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# Electroluminescence-detected magnetic resonance studies of Pt octaethyl porphyrin-based phosphorescent organic light-emitting devices

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The electroluminescence (EL)-detected magnetic resonance (ELDMR) of 0, 1, 2.5, 6, and 20 wt. % Pt octaethyl porphyrin (PtOEP)-doped tris(8-hydroxyquinolinate) Al ($\mathrm{Alq_3}$)-based phosphorescent multilayer organic light-emitting devices (OLEDs) is described. In 1 wt. %-doped devices, the ELDMR from the PtOEP and $\mathrm{Alq_3}$ emission are both very similar to that of undoped devices. They exhibit a positive (EL-enhancing) spin-$\frac{1}{2}$ polaron resonance at $10 \leqslant T \leqslant 50$ K, whose magnitude $\Delta I_{\mathrm{EL}}/I_{\mathrm{EL}}$ increases with current and weakens with increasing $T$, and a negative (EL-quenching) resonance at 50 K$\leqslant T$, which grows with $T$. At 295 K, $|\Delta I_{\mathrm{EL}}/I_{\mathrm{EL}}|$ decreases with current. The enhancing resonance is attributed to the magnetic-resonance reduction of singlet exciton (SE) quenching by a reduced population of polarons and host triplet excitons (TEs). The reduction in the TE and polaron populations is, in turn, due to the spin-dependent annihilation of host TEs by polarons, which is enhanced under magnetic resonance conditions. Since the polaron and host TE populations are much greater than the SE population, the polaron-host TE interaction is identified as one of the major interactions which govern the dynamics of the excited states in OLEDs. The quenching resonance is attributed to magnetic resonance enhancement of formation of dianions at the organic/cathode interface, which increases the charge density at that interface, and consequently the rate of field-induced host SE dissociation. Both the enhancing and quenching resonances weaken as the PtOEP concentration increases; at 6 wt. %, the enhancing resonance is undetectable and the quenching resonance is very weak ($|\Delta I_{\mathrm{EL}}/I_{\mathrm{EL}}| \sim 2\times10^{-5}$). The results can be explained by assuming that the ELDMR of the guest emission is due to the effect of magnetic resonance conditions on the host SEs. A rate equation model is established to explain the evolution of the ELDMR with dye concentration. Since the foregoing quenching mechanisms are believed to be responsible for the drop in the efficiency $\eta_{\mathrm{ext}}$ of fluorescent OLEDs at high current, the present results indicate that they are also responsible for the drop in $\eta_{\mathrm{ext}}$ of phosphorescent OLEDs at high current. In the 20 wt. %-doped devices, the spin-$\frac{1}{2}$ polaron resonance is negative at all $T$, and $|\Delta I_{\mathrm{EL}}/I_{\mathrm{EL}}|$ and the resonance linewidth decrease with increasing $T$; $|\Delta I_{\mathrm{EL}}/I_{\mathrm{EL}}|$ is weakly current dependent at both 20 K and 295 K. This behavior is consistent with the dianion model, if the dianion density decreases with increasing $T$. This is probably due to a low barrier for thermal dissociation of the dianions.

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## I. INTRODUCTION

The report on bright green electroluminescence (EL) from a bilayer device based on tris-(8-hydroxyquinolinate) Al ($\mathrm{Alq_3}$) (Ref. 1) spawned extensive studies on organic light emitting devices (OLEDs), both small molecule-[1,2] and polymer-based.[3,4] Extensive efforts have resulted in dramatic improvements in the brightness, efficiency, and lifetime of these devices. Doping the emitting layer with a guest molecule is one of the most effective approaches to improve device efficiency (as quantified by the external quantum efficienty $\eta_{\mathrm{ext}}$) and lifetime. While doping with a fluorescent dye restricts the internal quantum efficiency $\eta_{\mathrm{int}}$ to 25%,[2] doping with a phosphorescent dye removes that restriction.[5–9] The phosphorescent dyes incorporate a heavy metal atom, e.g., Pt or Ir, to enhance the spin-orbit interaction. Indeed, devices doped with Pt octaethyl porphyrin (PtOEP) and fac tris(2-phenylpyridine) iridium $[\mathrm{Ir(ppy)_3}]$ have achieved $\eta_{\mathrm{ext}}=9\%$ (Ref. 10) and 19.2%,[11] respectively. In principle, both fluorescence- and phosphorescence-based EL are due to the radiative decay of excitons generated by recombination of carriers injected from the electrodes in the emitting layer. This recombination and other processes involving the spin-$\frac{1}{2}$ negative and positive polarons ($p^-$ and $p^+$, respectively), into which the holes and electrons convert upon injection, are spin dependent. Hence, various optically detected magnetic resonance (ODMR) measurements such as photoluminescence (PL)-, EL-, and electrically (i.e., current-) detected magnetic resonance (PLDMR, ELDMR, and EDMR, respectively) have proven to be powerful tools in elucidating the photophysics of luminescent $\pi$-conjugated materials and OLEDs.[12–38] This paper describes an ELDMR study of PtOEP-doped $\mathrm{Alq_3}$-based phosphorescent OLEDs.

In poly($p$-phenylene vinylene) (PPV)- and poly ($p$-phenylene ethynylene) (PPE)-based OLEDs, the ELDMR and EDMR included narrow negative (i.e., current- and EL-quenching) and positive (i.e., current-enhancing and EL-enhancing) spin-$\frac{1}{2}$ polaron resonances, and half-field positive and negative triplet resonances.[14,15,21,23]

The positive spin-$\frac{1}{2}$ ELDMR was attributed to the reduction in the population of polarons at the field-for-resonance, and consequent reduced quenching of singlet excitons (SEs) by polarons (see Sec. III below).[19–23,27,29,34–36] The origin of the reduction in the population of polarons—and of the trip let excitons (TEs) as well—was very recently established to be due to the enhanced spin-dependent annihilation of TEs by polarons.[37,38] Since the TE and polaron populations are much larger than that of SEs under normal operating conditions (see Sec. III A below), the ODMR results identify the TE-polaron interaction as one of the major interactions which govern the dynamics of the excited states in $\pi$-conjugated materials and OLEDs.

