

Electroluminescence-detected magnetic-resonance study of poly(paraphenylenevinylene) (PPV)-based light-emitting diodes

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The strong electroluminescence (EL)-detected magnetic resonance of PPV-based light emitting diodes is compared to the conductivity (σ)- and photoluminescence (PL)-detected resonances. It provides direct evidence that polaron-to-singlet exciton conversion is responsible for the EL. In contrast to the narrow PL-enhancing resonance assigned to polaron recombination, strong EL- and σ -quenching resonances are attributed to the spin-dependent polaron-to-bipolaron decay. The half-field EL- and σ -detected resonances of two distinct triplet excitons is believed to result from triplet-triplet fusion to singlets.

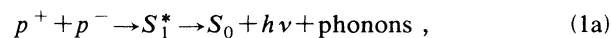
I. INTRODUCTION

Over the past 20 years, optically [i.e., photoluminescence (PL)]-detected magnetic resonance (ODMR) has provided invaluable insight into various radiative and nonradiative decay processes in a wide array of semiconductors.¹⁻⁶ In an ODMR experiment, microwave-induced changes in the PL are measured as the sample is subjected to a slowly swept dc magnetic field. Light-emitting diodes (LED's) have been available even longer than 20 years, yet the authors are aware of only one *electroluminescence* (EL)-detected magnetic-resonance study of any semiconducting system.⁷

EL in organic semiconductors has also been known for many years,⁸ but interest has been heightened by the recent improvements in efficiency that have been achieved in structures that use separate organic layers to control charge transport and provide the emissive layer.⁹⁻¹⁴ Some of the present authors recently reported that conjugated polymers could be used as the emissive layers in EL devices.¹⁵ Poly(paraphenylenevinylene) (PPV), prepared via a solution-processible precursor, was found to provide a robust material with high radiative quantum yield. The device structure was a ~ 100 -nm-thick polymer layer sandwiched between indium-tin oxide (ITO) or Al/Al₂O₃ as positive contact and Al as negative contact. The light generation efficiency of these devices could be raised to $\sim 1\%$ photon per electron through selection of a lower work-function metal for the negative electrode,¹⁶ and could also be raised by optimizing the emissive properties of the polymer layer through alteration to form copolymers.^{17,18} PPV and related polymers have considerable advantages over the traditional molecular materials since they are inherently stable and are well able to sustain the

high electric fields required for charge injection.

The electronic processes that govern the operation of these devices are of considerable interest. The nonlinear response of the π orbitals on the chain coupled to the chain geometry is believed to result in self-localization of the excited states. In nondegenerate ground-state systems such as PPV, these include singly charged spin- $\frac{1}{2}$ polarons (p^+ and p^-), doubly charged spinless bipolarons (bp^{++} and bp^{--}), and neutral singlet and triplet (polaronic) excitons (S_1 and T_1 , respectively).¹⁹⁻²² Burroughes *et al.*¹⁵ proposed that the operation of PPV-based LED's involved double charge injection of electrons and holes at opposite electrodes, transport through the polymer film as polarons, fusion of oppositely charged polarons to excitons, and radiative decay of the singlets,



where S_0 is the singlet ground state. Nonradiative intersystem crossing of singlets to a low-lying triplet state,



or direct nonradiative decay of the singlet excitons,



are clearly additional possible decay modes. If the lowest triplet level is within a phonon energy of half of that of S_1 , then fission of the latter into two triplets should also be considered:²³



Since the previous ODMR studies of poly(3-

alkylthiophenes) (P3AT's), PPV's, and polypara-phenyleneacetylenes (PPA's) (Refs. 3–6) indicated that the polaron levels are close to the singlet level, fission of singlets to polarons,

