltage and low efficiency. Subsequent research on OLEDs expanded to include various multilayer small \pi-conjugated molecule devices [19] and then to PLEDs [20].

The structure of typical materials used in OLEDs and PLEDs is shown in Fig. 10 and 11. The materials have advantages and disadvantages relative to each other. The polymers are generally better than the small molecules in terms of stability, the ease of processing from solution and device fabrication using techniques such as spin-coating and inkjet printing, and
Fig. 10. Molecular structure of some common $\pi$-conjugated polymer used in PLEDs.
Fig. 11. Molecular structure of some common π-conjugated molecules used in small molecular OLEDs.
operating voltage, which is generally lower due to their monolayer structure. Overall, however, the performance of the state-of-the-art small molecular OLEDs has consistently exceeded that of PLEDs, due to the ease of fabricating multilayer structures, including finely controlled doped guest-host layers, the availability of high purity materials, and a wide selection of materials. On the other hand, the amorphous small molecular layers are more susceptible to crystallization, a well-known degradation mechanism, than the polymer layers. It appears though, that the performance gap between the small molecular OLEDs and PLEDs is shrinking. Still, the recent advances in brightness, luminescent yield and lifetime of small molecular devices render them superior to PLEDs. It now appears that due to major differences in fabrication techniques, small molecular OLED technology will likely be more common in small-screen devices such as mobile phone and digital camera displays, while PLED technology will be more attractive for large displays.

Since the source of the EL in fluorescent (as opposed to phosphorescent) OLEDs is the radiative decay of SEs, simple spin statistics dictate a theoretical limit of 25% for the internal quantum efficiency $\eta_{\text{EL}}^{\text{int}}$ of both small molecular OLEDs and PLEDs. To overcome this limit, phosphorescent OLEDs, which utilize emissive triplet as the EL source, were developed [21]. In some of these phosphorescent devices, it was shown that $\eta_{\text{EL}}^{\text{int}}$ approaches 100%.

OLEDs began appearing in commercial products in 1999, mostly in competition with liquid crystal displays (LCDs). Currently, most of the commercialized OLEDs are used in small-screen displays such as mobile phones and digital cameras. They have several advantages over LCDs. (1) LCDs produce color through filtering white light through field-induced polarization by a liquid crystal. Hence the viewing angle is limited. (2) The LCDs
require additional backlighting, diffusers, and polarizers. (3) The inherent response time is slow. OLEDs are self luminescent, so the additional components are not needed, and their power efficiency will be much higher than that of LCDs. Additionally, they are brighter and viewable over a wider viewing angle, and attractive candidates for a flexible display. The only disadvantage of OLEDs vs LCDs is their current stability. The organic materials are sensitive to oxygen and moisture, and crystallization of the amorphous layer. Hence they must be encapsulated and their temperature kept below the lowest glass-transition temperature $T_g$ of the materials used in the devices. To that end, remarkable progress has been achieved in developing encapsulation techniques and high $T_g$ materials, and the stability of state-of-the-art OLEDs has dramatically improved in recent years.

**Basic OLED structure**

OLEDs are typically fabricated on glass substrates coated with a transparent conducting anode such as indium tin oxide (ITO). For small molecular devices, the organic layers are thermally evaporated on the anode substrate; the total thickness of the organic layer is $\sim$100 nm. For PLEDs, the layers are typically spin-coated on the anode; the total thickness of the organic layer is typically 100 - 400 nm. In both cases, a low-work-function metal cathode is evaporated on the organic layers. If a forward bias is applied to this structure, holes are injected from the anode, and electrons from the cathode (see Fig. 12).

ITO is used as an anode due to its high work function, transparency, and conductivity. Depending on the amount of indium oxide (InO$_2$), its work function varies from 3.5 to 4.3 eV and the conductance and transparency also depend on the thickness and the amount of tin oxide. Obviously, thicker ITO yields to higher conductivity and lower transparency. The
work function also dependent on various surface treatments, is 4.1 ~ 5.1 eV [22-24]. Since the typical HOMO of the hole transport layer (HTL) is 5 ~ 6 eV, these treatments will enhance hole injection by lowering the barrier for hole injection from ITO to HTL.

Hole injection is further improved by inserting a buffer layer between ITO and the HTL. High hole mobility copper phthalocyanine (CuPc; HOMO level is 5.1 eV) is evaporated for small molecular devices and poly(3,4-ethylenedioxythiophene) polystyrene sulphonate (PEDOT/PSS; HOMO level is 5.5 eV) is spin-coated for PLEDs (see Fig. 13). Hence efficient hole injection into these buffer layers is expected [25]. In PLEDs, hole injection and transport is further improved by treating PEDOT-PSS with ethylene glycol (EG), adding poly-alcohols (alcohols with more than two OH groups on each molecule), or adding high-dielectric solvents [26].

![Fig. 12. Basic structure of OLEDs](image_url)
Fig. 13. Role of PEDOT-PSS showing 6 fold enhancement in EL of PPZ doped PVK PLEDs
For the cathode, low work function materials such as Ca, Mg, and Al with work functions of 2.8, 3.7, and 4.3 eV, respectively, are used to minimize the energy barrier for electron injection from the cathode to the LUMO level of the electron transport layer (ETL). Typical LUMO levels of organic materials are 2 - 3 eV. When using the most common cathode material, Al, electron injection is dramatically improved by inserting a thin (~1 nm thick) alkali fluoride buffer layer, typically lithium fluoride (LiF) or cesium fluoride (CsF), between the ETL and the cathode [27]; it is found that the buffer layer reduces the barrier for electron injection by up to 1 eV [28].

The energy levels in a typical OLED are shown in Fig. 14. At an applied bias $V_{app} = 0$ V, the vacuum levels (VL) of the anode and cathode are shifted to align the Fermi energies of the anode and cathode. The bias needed to flatten the levels is called the built-in potential ($V_b$). Typical values of $V_b$ are 1.5 - 3 V. When $V_{app} < V_b$, the injected current is negligible, and most of the current is caused by free carriers in the organic layers or leakage current. When $V_{app} > V_b$, more charges are injected from both sides. Under this condition, the injected $e^-$ and $h^+$ move by hopping from site to site through the organic layers. Depending on the device structure, some of the carriers may accumulate at the organic-organic interface. This charge accumulation zone (CAZ) usually overlaps the recombination zone. If the charge accumulation is sufficiently high, then the distance between charges becomes sufficiently small for recombination to radiative SEs. By adjusting the thickness of each layer and choosing the right materials, the CAZ can be moved to the desired position to avoid SE quenching by the electrodes and achieve balance of electrons and holes to reach maximum efficiency. In addition, the hole blocking layer (HBL) can be inserted between HTL and ETL to achieve the same purpose. These are among the major reasons for a multilayer structure.
(a) Before contact

(b) $V_{app} < V_b$

(c) $V_{app} = V_b$

(d) $V_{app} > V_b$

Normal operating condition

Fig. 14. Energy level alignment.
The usual operating voltage of OLEDs is about 2 - 20 V, corresponding to an average electric fields of 0.1 - 2 MV/cm. These fields are very high compared to the typical ~ 10 kV/cm fields in the inorganic semiconductor devices. The reason for the large field in the organic devices is the high resistivity $\rho$ of the devices, which ranges over more than eight orders of magnitude, and with very high values of $10^5 - 10^{13}$ Ω cm in forward bias.

**Basic processes in OLEDs**

The basic processes that result in the EL of an OLED are: carrier injection, carrier transport, exciton forming and EL. The EL efficiency may be expressed as

$$\eta_{EL}^{int} = \eta_{PL} r_s \gamma k$$

(14)

and

$$\eta_{EL}^{ext} = \xi \eta_{EL}^{int}$$

(15)

where $\eta_{PL}$ is PL quantum efficiency, $\eta_{EL}^{int}$ and $\eta_{EL}^{ext}$ are internal and external quantum efficiency, respectively, $r_s$ is the yield of SEs (generally 1/4), $\gamma$ is the carrier balance, $k$ is the quenching factor, and $\xi$ is the external coupling factor.