The negative spin-$\frac{1}{2}$ resonance was attributed to the enhanced spin-dependent formation of positive or negative spinless bipolarons ($bp^{++}$ and $bp^{--}$, respectively).[14,15,18,21–23,34,35]

In Alq$_3$-based small molecular OLEDs, positive spin-$\frac{1}{2}$ ELDMR and EDMR are observed at $T \leqslant 60$ K and negative spin-$\frac{1}{2}$ ELDMR and EDMR, whose respective amplitudes $|\Delta I_{\mathrm{EL}}/I_{\mathrm{EL}}|$ and $|\Delta J/J|$ increase with $T$, are observed at $T \geqslant 60$ K.[34,35] $|\Delta I_{\mathrm{EL}}/I_{\mathrm{EL}}|$ and the current density ($J$) dependence of the room temperature quenching ELDMR are found to be strongly dependent on the organic/cathode buffer layer. These results suggest that dianions formed at the organic/cathode interface, predicted by several theoretical studies[39–41] and confirmed by experimental studies,[24,42,43] are responsible for the negative spin-$\frac{1}{2}$ EDMR and ELDMR.

The current ELDMR study of PtOEP-doped Alq$_3$-based OLEDs provides evidence that the quenching of guest TEs by polarons is negligible compared to the quenching of host SEs and TEs by these charges: The negative (EL-quenching) ELDMR of the phosphorescence is shown to be due to the same mechanism as the negative ELDMR of the source host SEs, which otherwise transfer their energy to the guest TEs. A rate equation model, which provides a quantitative assessment of this process, is described.

As the PtOEP concentration is increased, the polaron resonance becomes quenching at both 20 K and 295 K. At high PtOEP concentration, both the magnitude and the linewidth of the quenching resonance decrease as $T$ increases. This agrees well with the dianion model if the dianion density at low $T$ is higher than at room temperature. This is probably due to a low barrier for thermal dissociation of the dianions.

## II. EXPERIMENTAL PROCEDURE

The structure of the devices used in this study was [indium tin oxide (ITO)]/[5 nm copper phthalocyanine (CuPc)]/[50 nm 4,4′-bis((1-naphthyl)-phenylamino)-1,1′-biphenyl ($\alpha$-NPD)]/[40 nm $x$% PtOEP:Alq$_3$]/[10 nm Alq$_3$]/[1 nm CsF]/Al, where $x$=0, 1, 2.5, 6, and 20 wt. % (see Fig. 1). The CsF buffer layer improves electron injection and device efficiency dramatically.[44–46]

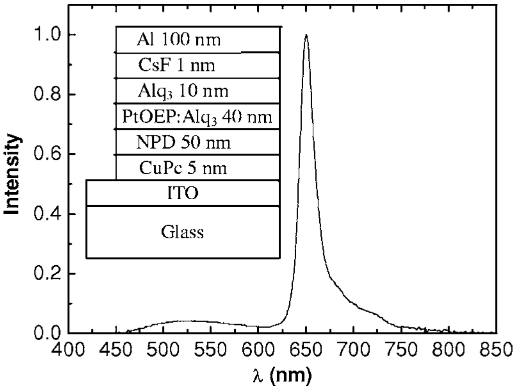

FIG. 1. The device structure and emission spectra of 1 wt. % PtOEP doped Alq$_3$ OLED. The PtOEP emission band around 650 nm dominates the EL, but the host Alq$_3$ emission band around 520 nm is still clearly visible.

The devices were fabricated in a $\sim 10^{-6}$ torr vacuum chamber, which is installed in a pure Ar-filled glove box, typically containing $<1$ ppm oxygen and water. Prior to deposition of the organic layers, the ITO-coated glass was etched in diluted aquaregia and thoroughly cleaned by detergent, distilled water, isopropanol, and acetone, and blown dry with Ar.[46,47] The deposition rates were monitored by a Maxtek TM-100 thickness monitor. The organic materials were deposited at $\sim 1.0$ Å/s by thermal vacuum evaporation. PtOEP and Alq$_3$ were codeposited and the deposition rates were carefully monitored to obtain the desired PtOEP concentration. The CsF and Al cathode were deposited at $\sim 0.1$ and $\sim 4.5$ Å/s, respectively. The active area of the OLED, defined by the overlap of the ITO and Al electrodes, was $\sim 20$ mm$^2$.

The ODMR system used in this study was described previously.[12–15,18,20,21,23,27–30,34–36] The OLED was inserted into the quartz dewar of an Oxford Instruments He gas flow cryostat; the quartz dewar was inserted into an optically accessible X-band microwave cavity. Bias was applied to the OLED and the EL was collected by a Si photodiode. The ELDMR was measured by lock-in detection of the changes in the EL induced by the $\sim 360$ mW, $\sim 9.45$ GHz microwaves chopped at 100 Hz.

## III. RESULTS AND DISCUSSION

Figure 1 shows the device structure and emission spectra of the 1 wt. %-doped device. Although the PtOEP guest emission band dominates the EL of this lightly doped device, the Alq$_3$ host emission is still clearly visible.