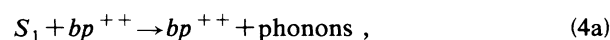
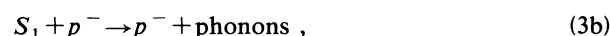
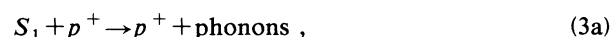


may also be significant. Reactions (1b)–(1e) clearly compete with the radiative decay. However, other decay mechanisms may also affect the EL and/or σ . If, as is widely believed,^{21,22} the mobility of bipolarons is significantly lower than that of polarons, the decay of polarons to bipolarons,

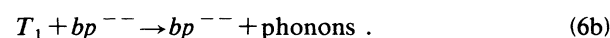
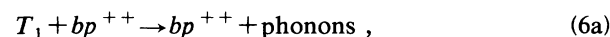
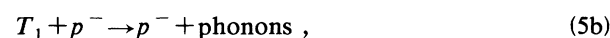
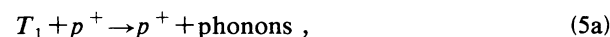


should decrease both the EL and σ .

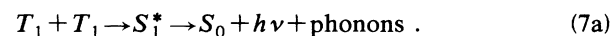
Charged excitations are also believed to act as effective nonradiative decay sites for singlet excitons:^{18,24,25}



Similar quenching of triplet excitons should also occur:



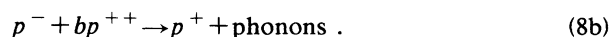
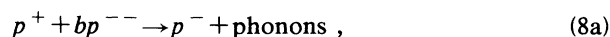
Of particular importance are triplet-triplet collisions that generate singlets:



These were established to be the source of the delayed fluorescence in, e.g., anthracene and related organic materials.^{23,26–31} They are thus suspected of being the source of the ODMR triplet powder patterns observed in P3AT's, PPV's, and PPA's.^{3–6} The spectral dependence of the half-field triplet ODMR of PPV is nearly identical to the PL spectrum, which is entirely consistent with Eq. (7a). The singlets may, of course, also decay according to reactions (1b)–(1e). Triplet-triplet pairs may obviously also directly decay nonradiatively:



It should be noted that reactions (1)–(7) do not exhaust the possible reactions and decay modes of singlets, triplets, polarons, and bipolarons. Others include, e.g., the decay of a bipolaron via collision with a polaron:



Detection of magnetic resonance through modulation of the EL may be particularly revealing since, in stark

contrast to conventional ODMR, all the excited states generated by carrier injection are inherently nongeminate, i.e., not created by geminate electron-hole pairs. The absence of any EL-detected magnetic-resonance study on any LED to date, save amorphous Si-based *p-i-n* structures,⁷ is therefore very surprising. The EL-detected resonance described in this paper is indeed strikingly different and much (~ 20 times) more intense than the ODMR. In addition to the ODMR (measured previously on PPV and its dialkoxy derivatives⁴) and EL-detected resonance, the conductivity (σ)-detected magnetic resonance is also described and compared to the EL-detected resonance. The results are entirely consistent with the above picture of transport of injected carriers as polarons and radiative decay via singlet generation [Eq. (1a)]. However, they also suggest that decay of polarons to bipolarons [Eq. (2)] is a significant competing process that may set an upper limit on the efficiency of such LED's. In addition, the EL- and σ -detected triplet-powder-pattern resonances suggest that singlet generation via triplet-triplet fusion [Eq. (7a)] may also contribute significantly to the EL. The dependence of the EL- and σ -detected magnetic resonance on the injected current and the temperature are consistent with the suggested role of charged excitations in the nonradiative quenching of singlet and triplet excitons [Eqs. (3)–(6)].