**Carrier injection**

(1) Electron injection at metal cathode/organic interface with the image force effects [29]

Electrons are injected from the metal electrode into the organic layer, and they must overcome the injection barrier $q\phi_m$, which is the energy difference between the Fermi level
$E_F$ of the metal and the LUMO level $E_{LUMO}$ of the adjacent organic layer. Likewise, holes generally encounter a barrier, which is the difference between $E_F$ of the ITO anode and $E_{HOMO}$ of the adjacent organic layer. After contact between the metal and organic layer is established, some electrons will fill trap sites in the organic layer. These induce equivalent holes in the metal layer. The electrons and the positive image charges result in an image-force potential $\phi_i$ due to the Coulomb attraction between them. This image potential lowers the barrier at the metal-organic interface and facilitates the transfer of electrons from the metal Fermi level to the organic LUMO. But $\phi_i$ will decrease as electrons penetrate deeper into the organic layer, therefore it is not energetically favorable for electrons to reach the bulk states deep in the organic layer. When the external field is applied, the energy of the available hopping site is lowered and the injection into bulk of the organic layer is enhanced. This image force lowering is more effective than in normal inorganic semiconductors due to the high applied field.

(2) Electron injection under applied field

Image-force lowering of the potential can not by itself account for the observed electron injection. To explain the observed behavior, the thermionic injection [29] is invoked for fields lower than 2 MV/cm and field dependent tunneling [30] is invoked for fields greater than 2MV/cm.

The thermionic injection occurs when the barrier at metal-organic interface is not too high for thermally stimulated electron injection. The thermionic current density $J_{th}$ is described by [30]

$$J_{th} = A T^2 e^{-\eta \Phi_i / kT}$$ (16)
where \( q\phi_b \) is the energy barrier modified by the image force and \( A^* \) is Richardson’s constant.

Under thermal equilibrium, there is a backflow of carriers which cancels out the thermal injection current. This backflow current density \( J_b \) at the interface is [31]

\[
J_b = \gamma p(0)
\]

(17)

where \( p(0) \) is the hole carrier density at the interface \( x = 0 \), and \( \gamma \) is determined by detailed balance between thermionic injection and interface recombination. At low applied bias, \( J_b \) is nearly equal to \( J_{th} \), thus the total current is only a small fraction of \( J_{th} \).

In a high electric field, carriers tunnel through the triangular a barrier at the interface (see Fig. 14(d)), a process called field emission. Tunneling through such a barrier is called Fowler-Nordheim (FN) tunnelling. This triangular barrier becomes narrower with increasing field. The tunneling current density \( J_{FN} \) is given by [29]

\[
J_{FN} \approx AV^{2} e^{-V_0/V}
\]

(18)

where \( V \) is the applied bias and \( A \) and \( F_0 \) given by

\[
A = \frac{mq^3}{8\pi\hbar m^* \phi_b}, \quad F_0 = \frac{8\pi\sqrt{2m^* \phi_b^3}}{3qh}.
\]

(19)
(3) Space charge limited current [18]

At sufficiently high fields, the triangular barrier at the metal-organic interface becomes so narrow that the current is controlled by the bulk properties. The bulk of the organic layer has a relatively high resistivity and contains traps. Furthermore, the low mobility and the carrier density of $\geq 3 \text{ mA/cm}^2$ in the bulk at high field render the charge accumulation unavoidable, which leads to the redistribution of the field, due to screening of the accumulated charges. The resulting current is called the space-charge-limited-current (SCLC) [32]. If the bulk is trap-free or has only a single shallow trap level, the SCLC is mainly the drift current which depends on the electric field as

$$J_{\text{SCLC}} \propto V^2$$  \hspace{1cm} (20)

If there are deep traps, at high field these traps will be filled, resulting in the absence of empty traps and an increase of $J$. This current is called the trapped-charge limited current (TCLC) and it is given by [33]

$$J_{\text{TCLC}} \propto V^\alpha$$  \hspace{1cm} (21)

where $7 \leq \alpha \leq 9$

Note that if an electron trap level $E_t$ lies above the Fermi level $E_F$, but $E_t - E_F > kT$, then the trap is considered as shallow; if $E_t - E_F < kT$, then it is considered as deep.
Carrier transport

(1) Traps

The organic material has an amorphous structure that is due to the fabrication method for small molecules and the intrinsic property of polymers. Thus a high density of trap sites is inevitable and difficult to determine in detail. Since the carrier transport process is then largely determined by traps in the organic material, without knowledge of the distribution and characteristics of these traps, it is impossible to describe the transport mechanism.

There are two types of traps, intrinsic and extrinsic. Intrinsic traps are due mostly to the amorphous structure of the organic material. They are conformational defects, grain boundary defects, and molecular structural defects. For small molecule films the distribution of trap energies is typically exponential and this distribution simplifies the analysis.

Extrinsic traps are typically generated by chemical impurities, so they can be avoided during the material synthesis or device fabrication processes. These traps are usually very deep traps and even at the low field they are promptly filled. Hence, they do not affect the transport process at the high fields.

A third type of trap is induced by intentionally doping the material with a guest molecule in a guest-host system. These will enhance the performance or control the emission spectrum. However, the aforementioned traps are the main reason for low carrier mobility, which is typically $10^{-7} - 10^{-3}$ cm$^2$/Vs for holes and one or two orders of magnitude lower for electrons.
(2) Mobility

If there are defects or traps, the carrier will be localized at a trap site and hop to another site through phonon-assisted hopping, resulting in a temperature dependence of the mobility \( \mu \) given by [34]

\[
\mu = \mu_0 e^{-E_a/kT}
\]  

(22)

where \( \mu_0 \) is the trap-independent or field-independent mobility and \( E_a \) is the activation energy to overcome the local energy barrier, typically about 0.15 eV for molecular crystals.

In an electric field, the trapped carrier in a potential well of activation energy \( E_a \) will experience an asymmetric change in barrier, as one side of the potential barrier increases, and the other side decreases; this change is proportional to \( \sqrt{F} \). Hence, carrier hopping becomes electric-field-assisted hopping and the electric field dependence of the mobility is [34]

\[
\mu = \mu_0 e^{\frac{\sqrt{F}}{F_0}}
\]

(23)

where \( \mu_0 \) is low-field mobility, typically \( 10^{-9} - 10^{-4} \, \text{cm}^2/\text{Vs} \) at room temperature, and \( F_0 \) is an empirically determined temperature-dependent coefficient.

Recombination

After electrons and holes are injected into organic layer from the electrode, they can recombine to form SEs, TEs, and charge transfer excitons (CTEs). In fluorescent devices,
the emission is from the radiative decay of SEs and in phosphorescent devices, it is due to the decay of TEs. The recombination sites are usually near the organic-organic interface, in the so-called recombination zone. This zone can be moved by changing the structure of the OLEDs. It is important to design the OLED so that the recombination zone is sufficiently far from the metal–organic interface, in order to avoid quenching of the SE by the cathode. This issue may be obviously problematic in monolayer devices.

We can apply the Langevin formalism [33, 35] if both carriers are statistically independent and the recombination process is random. The excitons in the molecular material are strongly bound Frenkel excitons, so the distance between $e^-$ and $h^+$, $\lambda_{h-e}$ is small. For recombination, $\lambda_{h-e}$ must be less than the Onsager radius $r_c$ which is the distance at which the Coulomb attraction energy and the thermal energy are equal [32], i.e.

$$r_c = \frac{q^2}{4\pi\varepsilon kT}.$$  \hspace{1cm} (24)

For most organic materials $\varepsilon \sim 3\varepsilon_0$, so the Onsager radius is $\sim 17$ nm at room temperature. The $e^- - h^+$ recombination is bimolecular process. Hence to maximize the recombination rate, the number of holes and electrons at the recombination zone should be equal and this is achieved through structure design and choice of suitable material.

**Efficiency**

If the recombination process is random and the probability of recombination of $e^- - h^+$ pairs in the singlet spin configuration to SEs ($\sigma_{SE}$) is equal to the probability of
recombination of $e^- - h^+$ pairs in the triplet spin configuration to TEs ($\sigma_{TE}$), then only 25% of the pairs will recombine to the radiative SEs. Then $\eta_{EL}^{int}$ will be theoretically limited to 0.25 with $r_s = 0.25$ for ideal carrier balance ($\gamma = 1$) and no quenching factor ($k = 1$). However, in reality, SEs are quenched by various processes such as charge transfer to another molecule, traps, and defects. In addition, generally $\eta_{PL} < 100\%$. For example, $\eta_{PL}$ of PPV film ranges from a few percent to $\sim 90\%$ [38]: in Alq₃ powder, typically $\eta_{PL} \sim 32\%$ [33].