### A. The negative and positive spin-$\frac{1}{2}$ ELDMRs

Figure 2 shows the spin-$\frac{1}{2}$ ELDMR at various levels of the injected current density $J$ at (a) 15 K and (b) 295 K of the PtOEP red emission in a 1 wt. %-doped device. At 15 K the resonance is positive (EL-enhancing), and as $J$ increases, its amplitude $\Delta I_{\mathrm{EL}}/I_{\mathrm{EL}}$ increases, approximately as $J^{0.5}$, indicating a bimolecular process.[29,34,35] At 295 K, the resonance is negative (EL-quenching) and $|\Delta I_{\mathrm{EL}}/I_{\mathrm{EL}}|$ decreases as $J$ increases. Both the low- and high-$T$ resonances behave similar to those of undoped Alq$_3$-based fluorescent OLEDs with a CsF buffer layer.[34,35] Hence, they are attributed to the same mechanisms, which we now discuss in detail.

As mentioned in Sec. I above, in all but the most heavily (20 wt. %) doped devices, the negative spin-$\frac{1}{2}$ ELDMR is attributed to the enhanced formation of negative bipolarons at the organic/cathode interface. In Sec. III C below we pro-

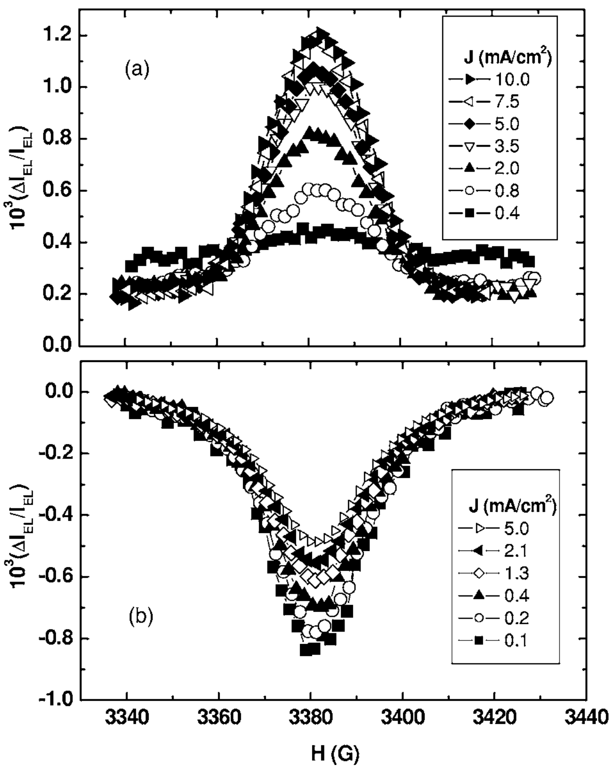

FIG. 2. The spin-$\frac{1}{2}$ ELDMR of the red PtOEP phosphorescence in 1 wt. % PtOEP-doped $Alq_3$ OLEDs at different currents at (a) $T=15-20$ K and (b) 295 K.

vide a rate equation analysis of this negative ELDMR.

The $g$-value, linewidth, temperature dependence, and current dependence of the low-temperature positive ELDMR are similar to the $g$-value, linewidth, temperature dependence, and laser power dependence of the positive PLDMR of $\pi$-conjugated polymers and $Alq_3$.[12,29,34,35] The positive ELDMR is therefore attributed to the same mechanism. This mechanism, however, has been controversial. It was initially suggested to be magnetic resonance enhancement of radiative polaron pair recombination.[12–15] This mechanism, however, is inconsistent with the voluminous evidence that polaron pairs do not decay directly to the ground state, but rather form SEs and triplet excitons (TEs).[4] A second mechanism was suggested to be magnetic resonance enhancement of the formation of TEs followed by TE-TE annihilation to SEs, resulting an enhanced PL due to enhanced delayed fluorescence.[26] This mechanism clearly requires that the population of TEs increase at the field-for-spin-$\frac{1}{2}$-resonance. Yet photoinduced absorption (PA)-detected magnetic resonance (PADMR) measurements showed clearly that at that field-for-resonance both the polaron and TE populations decrease.[16,29]

A third mechanism developed to account for the resonance invoked magnetic resonance enhancement of delayed PL due to nongeminate polaron pair recombination ("the delayed PL model").[31–33] This mechanism, however, requires that the cross section for SE formation by polaron pairs in the singlet configuration $\sigma_{SE}$ be greater than the cross section for TE formation by polaron pairs in the triplet configuration $\sigma_{TE}$.[31–33] This relation between $\sigma_{SE}$ and $\sigma_{TE}$ and the delayed PL model are inconsistent with various experimental results. (i) The relation between $\sigma_{SE}$ and $\sigma_{TE}$ is inconsistent with the various results that indicate that the yield of SEs in both $Alq_3$ and PPV OLEDs is not greater than 25%.[48,49] (ii) The delayed PL model is inconsistent with double modulation PLDMR (DM-PLDMR) measurements on a PPV derivative, which show that the contribution of the prompt PL to the PLDMR is similar to that of the delayed PL.[37,38] (iii) Combined thermally stimulated luminescence (TSL), which is due to delayed PL from (effectively) nongeminate polaron recombination, and PLDMR measurements, on another PPV derivative, show that the TSL increases ~30-fold but the PLDMR decreases ~6-fold when the excitation photon energy is increased from 2.7 to 3.4 eV.[50]