II. EXPERIMENTAL PROCEDURE

Two types of EL devices were studied. ITO-coated glass was used as the positive electrode in both cases. In type *A*, a layer of the methoxy-leaving group PPV precursor was then deposited by spin coating, and thermally converted to a ~ 60 -nm-thick partially conjugated copolymer, the PL of which is blueshifted with respect to PPV.¹⁷ The chemical structure of PPV and this copolymer are shown in Fig. 1. Thermally evaporated Al was then deposited on the polymer to provide the negative electrode. These devices have higher efficiency than equivalent devices fabricated with fully conjugated PPV, and allow some control of the emission color. Type-*B* LED's were prepared in a similar manner, but with a ~ 600 -nm-thick emissive layer of PPV prepared by the standard tetrahyrathiophenium-leaving group precursor.²² The negative contact was formed by a calcium layer deposited by thermal evaporation; this layer was pro-

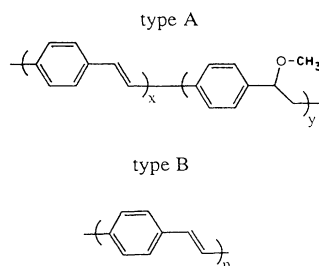


FIG. 1. Chemical structures of the emissive layers used in the two types of EL devices: (a) conjugated and/or nonconjugated copolymer (type-*A* LED); (b) PPV (type-*B* LED).

tected from oxidation and/or moisture by additional metallic layers. The additional complication involved in handling reactive calcium electrodes is offset by the improved efficiency and lowered forward-drive voltages. The spectra and resonances of type-*A* LED's were very similar to those of type *B*, but of poorer signal-to-noise ratio, due to the weaker EL. Unless otherwise noted, the results shown below were all obtained from type-*B* LED's.

The home-built ODMR spectrometer has been previously described.³⁻⁵ For EL- and σ -detected resonances, thin copper wire leads were inserted into the quartz dewar of the He gas flow cryostat to provide bias. The σ -detected resonance was recorded by lockin measurement of the microwave-induced changes in the current, resulting in similar changes in the voltage across a standard resistor connected in series with the LED.

III. RESULTS

The low-temperature EL and PL of both LED types is shown in Fig. 2. The EL closely matches the PL measured under the same conditions^{4,21} exhibiting strong vibrational coupling between the excited and ground states.

The full-field ODMR of a type-*B* LED is shown in Fig. 3. The main narrow ($\Delta H_{1/2} \approx 13G$) PL-enhancing resonance was previously assigned to magnetic-resonance enhancement of singlet exciton generation by intrachain "distant-pair" polaron recombination.³⁻⁶ The full- and half-field triplet powder patterns are also similar to the previously reported spectra⁴⁻⁶ and are consistent with magnetic-resonance enhancement of singlet generation from triplet-triplet fusion. The resulting zero-field-splitting parameters³² D ($\approx 540G$) and $0 \leq E \leq D/3$ suggest that the triplets in PPV and poly(3-alkylthiophenes),

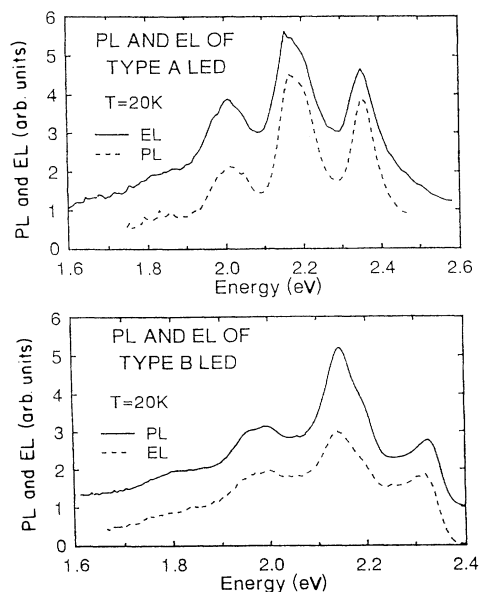


FIG. 2. PL and EL spectra of type-*A* (PPV copolymer) and type-*B* (PPV) LED's at 20 K. The EL of PPV (type *B*) is red-shifted by 100 meV relative to the room-temperature spectrum (see Ref. 14).