Eq. (14) and (15) then yield

$$\eta_{EL}^{ext} = \xi \eta_{PL} r_s \gamma k \quad (25)$$

The external coupling factor $\xi$ is another important factor. The photons generated in the emission zone of the OLEDs pass through other organic layers and the ITO coated glass substrate. Due to the refractive index mismatch between the organic layers and ITO substrate, the rate and the direction of emission are strongly modified by optical interference effects [39]. These effects depend on the direction of the dipole moment of the emitting molecules and the refractive index $n$ of the emitting layer. It can be shown that $\xi \approx 0.75 / n^2$ for isotropic dipoles of the emitter, and $\xi \approx 1.2 / n^2$ for in-plane dipoles which is the case for spin-coated PLEDs [38]. Since typically $n^2 = e / \varepsilon_0 \sim 3$, if $\eta_{PL} = 100\%$, then the maximum possible $\eta_{EL}^{ext}$ will be 7 - 8\%, as long as the spin ratio $r_s$ is 25\%. 

Dissertation organization

This dissertation consists mainly of papers published, and prepared for submission to forefront international journals.

Chapter 1 provided a general introduction and described the basic properties of ODMR and OLEDs. It included origin of the positive (PL-enhancing) spin 1/2 resonance, carrier injection, carrier transport, recombination mechanisms, and efficiency of devices. Chapter 2 is an article published in Physical Review Letters. Newly developed ODMR technique and measurements by that method are described in this paper. These measurements verify two different models and support the delay model. Chapter 3 describes an optimizing process to enhance and stabilize near UV emission from PVK based PLEDs. Treating the HTL layer with EG and optimizing thickness of HBL layer improve the device performance by 45 folds. Chapter 4 describes WPLED with red and blue small molecular dopant. Changing doping level and adjusting the layer thickness lead to bright white emitting small molecule and polymer hybrid LEDs. Chapter 5 is a follow up for the paper from chapter 2. The second harmonic measurements from DM-PLDMR is described. Finally, Chapter 6 presents the general conclusions and a summary of this work.

References


2. ON THE YIELD OF SINGLET EXCITONS IN ORGANIC LIGHT-EMITTING DEVICES;
A DOUBLE MODULATION PHOTOLUMINESCENCE-DETECTED MAGNETIC RESONANCE STUDY

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Abstract

Double modulation (DM) photoluminescence (PL) detected magnetic resonance (PLDMR) measurements on poly(2-methoxy-5-(2’-ethyl)hexoxy-1,4-phenylene vinylene) (MEH-PPV) are described. In these measurements, the laser excitation power is modulated at $1 < \omega_L/(2\pi) < 100$ kHz, and the spin 1/2 PLDMR of the PL response at $\omega_L$ is monitored by microwave modulation at $\omega_M << \omega_L$. The frequency response of the DM-PLDMR is inconsistent with the assumption that the PLDMR is due to delayed PL from nongeminate polaron recombination, which is the basis for previous predictions of the singlet exciton (SE)-to-triplet exciton (TE) ratio in organic light emitting devices. Rather, the frequency response is consistent with the assumption that the PLDMR is due to variations in the rate of quenching of SEs by TEs and polarons.

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**Introduction**

The internal quantum efficiency limits of fluorescent organic light-emitting devices (OLEDs) are determined by the relative formation rates of singlet (spin zero) and triplet (spin one) excitons. Consequently, understanding the spin dependence of exciton formation is one of the central issues in the science and technology of fluorescent OLEDs [1-5]. Optically-detected magnetic resonance (ODMR) is an experimental probe of exciton formation especially suited for studying spin-dependent phenomena [6]. Indeed, a model has been proposed in which the positive spin 1/2 photoluminescence (PL)-detected magnetic resonance (PLDMR) in π-conjugated materials is due to delayed PL from nongeminate polaron recombination (the “spin-dependent recombination (SDR) model”) [1-3]. A key prediction of the SDR model is that singlet exciton (SE) formation rates are higher than triplet exciton (TE) formation rates in π-conjugated polymers [1-3]. This model, however, continues to be debated [5]. In this paper, we provide experimental evidence that is inconsistent with the SDR model, and propose that the resonance results from reduced quenching of SEs by a reduced population of polarons and TEs. The reduced TE and polaron population is, in turn, due to enhanced annihilation of TEs by polarons [7-9].

The organic semiconductors that comprise OLEDs exhibit three categories of excited states: spin-0 SEs, spin-1 TEs, and spin-1/2 polarons. ODMR experiments probe the spin dependent interactions of these species. But the ~1 ns radiative lifetime of SEs is much shorter than that of either TEs or polarons, suggesting that under optical modulation, quenching interactions should have a significantly greater bandwidth than the recombination of long-lived polarons.
Experiments design and Background

We report two magnetic resonance experiments that exploit this distinction to distinguish between the SDR and quenching models. The experiments are shown schematically in Fig. 1. In the first experiment, only the microwave field is modulated at a frequency $f_M$, and the PLDMR is detected synchronously using lock-in #1. The second experiment is a novel double-modulation PLDMR (DM-PLDMR) experiment, in which both the microwave power and the laser power are modulated. Two lock-in amplifiers are used in series. The first, lock-in #2, is synchronized to the modulation frequency $f_l$ of the laser. Hence, any contribution to the PL from SDR of polarons with lifetime $\tau > 1/f_l$ is filtered out of the output by lock-in #2. That output is connected to lock-in #1, synchronized to $f_M = 200$ Hz. As $f_l$ increases to 100 kHz, the spin 1/2 PLDMR due to SDR of polaron pairs with $\tau \geq 10 \mu s$ should decrease to zero. In contrast, the PLDMR due to quenching should remain essentially unchanged.

The experimental design clearly distinguishes between the recombination and quenching models. To see this, we consider a simple general recombination model, which includes SEs with density $S$ and lifetime $\tau_S \sim 1$ ns, along with a species $X$ with spin $> 0$ and lifetime $\tau_X >> \tau_S$ which recombines into SEs at a rate $\gamma_{XX}$. Typically, $X$ is a polaron in SDR models and $\gamma_{XX}$ is determined by the fraction of polarons that are singlet paired. Given a SE generation rate $G_S$, at steady-state

$$\frac{dS}{dt} = G_S \frac{S}{\tau_S} + \gamma_{XX} X^2 = 0 \quad (\text{recomb}). \quad (1)$$

Since $\Delta PL \propto \Delta S$ is a small correction to $S = G_S \tau_S$,

$$\Delta PL = S^* - S = \tau_S \gamma_{XX} (X^*)^2 - \tau_S \gamma_X X^2 \quad (\text{recomb}) \quad (2)$$

**Fig. 1.** The experimental setup for testing the spin-dependent recombination (SDR) and quenching models of spin 1/2 ODMRs. The dynamics of the species involved in the resonance are determined by measuring the frequency response for modulation of microwave or laser power. Two experiments are performed. In the single modulation experiment, only the microwave power is modulated. In the double modulation experiment both the laser and microwave power are modulated.
where the star indicates resonance conditions. In SDR models, the cross-section for SE formation is greater than the cross section for TE formation [1-3], so off resonance the singlet pair population is depleted relative to the triplet pair population. Hence, rapid mixing at resonance converts triplet polaron pairs to singlet pairs and the recombination rate to SEs increases, i.e., $\gamma_{XX}^* > \gamma_{XX}$. Hence $S^* > S$, it is consistent with observations of a positive PLDMR.