The fact that the polaron population decreases at resonance invoked the "quenching model."[19–23,27,29,30] *This model, which is the only model consistent with all of the ODMR results reported to date, is based on quenching of SEs by polarons and TEs.* The reduction of the polaron and TE populations under the spin-$\frac{1}{2}$ resonance conditions reduces the quenching of SEs and thus results in a positive PLDMR and ELDMR. The quantitative quenching model developed by List *et al.*[29] was found to be in excellent agreement with experimental results. Very recently, Segal *et al.* developed a comprehensive rate equation model, which assumes that the reduction in the polaron and (host) TE population is due to enhanced annihilation of host TEs by polarons.[38] This is a well-known spin-dependent process.[51] It is spin dependent because the annihilation of the TE is allowed only if the composite TE-polaron state is in the doublet (spin-$\frac{1}{2}$) configuration. Yet only two of the six composite states of the TE-polaron are in the doublet configuration; the other four are in the quadruplet (spin-$\frac{3}{2}$) configuration. Thus, this annihilation is enhanced under magnetic resonance conditions. This enhancement not only reduces the population of the TEs. It also reduces the population of the polarons, because the polaron which annihilates the host TE is excited (probably from a trapped state) by the TE energy it absorbs. Hence, following its excitation, it contributes to the current (hence the positive EDMR) and the probability that it will recombine with another oppositely charged polaron increases (hence the reduction in the polaron population and the reduced quenching of SEs by either TEs or polarons). *Interestingly, this mechanism is the only mechanism proposed to date, which accounts for the positive low-temperature spin-$\frac{1}{2}$ EDMR.*[35] In this context, it should be noted that the TE-polaron interaction is not a marginal process in photoexcited $\pi$-conjugated materials or OLEDs: under normal photoexcitation conditions, the steady-state polaron and TE populations are much larger than the SE population: While the SE photogeneration rate is ~100 times that of the polaron and TE generation rates, the SE lifetime of ~1 ns is $>10^4$ times shorter than the $>10$ $\mu$s lifetime of the polarons and TEs.[20,37,38] We therefore attribute the enhancing spin-$\frac{1}{2}$ ELDMR to reduced quenching of SEs by a reduced population of polarons and host TEs, which, in turn, is due to enhanced annihilation of host TEs by polarons.

It is important to note that the ELDMR shown in Fig. 2 is due to the phosphorescent red emission from TEs in PtOEP.

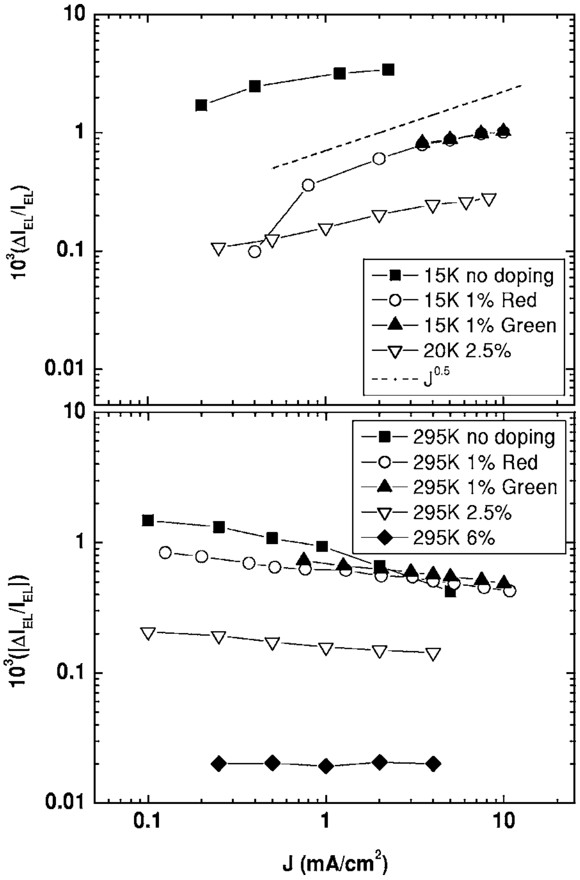

FIG. 3. The current $J$-dependence of the positive spin-$\frac{1}{2}$ ELDMR at 15–20 K and the negative spin-$\frac{1}{2}$ ELDMR at 295 K of 0, 1, 2.5, and 6 wt. % PtOEP-doped $Alq_3$ OLEDs.

However, we now demonstrate that the quenching of the guest TEs by polarons and host TEs is not likely to be as effective as the quenching of host SEs by these species. To this end, we compared the contributions of the red PtOEP phosphorescence and green $Alq_3$ fluorescence to the positive and negative spin-$\frac{1}{2}$ ELDMR.

Figure 3 shows the $J$ dependence of the positive (at 15 or 20 K) and negative (at 295 K) ELDMR of the 0, 1, 2.5, and 6 wt. % PtOEP: $Alq_3$ devices. In the 1 wt. % device, the behavior of the ELDMR of the red and green emission bands is identical, indicating either (a) direct quenching of the guest TEs by polarons and host TEs, as effective as the quenching of host SEs, or (b) an indirect quenching process, in which quenching of the PtOEP TE emission is due to quenching of the $Alq_3$ SEs which otherwise transfer their energy to PtOEP.

If the first scenario is correct, then the ELDMR should be largely independent of the PtOEP doping concentration. However, as seen in Fig. 3, both the positive and negative ELDMRs decrease rapidly as the PtOEP concentration increases. Indeed, in the 6 wt. % PtOEP-doped device, the positive spin-$\frac{1}{2}$ ELDMR is unobservable, and the negative resonance at 295 K is very weak ($|\Delta I_{EL}/I_{EL}| \sim 2\times 10^{-5}$) over the whole range of $J$. We therefore conclude that quenching of guest TEs by either polarons, host TEs, or dianions is far less significant than quenching of host SEs, and that the PtOEP phosphorescence ELDMR is due to quenching of the host SEs, which are a source of the PtOEP TEs.