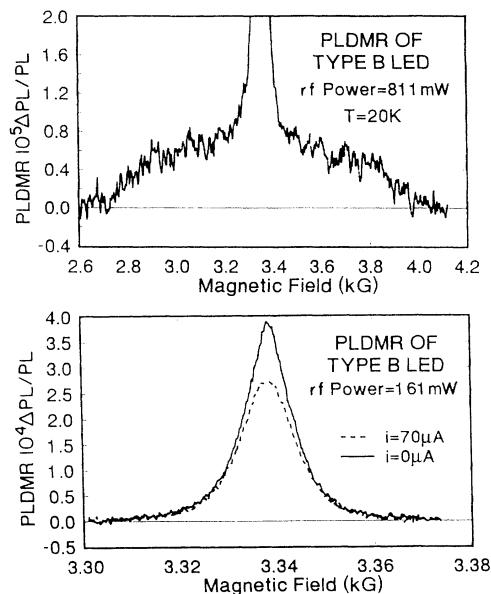


FIG. 3. (a) The photoluminescence (i.e., optically) -detected magnetic resonance (PLDMR or ODMR) of a type-*B* LED at 20 K, excited at 488 nm. Note the main narrow resonance and the broad triplet powder pattern underneath. (b) The main narrow ODMR without bias, and during $70\text{-}\mu\text{A}/\text{mm}^2$ current injection.

where $D \approx 620G$ and $E \approx D/3$, are only slightly larger than a phenylene or thiophene ring.

Figure 3 also shows the effect of a dc bias on the main narrow ODMR. As is clearly seen, it decreases $\Delta L/L$, in elegant agreement with the assignment to fusion of p^+ and p^- : As the bias sweeps the oppositely charged polarons in opposite directions, their recombination rate is reduced. Since the polaron levels are close to the singlet (weakly-coupled) exciton level,³⁻⁶ the applied bias may also induce fissions of singlets into p^+ and p^- ; on the other hand, its effect on the lower-energy, tightly coupled triplets is probably weaker. In addition, injection of carriers increases the charged excitation density, which may reduce the spin dependence of the decay processes (see Sec. IV below). Therefore, the applied bias not only reduces the PL, but also reduces the relative intensity $\Delta PL/PL$ of the narrow PL-enhancing resonance.

Figure 4 displays the main narrow EL-quenching resonance of a type-*B* LED at $J = 50 \mu\text{A}/\text{mm}^2$, $V = 30.7 \text{ V}$, and $T = 20 \text{ K}$. The main narrow EL-detected resonance of type-*A* LED's was similar; the line shape and g value were temperature independent from 20 to 296 K. The difference between this EL-quenching and the main narrow PL-enhancing resonances is obvious and striking. The temperature dependences of the relative amplitudes $\Delta L/L$ of the two resonances also differ sharply: When warming from 20 to 296 K, the PL-detected resonance decreases by over an order of magnitude, while the EL-detected resonance decreases by only $\sim 50\%$. Figure 4 also displays the main narrow σ -quenching resonance of the same type-*B* LED under the same conditions as in Fig. 3. The σ -detected resonance of type-*A* LED's was similar, and essentially identical to the EL-detected reso-

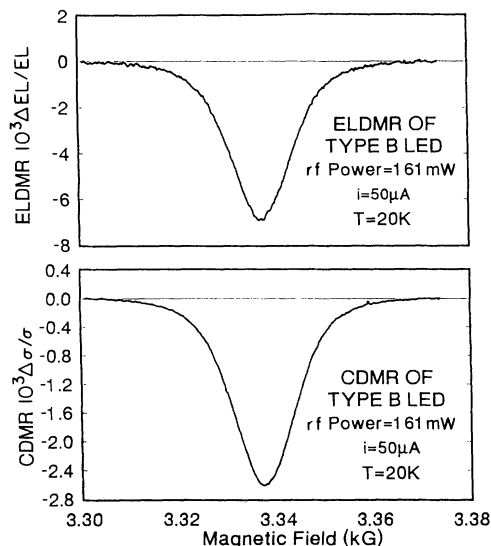


FIG. 4. The main narrow EL- and σ -detected magnetic resonance (ELDMR and CDMR, respectively) spectra of a type-*B* LED at 20 K and $50 \mu\text{A}/\text{mm}^2$.