Similarly, a simple general quenching model has SEs coupled to a quenching species $X$ with spin $> 0$ (i.e., a polaron or a TE) and lifetime $\tau_X \gg \tau_S$, which quenches SEs at a rate $\gamma_{XS}$. Indeed, quenching of SEs by polarons and TEs has been confirmed: a rate-equation treatment was used to quantify quenching of SEs by polarons [10], and PLDMR measurements of the half-field TE resonance in a guest-host polymer blend determined that the TE resonance is due to quenching of SEs by TEs [11]. The rate equation for SE quenching under steady state is

$$\frac{dS}{dt} = G_S - \frac{S}{\tau_S} - \gamma_{XX}XS = 0 \quad \text{(quench)},$$

and the change induced by resonance conditions is

$$\Delta PL = S^* - S = S\tau_S \gamma_{XX} (X - X^*) \quad \text{(quench)}.$$  

Photoinduced absorption detected magnetic resonance (PADMR) experiments show that the populations of both TE and polaron quenching species (i.e., $X$) decrease under resonance [1-3,10]. Thus, the quenching model is also consistent with observations of a positive PLDMR. The reduction in the polaron and TE populations is due to the spin-dependent annihilation of TEs by polarons. TE-polaron interactions are treated quantitatively elsewhere [9] and discussed further below.
We now consider modulation of the optical excitation source at frequencies \( f_i \) above the cutoff frequency of \( X \), i.e. \( f_i \gg 1/\tau_X \), but below the cutoff frequency of SEs, i.e. \( f_L \ll 1/\tau_S \). We exploit the orders of magnitude difference between \( \tau_X \) and \( \tau_S \). Under these conditions, \( X \) varies very little from its average value at or off resonance (\( \bar{X} \) and \( \bar{X}^* \), respectively). Thus, detection at \( f_L \) eliminates any PL due to the recombination terms of Eq. (2), yielding \( \Delta PL = 0 \).

In contrast, Eq. (4) for the quenching model has \( \Delta PL \propto S \), which follows the optical modulation, and leads to \( \Delta PL > 0 \), provided that \( \bar{X}^* < \bar{X} \), as observed independently under microwave modulation and rationalized below by annihilation processes involving spin-1 TEs and spin-1/2 polarons.

The expected frequency responses of the SDR and quenching models are given explicitly by considering the modulations of \( X \), \( S \), \( \gamma_{XX} \), and \( \gamma_{XY} \) under optical and microwave modulation to first order:

\[
X(t) = \bar{X} \left[ 1 + \alpha_{XL} F_{XL} (f_i) \cos(2\pi f_i t) \right] \left[ 1 + \alpha_{XM} F_{XM} (f_M) \cos(2\pi f_M t) \right] \tag{5}
\]

\[
S(t) = \bar{S} \left[ 1 + \alpha_{SL} \cos(2\pi f_i t) \right] \tag{6}
\]

\[
\gamma_{XY} (t) = \bar{\gamma}_{XY} \left[ 1 + \alpha_{YM} \cos(2\pi f_M t) \right] \tag{7}
\]

where bars indicate average values, \( \alpha_{AB} \) indicates modulation depth of the parameter \( A \) under excitation \( B \), and \( F_{XL} \) and \( F_{XM} \) are the frequency responses of \( X \) to light and microwave modulation, respectively, normalized to unity at zero frequency. The DM-PLDMR signals under the recombination and quenching models are found by substituting Eqs. (5) - (7) into Eqs. (1) and (3) respectively, and considering terms that vary as \( \cos(2\pi f_i t) \cos(2\pi f_M t) \):

\[
\Delta PL|_{f_i,f_M} = \bar{X}^2 \bar{\gamma}_{XX} \alpha_{XL} \left( 4\alpha_{XM} F_{XM} + 2\alpha_{YM} \right) F_{XL} \quad \text{(recomb)} \tag{8}
\]
\[ \Delta PL_{f_M, f_L} = \gamma_{XM} \alpha_{XM} X_{FM} \left( \alpha_{sL} + \alpha_{XL} F_{XL} \right) \text{ (quench)}, \]  

Thus, the SDR model predicts that \( \Delta PL_{f_M, f_L} \propto F_{XL} \), while the quenching model predicts that \( \Delta PL_{f_M, f_L} \propto (\alpha_{sL} + \alpha_{XL} F_{XL}) \). Recombination models predict that a simultaneous synchronously-detected optical and microwave modulation experiment with \( f_L \gg 1/\tau_X \) will give \( \Delta PL = 0 \) regardless of \( f_M \) because the optical modulation frequency is beyond the bandwidth of the slow recombining species, i.e., because \( F_{XL} \ll 1 \). Quenching models, in contrast, predict \( \Delta PL > 0 \) for such an experiment as long as \( f_M < 1/\tau_X \) and \( f_L < 1/\tau_5 \), because the optical modulation is within the bandwidth of short-lived SEs.

**Experimental results and discussions**

We now test both the SDR and quenching models by measuring the frequency response of the resonance in the two experiments shown in Fig. 1. The samples for all experiments were MEH-PPV films deposited onto the inner walls of an evacuated glass capillary and subjected to the spin 1/2 resonance conditions at \( T = 20 \) K. The films were optically excited at \( \lambda = 488 \) nm. The optical intensity at the sample was 500 mW/cm\(^2\). The laser power was modulated by a Cambridge Research Laser Stabilizer. We note that the behavior of the “regular” (i.e., single-modulation) PLDMR was essentially identical to that observed in the past [6, 12-15].

Fig. 2 shows the positive spin 1/2 PLDMR amplitude vs. \( f_M \). As shown by Graupner et al. [16], this frequency response yields the lifetimes of the spin-carrying species responsible for the resonance. Fits with two lifetimes are superior to one-lifetime fits, suggesting that two quenching species are involved in the resonance, i.e. TEs and polarons quench SEs. A least-
squares fit returns $24 \pm 2 \mu s$ and $244 \pm 66 \mu s$ as the two lifetimes. The best fit for a single quencher returns $38 \pm 4 \mu s$. In comparison, we previously measured the triplet lifetime to be $\sim 30 \mu s$ in a similar conjugated polymer [17]. The band-limited behavior seen in Fig. 2 is consistent with both the SDR and quenching model, and in both cases, the cut-off frequency ($\sim 1 \text{ kHz}$) is an indication of the lifetime of the long-lived species $X$ in Eqs. (1) through (4) above.

Fig. 3 shows the DM-PLDMR signal vs. $f_i$. The DM-PLDMR resonance had the same $g$-value and line shape as in Fig. 2, confirming that the same resonance was measured in the two measurements. The observed DM-PLDMR and PLDMR amplitudes are approximately equal even at $f_i = 100 \text{ kHz}$, which is far higher than the $\sim 10 \text{ kHz}$ cut-off for the slow species. The dashed line in Fig. 3, however, is the first-order SDR result, Eq. (8), normalized at $1 \text{ kHz}$ for quenchers with $\tau_X = 38 \mu s$.

To confirm that the flat frequency response of the DM-PLDMR for $1 \text{ kHz} < f_i < 100 \text{ kHz}$ is consistent with quenching theory, we measure the frequency response of the quencher under optical modulation using photo-induced absorption (PIA). Fig. 4 shows the PIA of a drop-cast MEH-PPV film at $T = 20 \text{ K}$. The optically modulated pump beam had a wavelength $\lambda = 405 \text{ nm}$ and optical intensity of $I_{exc} = 5 \text{ mW/cm}^2$, and the probe beam had $\lambda = 808 \text{ nm}$ and $I_{exc} = 150 \text{ mW/cm}^2$. The probe wavelength was selected as close as practical to the PL spectrum of MEH-PPV while minimizing cross talk from optically modulated MEH-PPV PL, thereby detecting quenchers with the best overlap with SEs. The normalized magnitude of the PIA data at low frequency is expected to be approximately $\alpha_{sl}$, Eq. (9) demonstrates that $\alpha_{sl} F_{XL} \ll \alpha_{sl}$ at $f_L = 1 \text{ kHz}$. Consequently, Eq. (9) predicts a DM-
PLDMR signal with no dependence on $f_i$, as seen in Fig. 3. This data is fully analyzed elsewhere [9].