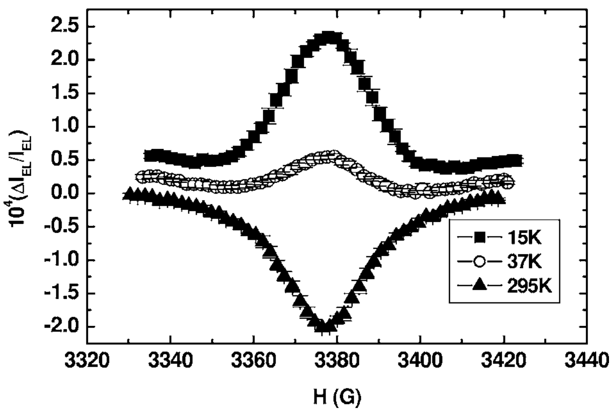

FIG. 4. The spin-$\frac{1}{2}$ ELDMR of 2.5 wt. % PtOEP: $Alq_3$ OLED at 15, 37, and 295 K.

Figure 4 shows the spin-$\frac{1}{2}$ polaron ELDMR of the 2.5 wt. %-doped OLED at three temperatures. Not only is the magnitude of the resonances small compared to the 1 wt. %-doped devices, but the resonance has a negative component even at 15 K. Figure 4 suggests that the "transition temperature" from the low-$T$ positive to the high-$T$ negative resonance is ~30 K; in undoped $Alq_3$ OLEDs this transition occurs at ~60 K rather than ~30 K.[34,35]

In the previous study by Li *et al.*,[35] the enhanced dianion formation was suggested to generate the negative resonance simply through its negative effect on the injected current. However, this scenario would entail that the negative resonance be largely independent of the PtOEP concentration, in contrast to the observed dependence, in which the negative resonance weakens with increasing PtOEP content. *Consequently, it is believed that the enhanced dianion formation induces the negative resonance due to its effect in enhancing the charge density of the sheet of charge at the organic-cathode interface. This enhanced charge density enhances the field-induced host SE dissociation rate*. At low PtOEP content, this field-induced quenching competes with the Förster energy transfer much more effectively than at high PtOEP content, where both the Förster and Dexter transfer rates are much higher.

### B. The half-field TE ELDMR

The ODMR of luminescent $\pi$-conjugated materials and OLEDs usually includes not only positive and/or negative spin-$\frac{1}{2}$ polaron resonances at $g \sim 2.002$, but (generally positive) full- and half-field TE resonances as well.[12–15,17,18,21–23,30] As in the case of the positive spin-$\frac{1}{2}$ polaron resonance, different mechanisms were proposed to explain the half-field resonance, including (i) enhanced TE-TE annihilation to SEs, (ii) enhanced ground-state recovery from TEs, and (iii) reduced quenching of SEs by a reduced population of TEs at resonance. By monitoring the separate guest and host contributions to the distinct guest and host half-field TE resonances, List *et al.*[30] provided strong evidence that excluded mechanisms (i) and (ii). They also provided a model of long-range SE-TE annihilation due to a

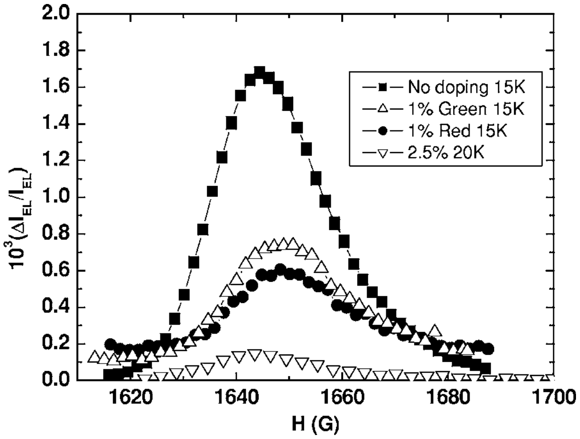

FIG. 5. The half-field TE ELDMR of 0%, 1%, and 2.5% PtOEP:Alq$_3$ at low temperature.

dipole-dipole transfer mechanism which established the quenching model (iii) as the origin of the half-field resonance. As mentioned above, it has now been established that the reduction in the polaron and (host) TE populations is due to enhanced annihilation of (host) TEs by polarons.[37,38,51]

Figure 5 shows the half-field ELDMR of the 0, 1, and 2.5 wt. % PtOEP: Alq$_3$. The current-dependence of the half-field resonance is relatively weak, but the amplitude of the resonance decreases from $1.7\times10^{-3}$ in the undoped device to $<1.5\times10^{-4}$ in the 2.5 wt. % device. In the 6 wt. % device, the half-field resonance is undetectable. In the 1 wt. % device, the amplitude of the green band half-field ELDMR is larger than that of red band.

Recapping, we have attributed the (a) low-$T$ positive spin-$\frac{1}{2}$, (b) high-$T$ negative spin-$\frac{1}{2}$, and (c) low-$T$ half-field triplet resonances to (a) reduced quenching of host SEs by polarons and host TEs, (b) enhanced formation of dianions at the Alq$_3$/cathode interface, and (c) reduced quenching of host SEs by TEs, respectively. Hence, the red PtOEP phosphorescence ELDMR is due to an indirect process, i.e., quenching of the source host SEs, which otherwise transfer their energy to the PtOEP molecules. All three resonances weaken rapidly with increasing PtOEP concentration. We now provide a rate equation model to account for this behavior.

### C. Rate equation analysis of the ELDMR

Figure 6 shows the photophysical processes in PtOEP-doped Alq$_3$ OLEDs. Reverse energy transfer from PtOEP TEs to Alq$_3$ is ignored due to the high efficiency of the devices.[52] The terms used are as follows:

[$^1S_1$], [$^3T_1$] [$^1S_0$] are the populations of the lowest SE state, lowest TE state, and ground state, respectively. A PtOEP subscript refers to populations of states in PtOEP. The other states are states in Alq$_3$.