nance. Its intensity $|\Delta\sigma/\sigma|$ was essentially temperature independent. When biasing below the EL forward bias threshold voltage, an identical photoconductivity (σ_{ph})-detected resonance was also observed. Finally, we note that the g values of the PL-, EL-, σ -, and σ_{ph} -detected resonances are all identical within the available experimental precision of ± 0.0003 .

The EL- and σ -detected resonances saturate at quite low current densities ($\sim 25 \mu\text{A}/\text{mm}^2$) for a type-*B* LED (Fig. 5): $|\Delta EL/EL|$ and $|\Delta\sigma/\sigma|$ decrease from 5.7×10^{-3} and 3.5×10^{-3} , respectively, at $I \leq 25 \mu\text{A}$ ($V \leq 36.6 \text{ V}$) to 1.85×10^{-3} and 5.3×10^{-4} , respectively, at $I = 803 \mu\text{A}$ ($V = 43.5 \text{ V}$).

The EL- and σ -detected resonances of type-*B* LED's also clearly display the half-field $\Delta m_s = 2$ transitions of triplet (polaronic) excitons (Fig. 6); the strong main narrow quenching resonance obscures the full-field powder patterns due to the $\Delta m_s = 1$ transitions. Both LED types show similar behavior, but the EL-detected resonance is strikingly different from the σ -detected resonance: Both are clearly due to two distinct triplets, yet while one is

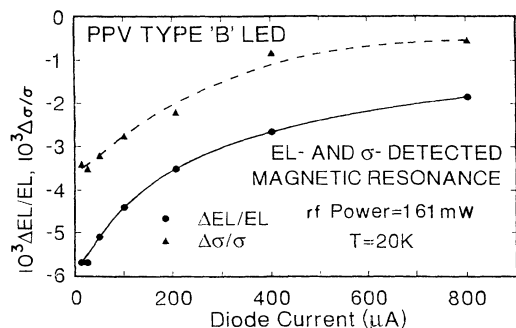


FIG. 5. The dependence of the intensity of the main narrow EL- and σ -detected magnetic resonance on the injected current.

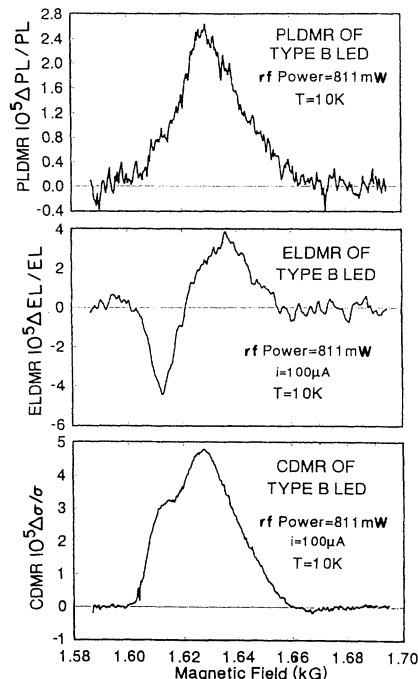


FIG. 6. The half-field PLDMR (i.e., ODMR) without bias, and EL- and σ -detected magnetic resonance (ELDMR and CDMR, respectively) of a type-*B* LED at 5 K and $100 \mu\text{A}/\text{mm}^2$ forward current injection. The resonance is due to the $\Delta m_s = 2$ transitions of two distinct triplet excitons at 1.61 and 1.63 kG. See also Refs. 4–6.