Although the above analysis of the PLDMR frequency dependence demonstrates that SEs are involved in the resonance, bimolecular interactions involving SE are not themselves spin dependent. Rather, the origin of the spin dependence must lie in the TE and polaron quenching species, whose populations are both observed to decrease in PADMR experiments [1-3, 10]. We propose that TE-polaron interactions are the origin of the spin dependence. TE-polaron interactions are spin-dependent, as discussed in anthracene [7]. Of the six composite spin states, only two are doublets that allow TE annihilation by the polaron. Since resonance mixes the doublet and quartet spin states, the TE-polaron annihilation rate increases and the TE population decreases. Resonance also reduces the population of polaron pairs (see below). The TE-polaron interaction was shown to be the source of the positive spin 1/2 PLDMR in C$_{60}$ [8]. It can also account for the PLDMR observed here. Under optical excitation, polarons are formed in pairs by the dissociation of a SE, and at low temperature in a disordered organic semiconductor, each oppositely charged polaron is frequently trapped within a short radius of the other. The lifetime of the polaron pair is then limited by the detrapping rate. TE-polaron interactions, which transfer energy from the TE to the polaron, can detrap the polaron and assist polaron recombination; the TE is annihilated in the process. Since the rate of TE-polaron interactions increases under resonance [9], TE annihilation and polaron recombination rates increase, and as a result the SE quenching rates decrease. We show elsewhere that the frequency dependence of the PLDMR signal in MEH-PPV, along with the frequency dependence of the PIA (Figs. 2-4), can be completely quantitatively modeled using a TE-polaron based quenching theory and parameters from the literature [9].
Fig. 2. Single modulation PLDMR $\Delta PL/PL$ for an MEH-PPV film vs the microwave modulation frequency $f_M$. The dashed line is a single lifetime $\tau = 38 \mu$s fit; the solid line is a two-lifetime fit with lifetimes 24 $\mu$s, and 244 $\mu$s.
Fig. 3. Double modulation data $\Delta PL/PL$ for the same sample vs the laser modulation frequency $f_L$, with $f_m = 200$ Hz. The dashed line is the behavior predicted by the delayed PL (i.e., SDR) model to first order, scaled to match the data.
Fig. 4. Normalized photoinduced absorption of a drop-cast MEH-PPV sample at $T = 20$ K, versus pump chop frequency. The PIA is excited at a wavelength of $\lambda = 405$ nm, while the probe beam has a wavelength of $\lambda = 808$ nm.
It has been argued that the measured excitation intensity dependence of the PLDMR in ρ-conjugated polymers is inconsistent with a quenching model [3]. But since the quenching rate increases with the densities of both quenchers and singlet excitons, both models predict a resonant signal which increases with the square of excitation intensity at low power (where the PL increases linearly with excitation intensity). At high excitation intensity, the PL increases sublinearly with excitation intensity, consistent with strong SE quenching phenomena. In this context, it should be noted that the steady state populations of the TEs and polarons, with generation rates that are ~1/100 those of SEs, but lifetimes that are > 20 μs, are consequently > 200 times greater than the steady state population of the SEs, whose lifetime is ~1 ns.

Conclusions

In conclusion, the microwave- and laser-modulation-frequency dependence of the PLDMR and DM-PLDMR, respectively, in MEH-PPV, invalidates SDR models, questioning reports of SE yields exceeding 25% in fluorescent OLEDs. Rather, the results are consistent with a quenching model where SEs are annihilated by TEs and polarons.

Acknowledgments

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References


3. COMBINATORIAL SCREENING OF NEAR UV POLYMER ORGANIC LIGHT-EMITTING DEVICES (PLEDs)

Abstract

Combinatorial screening of poly (9-vinyl carbazole) (PVK) OLEDs is described. The brightness of the devices improved 10 fold by treating the poly (3,4-ethylenedioxythiophene)/poly (styrene sulfonate) (PEDO/PSS) hole injecting layer with ethylene glycol (EG) and 5 fold with optimizing the thickness of the hole blocking layer (HBL) and electron transport layer (ETL) which results in increased electron injection. The optimized device exhibited a maximal radiance $R \sim 200 \text{ mW/cm}^2$ and external quantum efficiency $\eta_{exl} \sim 1.0 \%$ with an electroluminescence (EL) spectrum edge at 350 nm and peak at 410 nm.

Introduction

PVK has been studied since 1946 and since the 70s it is used as the thin photoconductive layer in xerography [1]. Only recently, with developing interests in OLEDs, it is being considered as a hole transport layer (HTL) or as a host material for several other doping materials [2], due to its large gap and high triplet energy [3]. Excimer emission from PVK was reported as earlier as 1969 [4]. However, it has not been used as an actual emitting material in OLEDs, due to its large highest occupied molecular orbital (HOMO) – lowest unoccupied molecular orbital (LUMO) gap of 4.9 eV [5].

The HOMO of PVK, measured from the vacuum level, is 6.1 eV. Since the work function of indium-tin oxide (ITO) is \~ 5 eV, the barrier to hole injection is \> 1 eV, and hole injection
is very limited, and a simple structure of ITO/PVK/Al cannot produce any EL. However, PEDOT/PSS, whose work function is 5.5 eV, inserted between ITO and PVK, becomes a hole-injecting stepping stone, and hole injection is improved and sufficient to produce sizable EL.

**Device structures and measurement methods**

Three types of devices were fabricated to optimize the performance of PVK-based OLEDs. Type 1 was a standard ITO/PEDOT-PSS/PVK/CsF/Al control device. In Type 2 devices, the PEDOT-PSS was treated with EG to improve hole injection. Type 3 devices included a hole blocking layer, which prevents holes from reaching the cathode and consequently results in nearly 100% electron-hole recombination.

For Type 1 devices, the PEDOT/PSS layer was spin-coated at 4000 rpm and heated for 1 hour at 100 ± 10 °C on ozone-treated 2×2cm² ITO substrates inside an Ar-filled glove box; the oxygen and water levels in the glove box were below 1 ppm. After that a solution of PVK in toluene was spin-coated at 2000 rpm. Next, to improve electron injection from the cathode, a 1 nm thick CsF layer was thermally evaporated on the PVK in a vacuum chamber (pressure <10⁻⁶ Torr) installed in the glove box. It was followed by thermal evaporation of a 150 nm thick Al cathode layer, evaporated through a 2”×2” mask containing 21×21 ~1.5 mm diameter holes, yielding 441 PLED pixels.

For a Type 2 device, immediately after the PEDOT-PSS layer was spin-coated, it was directly immersed in EG and heated or heated first and immersed for various periods. The other layers of the devices were identical to those of Type 1 devices.
For Type 3 devices, were similar to Type 2, but in addition an HBL of 2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) was thermally evaporated on the PVK, followed by 5 nm thick tris-(8-hydroxyquinoline) aluminum (Alq3) ETL, 1 nm CsF, and an Al cathode. For combinatorial screening, a sliding shutter was used to deposit the BCP with a systematically varying thickness [6]. As the shutter was opened, a 2 nm layer of BCP was deposited in each of four steps. Thus the OLED pixels in the various columns of the OLED matrix contained BCP layer thickness $t_{BCP} = 0, 2, 4, \text{ and } 6 \text{ nm}$. Following the deposition of the BCP layer, the substrate was rotated by 90° and the process was repeated in 3 steps with $t_{BCP} = 0, 8, \text{ and } 16 \text{ nm}$, resulting in final thicknesses $t_{BCP} = 0, 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, \text{ and } 22 \text{ nm}$ (see Fig. 1). It should be noted that the gap between the substrate and shutter was ~2 mm, so the shadow effect may have affected the real thickness. However, the variation in $t_{BCP}$ was still systematic. The EL was measured by a Minolta LS110 luminance meter and the EL spectra were measured using an Ocean Optics CHEM2000 integrated spectrometer.

![Diagram](image-url)

**Fig. 1.** Thickness of the BCP layer across the matrix array of OLEDs
Experimental results and discussions

The EL spectrum of all of the devices was identical, and is shown in Fig. 2. Type 2 devices were screened to determine the optimal EG treatment. One set of Type 2 were heated for 1 hour at 100 ± 10 °C then immersed in EG for up to 4 minutes. Another set were immersed in EG first and heated also for 1 hour. The highest performance devices were those that were immersed in EG for 1 min immediately following spin-coating of the PEDO-PSS layer, and heated for 1 hour. The radiance $R$ (in mW/cm$^2$, determined from the brightness $L$, in Cd/m$^2$, measured by the luminescence meter, the EL spectrum, and the photopic response curve) and efficiency of these devices were ~ 10 times that of the untreated devices. The maximal radiance and brightness were 45 mW/cm$^2$ and ~3000 lm/W$^2$, respectively, which is equivalent to 1000 Cd/m$^2$ at 555 nm.