$k_{\text{ISC1}}$ is the intersystem crossing (ISC) rate from Alq$_3$ [$^1S_1$] states to Alq$_3$ [$^3T_1$] states.

$k_{\text{ISC2}}$ is the ISC rate from Alq$_3$ [$^3T_1$] states to Alq$_3$ [$^1S_0$] states.

$k_{\text{Förster}}$ and $k_{\text{Dexter}}$ are the Förster[51,53] and Dexter[51,54] energy transfer rates, respectively, from Alq$_3$ to PtOEP.

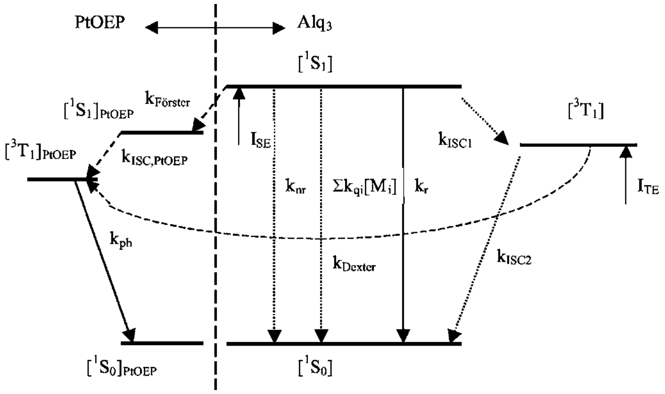

FIG. 6. The photophysical processes in PtOEP-doped Alq$_3$ OLEDs.

$k_r=A$ is the Einstein coefficient of spontaneous emission from $^1S_1$.

$[M_i]$ is the population of quenching species (polarons, host TEs, dianions, etc.).

$\Sigma k_{qi}[M_i]$ is the total quenching rate of host SEs.

$k_{nr}$ is the total nonradiative decay rate, excluding quenching channels.

$k_{ph}$ is the phosphorescence transition rate in PtOEP.

$I_{\text{SE}}$ and $I_{\text{TE}}$ are the SE and TE generation rates due to charge injection, respectively.

The rate equations are consequently written as follows.

In Alq$_3$,

$$\frac{d[{}^1S_1]}{dt} = I_{\text{SE}} - \left(k_{nr} + \sum k_{qi}[M_i] + k_r + k_{\text{ISC1}} + k_{\text{Förster}}\right)[{}^1S_1] \tag{1}$$

$$\frac{d[{}^3T_1]}{dt} = I_{\text{TE}} + k_{\text{ISC1}}[{}^1S_1] - (k_{\text{ISC2}} + k_{\text{Dexter}})[{}^3T_1]. \tag{2}$$

In PtOEP,

$$\frac{d[{}^1S_1]_{\text{PtOEP}}}{dt} = k_{\text{Förster}}[{}^1S_1] - k_{\text{ISC,PtOEP}}[{}^1S_1]_{\text{PtOEP}} + O_1 \tag{3}$$

$$\frac{d[{}^3T_1]_{\text{PtOEP}}}{dt} = k_{\text{ISC,PtOEP}}[{}^1S_1]_{\text{PtOEP}} + k_{\text{Dexter}}[{}^3T_1] - k_{ph}[{}^3T_1]_{\text{PtOEP}} + O_2, \tag{4}$$

where

$$k_{\text{Förster}} \propto r^{-6}, \tag{5}$$

$$k_{\text{Dexter}} \propto e^{-\alpha r}, \tag{6}$$

and $O_1$ and $O_2$ are higher-order terms. In steady state, the Alq$_3$ emission will be governed by

$$d[{}^1S_1]/dt = 0, \tag{7}$$

$$I_{\mathrm{EL}} = k_r[{}^1S_1] = \frac{k_r I_{\mathrm{SE}}}{k_{nr} + \sum k_{qi}[M_i] + k_r + k_{\mathrm{ISC1}} + k_{\mathrm{F\ddot{o}rster}}}. \tag{8}$$

Similarly,

$$\frac{d[{}^3T_1]}{dt} = 0 \Rightarrow [{}^3T_1] = \frac{I_{\mathrm{TE}} + k_{\mathrm{ISC1}}[{}^1S_1]}{k_{\mathrm{ISC2}} + k_{\mathrm{Dexter}}}. \tag{9}$$

At resonance, if the population of SE quenching species $[M_i]$ changes to $[M_i]+\Delta[M_i]$, the normalized EL change will be

$$\frac{\Delta I_{\mathrm{EL}}}{I_{\mathrm{EL}}} = \frac{-\sum k_{qi}\Delta[M_i]}{k_{nr} + \sum k_{qi}([M_i] + \Delta[M_i]) + k_r + k_{\mathrm{ISC1}} + k_{\mathrm{F\ddot{o}rster}}}. \tag{10}$$

As mentioned above, PADMR measurements demonstrate that the population of polarons and TEs decreases at the field-for-spin-$\frac{1}{2}$ resonance. If polarons and host TEs are quenching centers of emissive SEs (thus they are $M$'s), a negative $\Delta[M_i]$ will yield a positive ELDMR.

In OLEDs, mobile polarons are on the one hand the source of SEs, and on the other hand quenchers of SEs. Their lifetime, however, is short (typically ~100 ns, as determined by OLEDs' response to pulsed bias[55]). In contrast, the lifetime of trapped polarons is much longer (typically 10 $\mu$s–10 ms, as determined by measurements of the PLDMR vs the microwave chopping frequency[20,37,38]). Hence the quenching of SEs due to mobile polarons can be neglected relative to quenching by trapped polarons.