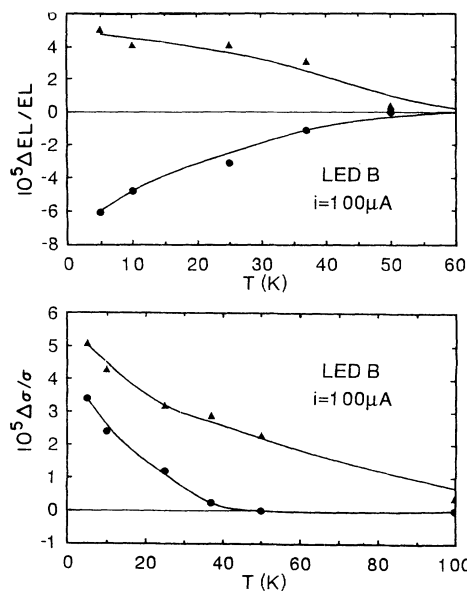


FIG. 7. The temperature dependence of the intensity of the half-field triplet exciton EL- and σ -detected magnetic resonances (ELDMR and CDMR, respectively). Triangles are the values of the higher-field pattern at 1.63 kG, whereas circles are those of the lower-field pattern at 1.61 kG.

EL quenching and the other EL enhancing, both are σ enhancing. Figure 7 shows that the signals from both excitons sharply weaken with increasing temperature, but with distinct behavior. The EL-detected resonance of neither is observable above 50 K, while the σ -detected resonance of the broader (higher-field) triplet is still faintly observable at 100 K.

IV. DISCUSSION

The foregoing results, which are summarized in Table I, all illustrate the wealth of detailed information on the electronic processes that govern the EL of polymer-based LED's that can be obtained from EL- and σ -detected magnetic resonance. The first noteworthy observation is that the g value of the strong narrow symmetrical EL- and σ -detected resonances (Figs. 3 and 4) is identical to that of the main narrow PL-enhancing ODMR. The latter was previously assigned to magnetic-resonance enhancement of nongeminate intrachain p^+p^- fusion to singlet excitons [Eq. (1a)].³⁻⁶ Within this assignment, the narrow EL- and σ -detected resonances then provide the clearest evidence to date for the mode of generation of the singlets that produce the EL, i.e., that of double charge injection, followed by polaron formation, and nongeminate p^+p^- fusion to form excited singlet excitons. The response of the two types of LED's fabricated with different emissive layers and different electron-injecting contacts was essentially identical. It is therefore believed that this response is intrinsic to the polymers, and not specific to the nature of defects in the polymer or to the character of the electrodes or electrode interfaces.

The quenching nature of the narrow σ - and EL-detected resonances at $g \approx 2.0023$ clearly suggest an intrinsic underlying spin-dependent decay mechanism competing with the transport and EL. Although spin-dependent nonradiative trapping by interface defects would also yield such resonances, they would be expected to vary within the diode structure. In addition, they should also exhibit an ESR or light-induced ESR; yet no such signals could be detected from these diodes. In searching for an intrinsic mechanism, it is clear that the sought after picture must be able to account for the signs that are opposite to that of the PL-detected resonance, since both the EL and PL involve singlet excitons produced via p^+p^- fusion.

An intrinsic process consistent with much of the available results is the spin-dependent fusion of two like-charged spin- $\frac{1}{2}$ polarons to spinless bipolarons [Eq. (2)].

Bipolarons are believed to be the long-lived charged excitations in PPV, of mobility much lower than that of polarons.^{21,22} Magnetic-resonance enhancement of bipolaron production would then reduce both the current through the polymer and the polaron population available for EL. In addition, we note that charged excitations are believed to act as effective nonradiative decay sites for singlet excitons [Eqs. (3) and (4)],^{18,24,25} and this should also contribute to the EL-quenching effect.