![Spectrum from EG treated PVK at 7V and response curve of the typical human eye](image)
Figure 3 shows the power efficiency $\eta_{\text{power}}$ (%), external quantum efficiency $\eta_{\text{ext}}$ (%), and radiance $R$ (mW/cm$^2$) of untreated and EG treated PVK OLEDs. The radiance of treated devices increased steadily up to 11 V and gradually decreases at higher bias. The behavior of the untreated devices is very different: the efficiency of the untreated devices peaks at 4-5 V, whereas that of the EG treated devices peaks at $\sim$ 7 V. Even more importantly, though, the efficiency of the treated OLEDs decreases more gradually than that of the untreated devices. Consequently, at high bias ($\geq$ 10 V), the radiance of the treated devices is more than $\sim$20 times that if the untreated OLEDs. This improvement of radiance due to EG treatment is expected earlier but less than predicted [7]. The reason for weaker improvement is probably the nature of PVK emission, which is excimer emission, which requires two adjacent molecules to produce the EL, Therefore the EL efficiency is affected by the morphology of the film, and in the present case, by the concentration of the PVK in the solution. The operating lifetime of the device was also poor, and this is believed to result from the proximity of the emission zone to the cathode. The modification introduced into Type 3 devices addressed this problem.

For Type 3 devices, total 12 different thickness of BCP layer was evaporated using the combinatorial method mentioned above and screened to determine the optimum layer thickness for device brightness, efficiency, and stability. Mainly because of the large size of the substrate, Type 3 devices for combinatorial screening study were intentionally untreated to make sure of the uniform thickness of the PEDOT-PSS layers and to prevent possible abnormality due to the partial aggregation of PEDOT-PSS during EG treatment, which happens on the spin-coated large substrate. As shown in Fig. 4, the maximal brightness of $\sim$5 times of $t_{\text{BCP}} = 0$ was achieved at $t_{\text{BCP}} = 12$ nm. The efficiency was maximum at $t_{\text{BCP}} = 2$, but
Fig. 3. The power efficiency $\eta_{\text{power}}(\%)$, external efficiency $\eta_{\text{ext}}(\%)$, and radiance $R(\text{mW/cm}^2)$ for PEDOT/PSS and EG treated PEDOT/PSS.
Fig. 4. Normalized to value at $t_{bcp} = 0$, the maximal Brightness and Efficiency
Fig. 5. The current $I(V)$ and EL for selected thickness of the BCP layer.
the behavior of current $I(V)$ (Fig. 5) indicates the actual efficiency maximum will be at $t_{BCP} = 10$ nm which was ~7 times. The maximal efficiency at low $t_{BCP}$ ($\leq 4$ nm) is high and does not follow the trend of the brightness. The current at this thickness is even lower than $t_{BCP} = 0$, but there is a slight increase in the brightness. It is believed that the thin HTL makes the emission zone away from the cathode and leads to less quenching of singlet excitons (SEs) by the metal layer, but it is not enough to block a sufficient number of holes at the PVK-HTL interface. With thicker BCP layers, the electron-hole valence at the interface and carrier injection is improved. The operating voltage is also lowered to ~15 V but with a more than 18 nm thick BCP layer it goes back to ~20 V.

Finally, using results from the combinatorial method, Fig. 6 showed performance from the Type 3 devices with EG treated PEDOT-PSS and a 12 nm BCP layer. The maximum radiance was 200 mW/cm$^2$ and the brightness was 14000 lm/m$^2$, which is the same as 4500 Cd/m$^2$ at 555 nm. The maximum $\eta_{power}(\%)$ was 0.16%, and the maximum $\eta_{ext}(\%)$ was 1.0 % with the improved stability due to addition of the BCP and Alq$_3$ layer. Compared to Type 1 devices, the operating voltage was 8 volts higher with the thicker BCP layer and the Alq$_3$ layer. The improvements in the efficiency were only shown at device 3. That is because only hole injection was improved for device 2 and both hole and electron injection was improved in device 3.
Fig. 6. The power efficiency $\eta_{\text{power}}(\%)$, external efficiency $\eta_{\text{ext}}(\%)$, and radiance $R(\text{mW/cm}^2)$ for Type 3 devices.
Conclusions

In conclusion, the proper procedure for the treatment of the PEDOT-PSS layer with EG is suggested and a 10 fold enhancement was shown. The radiance of the device of [EG-treated PEDOT/PSS]/[PVK]/[12 nm thick BCP]/[Alq3]/[CsF]/[Al] showed ~ 10 fold improvement with an addition of EG treated PEDOT/PSS layer and ~ 5 fold with 12 nm thick BCP and Alq3 layer. With both layers, a 45 fold improvement in the brightness, 8 fold in the external quantum efficiency, and 7 fold in the power efficiency were achieved.

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References

4. STUDY OF WHITE-EMITTING HYBRID POLYMER/SMALL MOLECULE OLEDs BASED ON GUEST RED AND BLUE EMITTERS DOPED IN HOST PVK

Abstract

White OLEDs (WOLEDs) based on red-emitting [2-methyl-6-[2-(2,3,6,7-tetrahydro-1H,5H-benzo[i,j]quinolizin-9-yl)ethenyl]-4H-pyran-4-ylidene]propane-dinitrile (DCM2) and blue-emitting 4,4'-bis(2,2'-diphenylvinyl)-1,1'-biphenyl (DPVBi)-doped poly (9-Vinyl Carbazole) (PVK) is described. With increasing bias, the color coordinate evolves from orange to white. The performance of the devices is improved by inserting an additional 30 nm thick layer of DPVBi. The highest-performance device exhibited a maximal white brightness of $L \sim 9000 \text{ Cd/m}^2$ and an external quantum efficiency $\eta_{\text{ext}} \sim 2.2 \%$.

Introduction

Polymer-based white OLEDs (WOLEDs) based on PVK were first reported in 1994 [1]. The PVK layer was doped with a fluorescent dye, resulting in a white-emitting monolayer OLED. The monolayer polymer-based WOLED is advantageous over multilayer small molecular WOLEDs in manufacturing ease and lower operating voltage [2]. However, its performance is not good as the latters [3, 4].

Since this WOLED is a monolayer device and PVK is a hole transporter, the recombination zone is close to the cathode and will lead to the quenching of electroluminescence (EL) by the cathode. This quenching maybe overcome by inserting an
additional layer to move the recombination zone away from the cathode. In addition, since the performance of WOLED largely depends on the blue emitting layer, instead of a fluorescent dye or PVK host, DPVBi doped into PVK should enhance the blue emission; the red emission is controlled by adjusting the doping level of red dye \([2\text{-methyl-6-[2-(2,3,6,7-tetrahydro-1H,5H-benzo[i,j]quinolizin-9-yl)ethenyl]-4H-pyran-4-ylidene]propane-dinitrile (DCM2)}\). 

**Device structures and measurement methods**

Two sets of devices were fabricated to determine the optimal structure of these WOLEDs. Set 1 was a set of undoped blue-emitting OLEDs to determine the optimal structure for blue emission; Set 2 was a set of DCM2-doped WOLEDs fabricated to determine optimal DPVBi layer thickness.