In PtOEP, under steady-state condition, we set Eqs. (3) and (4) to 0, and ignore the $O_1$ and $O_2$ terms, since the internal quantum efficiency of the PtOEP emission is almost 100%.[5] We get two equations,

$$[{}^1S_1]_{\mathrm{PtOEP}} = \frac{k_{\mathrm{F\ddot{o}rster}}[{}^1S_1]}{k_{\mathrm{ISC,PtOEP}}}, \tag{11}$$

$$I_{\mathrm{EL,PtOEP}} = k_{ph}[{}^3T_1]_{\mathrm{PtOEP}} = k_{\mathrm{ISC,PtOEP}}[{}^1S_1]_{\mathrm{PtOEP}} + k_{\mathrm{Dexter}}[{}^3T_1]. \tag{12}$$

Combining these two equations, we get

$$I_{\mathrm{EL,PtOEP}} = k_{\mathrm{F\ddot{o}rster}}[{}^1S_1] + k_{\mathrm{Dexter}}[{}^3T_1]. \tag{13}$$

Note that although Dexter energy transfer can also occur from a host SE to a guest SE, it is negligible compared to Förster SE-SE energy transfer.

When the PtOEP concentration is low, only long-range Förster energy transfer occurs,

$$I_{\mathrm{EL,PtOEP}} = k_{\mathrm{F\ddot{o}rster}}[{}^1S_1]. \tag{14}$$

Note that the intensity of the PtOEP phosphorescence differs from the host Alq$_3$ fluorescence only by the constant $(k_{\mathrm{F\ddot{o}rster}}/k_r)$. Hence the normalized change in the phosphorescence intensity will also be given by an expression analogous to Eq. (10).

Thus this model accounts for the observed identical dependence of the host and guest ELDMR on the current, at both low and high $T$.

When the PtOEP concentration increases, the intermolecular distance $r$ decreases, and both $k_{\mathrm{F\ddot{o}rster}}$ and $k_{\mathrm{Dexter}}$ increase. Consequently, as expected and predicted by Eq. (8), the host EL decreases. Equation (10) of the model predicts that the magnitude of the normalized EL change will decrease as well, which agrees well with the experimental results (see Fig. 3).

When the PtOEP concentration increases, Dexter energy transfer becomes significant. Then the simplified relation

$$\Delta I_{\mathrm{EL}}/I_{\mathrm{EL}} = \Delta[{}^1S_1]/[{}^1S_1] \tag{15}$$

derived from Eq. (14) when Dexter energy transfer is negligible, must be replaced by the relation

$$\frac{\Delta I_{\mathrm{EL}}}{I_{\mathrm{EL}}} = \frac{k_{\mathrm{F\ddot{o}rster}}\Delta[{}^1S_1]}{k_{\mathrm{F\ddot{o}rster}}[{}^1S_1] + k_{\mathrm{Dexter}}[{}^3T_1]}. \tag{16}$$

The additional Dexter term in the denominator results in $|\Delta I_{\mathrm{EL}}/I_{\mathrm{EL}}|$ decreasing even faster in the PtOEP phosphorescence than in the Alq$_3$ fluorescence ELDMR. When the Dexter term dominates, the phosphorescence ELDMR will be very small. This is in excellent agreement with the observation that the ELDMR in the 6 wt. % PtOEP-doped OLED is very weak and undetectable at low $T$. The observed weak negative ELDMR at 295 K may indicate either a weak negative EDMR, which results in a weak negative ELDMR, or that the dianions at the organic/cathode interface quench TEs slightly.

In the undoped devices, the ELDMR signal is given by Eq. (10) but without the Förster term. Due to the absence of heavy metal and consequent weakness of the spin-orbit coupling, and the large energy difference between $S_1$ and $T_1$ states, $k_{\mathrm{ISC}} \ll k_r$, $k_{nr}$. Taking $k_r = 10^9$ s$^{-1}$ and a PL quantum yield of Alq$_3$ of ~0.2,[56] we get $k_{nr} = 4 \times 10^9$ s$^{-1}$. The SE-polaron interaction rate $k_{qp}$ was ~$10^{-9}$ cm$^3$ s$^{-1}$ in the polyparaphenylenes studied by List *et al.*[29] Assuming a polaron population of about $10^{17}$ cm$^{-3}$ (see Ref. 29), and a ~5% reduction in that polaron population at magnetic resonance,[16,29] the ELDMR amplitude is found to be ~$10^{-3}$, in agreement with the observed amplitude.

We now consider the low temperature ELDMR at $J$ ~2 mA/cm$^2$. Assuming a fixed polaron density, $k_{qp}$ and a 5% reduction in the polaron density at resonance, we get $k_r + k_{nr} = 1.6 \times 10^9$ s$^{-1}$. For ~1% doping, at ~2 mA/cm$^2$, the ELDMR signal is $8 \times 10^{-4}$. $k_{\mathrm{F\ddot{o}rster}}$ in the 1% device can then be calculated to be $4.5 \times 10^9$ s$^{-1}$. Since $k_{\mathrm{F\ddot{o}rster}} \sim r^{-6}$, it can be seen that $k_{\mathrm{F\ddot{o}rster}}$ in the 2.5% device is 6.25 times that in 1% device. Equation (10) then predicts that the ELDMR signal will be ~$1.7 \times 10^{-4}$, in good agreement with the observed value of $2 \times 10^{-4}$. The calculation also indicates that Dexter energy transfer is not significant at doping levels below 2%–3%. We estimate that in the 2.5% device, the average distance between two PtOEP molecules is ~2.9 nm.

### D. The ELDMR of 20 wt. % PtOEP-doped Alq$_3$ OLEDs

In the 20 wt. % PtOEP-doped device, the spin-$\frac{1}{2}$ ELDMR is quenching at all $T$. Figure 7 shows the temperature dependence of that quenching resonance at $J$ ~2 mA/cm$^2$.