The observed saturation of the quenching EL- and σ -detected resonances at higher current densities is not entirely understood at present, but three possible explanations should be considered: (i) The imbalance of electron and hole injection is probably reduced at higher current densities, thus weakening these resonances; (ii) a higher frequency of like-charged polaron-polaron scattering events reduces the spin dependence of bipolaron formation at high current densities; (iii) higher charge-injection rates may be saturating bipolaron generation, if it preferentially occurs at charge-trapping sites.

The weak temperature dependence of the EL- and σ -quenching resonances contrast sharply with the strong decay of the PL-detected resonance upon warming to room temperature. It was previously suggested that the latter may reflect the temperature dependence of the polaron spin-lattice relaxation rate T_1^{-1} .^{3,4} This interpretation would imply a similarly strong temperature dependence of the EL- and σ -detected resonances. We are thus compelled to reexamine the source of the temperature dependence in both cases. In an alternative picture, consistent with the behavior of all resonances, the observed dependence is governed by the dynamics of polarons and mobile triplet excitons. As the temperature increases, their diffusivity increases (due, e.g., to thermally activated hopping), resulting in a weaker spin dependence of the PL. In the diodes, however, polaron motion is determined by the product of their drift mobility and the electric field, while that of the neutral excitons is limited by their diffusivity, as in ODMR measurements. These two very different conditions may be responsible for the distinct temperature dependence of the ODMR as compared to the EL- and σ -detected resonances. The strong temperature dependence of the EL- and σ -detected half-field triplet resonances (Fig. 7) is entirely consistent with this interpretation.

The appearance of two EL- and σ -detected half-field triplet resonances (Fig. 6) is also striking. The lower field implies a more strongly localized triplet than the higher-field one. These more localized triplets may possibly de-

TABLE I. Summary of the various resonances.

ODMR type	Narrow resonance	Full-field triplet pattern	Half-field triplet pattern
PL detected	enhancing	enhancing	higher-field enhancing
EL detected	quenching	unobserved ^a	lower-field quenching
σ - detected	quenching	unobserved ^a	higher-field enhancing
			lower-field enhancing
			higher-field enhancing

^aObscured by the strong narrow quenching resonance.

cay by triplet-triplet fusion [Eq. (7)] near the electrode-film interfaces. As they fuse, the resulting singlets [Eq. (7a)] either rapidly decay or separate into p^+ and p^- . However, the presumably higher density of bipolarons and proximity of the electrode, which sweeps the appropriate polarons from this region, would reduce the radiative yield from these singlets [Eq. (4)].^{18,23,24} The overall effect of these processes occurring near the electrodes would be to reduce the contribution of triplets to the EL but add to their contribution to σ .

V. SUMMARY

In summary, the effects of X-band magnetic-resonance conditions on the PL, EL, and conductivity (σ) of two types of PPV-based LED's were described and discussed. The optically (i.e., PL)-detected magnetic resonance (ODMR or PLDMR) is identical to that of films of PPV and its derivatives, which was previously reported. It includes a main narrow PL-enhancing resonance at $g \approx 2.0023$ attributed to fusion of polarons to singlet excitons which then decay radiatively, and PL-enhancing full- and half-field triplet pattern resonances attributed to singlet generation via triplet-triplet fusion. The main EL- and σ -detected magnetic resonance (ELDMR and CDMR, respectively) features are intense narrow EL- and σ -quenching lines at the same g value. Their temper-

ature and current-injection dependence are consistent with their tentative assignment to magnetic-resonance enhancement of fusion of like-charged polarons to spinless bipolarons. While these intense resonances obscure any full-field (i.e., at $g \sim 2$) triplet powder patterns, the half-field resonances of two distinct triplets are clearly observed. While both are σ enhancing, the lower-field triplet, which is less symmetric and more localized, is EL quenching. Their temperature dependence is consistent with assignment to bulk- and near-interface triplet fusion. Further studies of PL-, EL-, σ -, and σ_{ph} -detected magnetic resonance in other polymer LED's are in progress, and should provide important information needed to construct a detailed model of the many electronic processes present in these devices.

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