In Set 1, three different structures were tested; 1 wt% DPVBi-doped PVK, 1 wt% DPVBi-doped PVK followed by a 25nm DPVBi layer, and PVK followed by a 25nm DPVBi layer. In all devices, a poly (3,4-ethylenedioxythiophene)/poly (styrene sulfonate) (PEDO-PSS) layer was spin-coated at 4000 rpm and heated for 1 hour at 100 ± 10 °C on aqua-regia-treated 2 cm×2 cm ITO substrates inside an Ar-filled glove box; the oxygen and water levels in the glove box were below 1 ppm. The PVK and doped PVK layers were spin-coated at 2000 rpm and the 25 nm DPVBi layer in the 2nd and 3rd devices was deposited by conventional thermal evaporation in a vacuum chamber (<10⁻⁶ Torr) installed in the glove box. Finally, a 1 nm-thick cesium fluoride (CsF) layer was evaporated to improve electron injection from the cathode. It was followed by a 150 nm-thick Al layer, which was deposited through a 2”×2” mask containing 21×21 hole pixels, each ~1.5 mm in diameter [5].
Before starting with device set 2, devices with 1 wt% to 50 wt% of DPVBi without DCM2 were tested to determine the optimal doping level of DPVBi. Also 0.5 wt% and 1 wt% of DCM2 with 10 wt% DPVBi were fabricated to adjust red emission.

For device set 2, 10 wt% DPVBi- and 0.5 wt% DCM2-doped PVK was spin-coated on top of the ethylene glycol (EG) treated PEOT-PSS layer and DPVBi layer was thermally evaporated using the combinatorial methods which result in 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, and 55 nm [5]. Rest of layer was 5 nm thick Tris-(8-hydroxyquinoline) aluminum (Alq3) as an electron transporting layer followed by 1 nm CsF and 150 nm Al layers.

The EL was measured by a Minolta LS110 luminance meter and the EL spectra were measured using an Ocean Optics CHEM2000 integrated spectrometer.

**Experimental results and discussions**

For set 1 devices, they yield the maximum EL of 250 Cd/m\(^2\), 950 Cd/m\(^2\) and 600 Cd/m\(^2\), the maximum external quantum efficiency \(\eta_{\text{ext}}\) of 0.5%, 1.4% and 1.7%, and peak emission wavelength \(\lambda_{\text{em-max}}\) = 430 nm, 450 nm to 440 nm, respectively (see Fig. 1 and 2). Thus, inserting a DPVBi layer improves the blue emission. From these results, we conclude that in the DPVBi-doped PVK-only device, significant emission is quenched by the cathode layer, and insertion of the additional DPVBi layer, which shifts the recombination zone away from the cathode, weakens this quenching process and improved the devices performance. In addition, even the undoped PVK, followed by the neat DPVBi layer, is better than the DPVBi- doped PVK, but it is worse than the DPVBi-doped PVK followed by the neat DPVBi. This indicates that the recombination zone is at the interface of the spin-coated DPVBi-doped PVK layer and the evaporated DPVBi layer. The behavior of \(\lambda_{\text{em-max}}\) is also
consistent with this assumption, as the shifts of $\lambda_{\text{em-max}}$ are suspected to be due to the contribution of PVK to the emission. Increasing the DPVBi doping level in PVK improves the performance of blue OLEDs: the optimal doping level is at 10% (see Fig. 3).

**Fig. 1.** The normalized EL spectrum of Set 1 devices; 1 wt% DPVBi doped PVK, 1 wt% DPVBi doped PVK/25nm DPVBi, and PVK/25nm DPVBi
Fig. 2. External quantum efficiency $\eta_{\text{ext}}(\%)$ of Set 1 devices; 1 wt% DPVBi doped PVK, 1 wt% DPVBi doped PVK/25nm DPVBi, and PVK/25nm DPVBi
Fig. 3. The brightness of DPVBi doped PVK/30 nm DPVBi devices, normalized to the value at 1 wt% DPVBi doping level.

For Set 2 devices, 11 devices, with different DPVBi thicknesses $t_{DPVBi}$, were evaporated by the combinatorial method and screened to find the optimal value. Mainly because of the large size of the substrate, Set 2 devices for combinatorial study were intentionally non-EG treated to make sure of a uniform thickness of the PEDOT-PSS layer and to prevent possible
abnormality due to the partial aggregation of PEDOT-PSS during EG treatment, which happens on the spin-coated large substrate. The brightest OLED, obtained with $t_{DPVBi} = 30$ nm, was ~3.5 times brighter than that with $t_{DPVBi} = 5$ nm (see Fig. 4). The highest efficiency, obtained at $t_{DPVBi} = 35$ nm was ~5 times that with $t_{DPVBi} = 5$ nm. So the optimal $t_{DPVBi}$ is 30 nm.

The emission from Set 2 was orange for $V < 15$V, but at higher bias the intensity of the blue DPVBi emission band increased, so the overall color of the OLEDs evolved to white (see Fig. 5). Below ~15V, it appears that the red emission band is stronger than the blue. Thus the recombination is more in the PVK layer: Since the HOMO level of PVK is 6.1 eV and that of DPVBi is 5.9 eV, the 0.2 eV barrier is a small barrier for hole transfer from PVK to DPVBi, especially compared to the 0.6 eV barrier from PEDOT-PSS to PVK. However, DCM2 is a very efficient energy transfer material, so holes will first fill the DCM2 sites and will migrate to the DPVBi layer only at higher bias. Another possible but unverified explanation is that the thermal evaporation of DPVBi layer may affect the morphology at the PVK/DPVBi interface and result in an increased barrier.

Finally, we consider devices with an EG-treated PEDOT-PSS hole injecting layer and a 30 nm-thick DPVBi layer. Figure 6 shows performance from this device. The maximum brightness is 9000 Cd/m$^2$, the maximum power efficiency $\eta_{\text{power}}$ is 0.3 %, and the maximum quantum efficiency $\eta_{\text{ext}}$ is 2.2 % with a lower operating voltage than Set 2 devices. Clearly, the additional EG treatment of the PEDOT-PSS layer lowered the threshold voltage from 15 V to 13 V and increased the brightness by 50%, through improved hole injection.
Fig. 4. The brightness and efficiency of Set 2 devices, normalized to the values at $t_{DPVBi} = 5$ nm.
Fig. 5. Color evolution of Set 2 devices for $V = 15, 20, \text{ and } 25 \text{ V at } t_{DPVBi} = 30 \text{ nm}$
Fig. 6. The power efficiency \( \eta_{\text{power}}(\%) \), external efficiency \( \eta_{\text{ext}}(\%) \), and brightness \( L(\text{Cd/m}^2) \) for last device.
Conclusions

In conclusion, the addition of the DPVBi layer on top of the DPVBi doped PVK improves device performance ~3 fold by reducing quenching by the cathode. The optimized device consist of [EG-treated PEDOT/PSS]/[0.5% DCM2 and 10% DPVBi-doped PVK]/[30 nm DPVBi]/[Alq3]/[CsF]/[Al]. They exhibit white emission with a brightness of 9000 Cd/m$^2$ at a current density of 1000 mA/cm$^2$ and the maximal quantum efficiency of 2.2% at 16 V.

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5. A DOUBLE-MODULATION PHOTOLUMINESCENCE-DETECTED MAGNETIC RESONANCE STUDY of MEH-PPV: THE SECOND HARMONIC RESONANCE

Abstract

Double-modulation (DM) photoluminescence (PL)-detected magnetic resonance (PLDMR) measurements on poly(2-methoxy-5-(2'-ethyl)-hexoxy-1,4-phenylene vinylene) (MEH-PPV) are described. The second harmonic signal obtained by DM-PLDMR shows that the process involved in the positive spin 1/2 resonance can be explained by the triplet-polaron quenching (TPQ) model.

Introduction

As shown in the previous chapter, ODMR is a very sensitive measurement technique, which can detect very small changes in an optical quantity (typically $5 \times 10^{-6} \leq \Delta I/I \leq 2 \times 10^{-3}$) induced by the magnetic resonance condition; the lock-in amplifier is one of the most essential components in the experiment. In lock-in detection, which compares the input to a reference signal that is modulated at a frequency $f_m$, only the component of the input affected by this modulation can be detected. Usually the Fourier component of the input at $f_m$ is detected, but the signal associated with the second harmonic at $2f_m$ also can be measured. These measurements reveal the contribution of bimolecular process to the quantity that is being modulated at $f_m$. 
Second harmonic measurements of the PL modulated at $f_l$ were reported by Partee et al. [1]. They showed that there is a bimolecular contribution to the PL and assigned it to delayed fluorescence (DF) from triplet-triplet annihilation to SEs. However, the DF could also be assigned to nongeminate polaron recombination to SEs. Extending the DM-PLDMR study described in the previous chapter to the response at $2 f_l$ enables us to determine the contribution of bimolecular process to the positive spin $1/2$ PLDMR.

**Experiments setup and background**

The measurement setup is similar to the DM-PLDMR, but the 2nd harmonic signal from the first lock-in amplifier is monitored rather than the signal at $f_l$. Since the measurements were limited ~100 kHz, the measurements on the 2nd harmonic were limited to 50 kHz. In this chapter, we focused on the behavior at $f_l = 10$ kHz at 20 K.

As discussed in the previous chapter, the two mechanisms assigned to the positive spin $1/2$ PLDMR are the delayed PL and the quenching mechanisms. In viewing these mechanisms, we recall that the delayed PL model starts with the assumption that the cross section for SE formation $\sigma_{SE}$ is higher than that for TE formation $\sigma_{TE}$. Consequently, off resonance the triplet polaron pair population is higher than the singlet polaron pair population, so at resonance there will be a net conversion of triplet polaron pairs to singlet polaron pairs due to spin mixing by the microwaves. The higher population of nongeminate singlet-polaron pairs results in the enhanced (delayed) PL.

The quenching model assigns the resonance to reduced quenching of SEs by the reduced TE and polaron population, as conformed by List et al. [2]. The reduction of TE and polaron population was further analyzed by Segal et al. [3]. They invoked TE-polaron quenching
(TPQ) model, a well-known interaction that results in quenching of the TE and excitation of the polaron to a higher energy state \( p^* \).

\[
T_1 + p^\pm \rightarrow p^{*\pm}. \tag{1}
\]

Then \( p^* \) will either relax to the lower state \( p \), or recombination with oppositely charged polaron to form a SE or TE:

\[
p^{*\pm} \rightarrow p^{\pm} + \text{phonons}, \tag{2}
\]

\[
p^+ + p^- \rightarrow S_1 \rightarrow S_0 + h\nu + \text{phonons}. \tag{3}
\]

with a similar reaction for forming a TE. However, quenching of a TE by a polaron is a spin-dependent process: When the spin 1 TE and the spin 1/2 polaron combine to form a composite state, that state will either be one of four spin 3/2 states, or one of two spin 1/2 states. However, due to spin conservation, the TE can be quenched to leave an excited \( p^* \) state only if the combined TE-polaron state is a spin 1/2 state. Hence, TE annihilation resulting in an excited \( p^* \) will occur only in 1/3 of the TE-polaron collisions. Under spin 1/2 (1) resonance condition, the polaron (TE) spin is flipped, converting spin 3/2 states to spin 1/2 states, enabling quenching of TEs and excitation of the polaron. Thus, the population of both TEs and polarons is thereby reduced by the magnetic resonance conditions.
Experimental results and discussions

The DM-PLDMR-detected of the PL component at $2f_i$ is shown in Fig. 1. As is clearly seen, the amplitude of the resonance $\Delta PL/PL \sim 10^{-1}$, i.e. it is much stronger than the resonance of the component at $f_i$ where $\Delta PL/PL \sim 10^{-3}$. Hence, it demonstrates that the resonance involves a bimolecular process. However, we note that both the delayed PL and TPQ models involve a bimolecular process: In the former, that process is nongeminate-polaron recombination; in the latter, it is the TE-polaron interaction. Hence, interestingly enough, DM-PLCMR at $f_i$ can discriminate between these two models, but the second harmonic detection at $2f_i$ cannot, at least not qualitatively. However, as shown by Segal et al. [3], the magnitude of the resonance at $2f_i$ is consistent with TPQ model.

Conclusions

The DM-PLDMR at the second harmonic of the PL, which is modulated at $f_i$ and monitors the contribution of bimolecular process to the PLDMR, is a very strong resonance ($\Delta PL/PL \sim 10^{-1}$). It is consistent with the model in which the spin 1/2 resonance is due to TE-polaron quenching mechanism, which is a bimolecular mechanism. However, since the delayed PL mechanism is also a bimolecular mechanism, it is also qualitatively consistent with the results at the second harmonic. We therefore conclude that the only measurement performed to date, which discriminates between the two models, is the DM-PLDMR described in the previous chapter. That measurement clearly supports the TPQ model, and invalidates the delayed PL model.
Fig. 1. Double-modulated PLDMR lineshape detected at $2 f_i = 2 \times 10$ kHz.
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6. SUMMARY AND GENERAL CONCLUSIONS

The Origin of the PLDMR enhancing signal and various aspects of the device physics of small molecular doped PLEDs were described and discussed. The difference between The delay model and the quenching model was explained. The microwave- and laser-modulation-frequency dependence of the PLDMR and DM-PLDMR, respectively, in MEH-PPV, invalidated the delay models, questioning reports of SE yields exceeding 25% in fluorescent OLEDs. Rather, the results were consistent with the quenching model where SEs are annihilated by TEs and polarons. For the device, the proper procedure for the treatment of the PEDOT/PSS layer with EG was suggested and a 10 fold enhancement was shown. The radiance of the device showed ~ 10 fold improvement with an addition of EG treated PEDOT/PSS layer and ~ 5 fold with 12 nm thick BCP and Alq₃ layer. With both layers, a 45 fold improvement in the brightness, 8 fold in the external quantum efficiency, and 7 fold in the power efficiency were achieved. Also, for WOLED, the addition of the DPVBi layer on top of the DPVBi doped PVK improved device performance ~3 fold by reducing quenching by the cathode. The optimized device structure was suggested and tested. They exhibited white emission with a brightness of 9000 Cd/m² at a current density of 1000 mA/cm² and the maximal quantum efficiency of 2.2% at 16 V.

Following the introduction to ODMR and OLEDs given in Chapter 1, new experimental method to verify two different models was described in Chapter 2. Double modulation PLDMR measurements on MEH-PPV were described. In these measurements, the laser excitation power was modulated at 1 kHz < ω_L/(2π) < 100 kHz, and the spin 1/2 PLDMR of the PL response at ω_L was monitored by microwave modulation at ω_M << ω_L. The frequency
response of the DM-PLDMR was inconsistent with the assumption that the PLDMR was due to delayed PL from nongeminate polaron recombination, which is the basis for previous predictions of the singlet exciton (SE)-to-triplet exciton (TE) ratio in organic light emitting devices. Rather, the frequency response is consistent with the assumption that the PLDMR was due to variations in the rate of quenching of SEs by TEs and polarons.

In chapter 3, combinatorial screening of PVK OLEDs was described. The brightness of the devices improved 10 fold by treating PEDO/PSS hole injecting layer with ethylene glycol (EG) and 5 fold with optimizing the thickness of the hole blocking layer (HBL) and electron transport layer (ETL) which results in increased electron injection. The optimized device exhibited a maximal radiance $R \approx 200 \text{ mW/cm}^2$ and external quantum efficiency $\eta_{\text{ext}} \approx 1.0 \%$ with an electroluminescence (EL) spectrum edge at 350 nm and peak at 410 nm.

WOLEDs based on red-emitting DCM2- and blue-emitting DPVBi-doped PVK was described in chapter 4. With increasing bias, the color coordinate evolved from orange to white. The performance of the devices was improved by inserting an additional 30 nm thick layer of DPVBi. The highest-performance device exhibited a maximal white brightness of $L \approx 9000 \text{ Cd/m}^2$ and an external quantum efficiency $\eta_{\text{ext}} \approx 2.2 \%$.

The last chapters of this thesis, Chapter 5, focused on the second harmonic signal measurements from double-modulation PLDMR measurements on MEH-PPV were described. The DM-PLDMR at the second harmonic of the PL, which was modulated at $f_L$ and monitors the contribution of bimolecular process to the PLDMR, was a very strong resonance ($\Delta PL/PL \approx 10^1$). It was consistent with the model in which the spin 1/2 resonance was due to TE-polaron quenching mechanism, which was a bimolecular mechanism. However, since the delayed PL mechanism was also a bimolecular mechanism, it was also
qualitatively consistent with the results at the second harmonic. We therefore concluded that the only measurement performed to date, which discriminated between the two models, was the DM-PLDMR described in chapter 3. That measurement clearly supported the quenching model, and invalidates the delayed PL model.
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