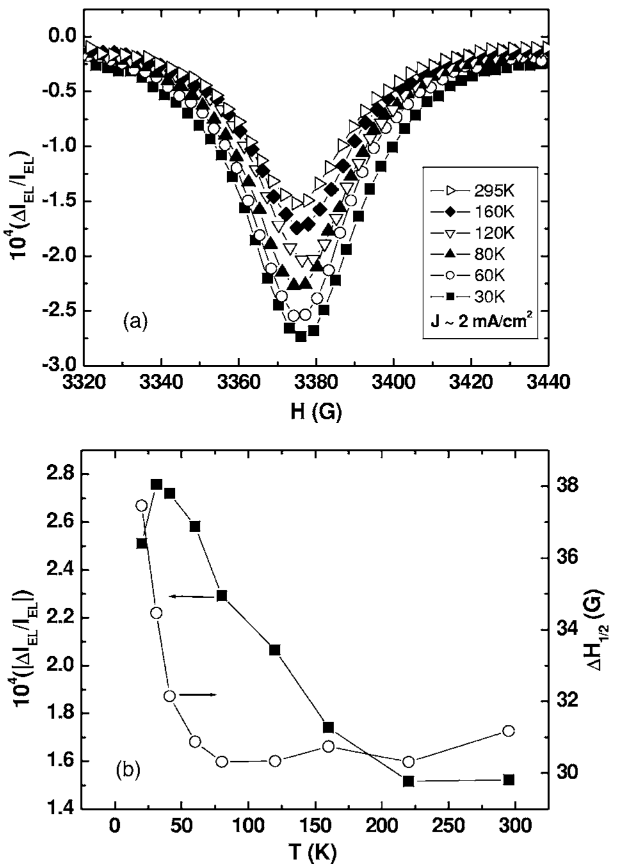

FIG. 7. (a) The temperature dependence of the spin-$\frac{1}{2}$ ELDMR signal of 20 wt. % PtOEP OLEDs; $J\sim 2$ mA/cm$^2$. Note that the magnitude of the negative resonance decreases when $T$ increases. (b) The temperature dependence of the resonance linewidth $\Delta H_{1/2}$ (open circles) and resonance amplitude $|\Delta I_{\mathrm{EL}}/I_{\mathrm{EL}}|$ (solid squares). $|\Delta I_{\mathrm{EL}}/I_{\mathrm{EL}}|$ is largely independent of the injected current at both 20 K and room temperature (not shown).

$|\Delta I_{\mathrm{EL}}/I_{\mathrm{EL}}|$ and the linewidth both decrease when $T$ increases; it is observed (not shown) that $|\Delta I_{\mathrm{EL}}/I_{\mathrm{EL}}|$ is largely independent of the injected current at both 20 K and room temperature. This behavior is qualitatively different from that of the negative resonance in the undoped devices. In that case, $|\Delta I_{\mathrm{EL}}/I_{\mathrm{EL}}|$ increases as $T$ increases, and decreases as $J$ increases. The qualitatively different behavior in the 20 wt. % PtOEP-doped device suggests a new mechanism.

In attempting to identify the new mechanism, we note that the lifetime of PtOEP TEs was observed to decrease as the PtOEP concentration increases.[52] This is believed to be due to enhanced nonradiative decay paths for TEs in PtOEP aggregates. At the same time, the TE-TE annihilation rate also increases with PtOEP concentration.[55] It is therefore plausible that the new quenching ELDMR is related to these two processes. However, the ELDMR of Ir(ppy)$_3$-doped 4,4′-bis(9-carbazolyl)biphenyl (CBP) OLEDs exhibits a similar quenching resonance from 20 K to 295 K, even at 2 wt. % doping.[56] Since the Ir(ppy)$_3$ TEs exhibit a phosphorescence lifetime of $\sim 1$ $\mu$s (Ref. 6) [compared to $\sim 100$ $\mu$s in PtOEP (Ref. 5)], the TE-TE annihilation rate must be much lower in Ir(ppy)$_3$-based devices. In addition, aggregation should be negligible in 2 wt. % Ir(ppy)$_3$-doped devices. Hence it is improbable that the new mechanism is related to aggregation effects.

In light of the foregoing considerations, the origin of the negative resonance in 20 wt. % PtOEP in Alq$_3$ OLEDs is tentatively assigned to magnetic resonance enhanced formation of dianions in the bulk of the doped layer. As $T$ decreases, the mobility of the TEs decreases, and the stability of the dianions increases. Thus, the density of dianions will increase with decreasing $T$. Hence, the magnitude and linewidth of the negative resonance will increase with decreasing $T$, in qualitative agreement with the observed behavior.

It is interesting to consider the correlation between the magnitude of the room temperature negative ELDMR and the efficiency of the PtOEP-doped devices. The 6 wt. % PtOEP-doped device is the highest efficiency device, and it has the weakest room temperature negative resonance.

In our previous ELDMR and EDMR study of Alq$_3$ OLEDs, we suggested that formation of dianions at the organic/cathode interface, which is a carrier trapping mechanism which reduces $J$ and consequently the EL, is an important mechanism in OLEDs. The sheet of charge at the organic/cathode interface also quenches SEs, and this process may also be significant. The current results support this suggestion. Thus, the improved efficiency of optimized phosphorescent OLEDs is probably due to the following two effects: (i) The contribution of both Förster and Dexter energy transfers, which exploit 100% of the host excitons, resulting in virtually 100% internal quantum efficiency. (ii) The relative immunity of guest TEs to quenching due to the sheet of charge at the organic/cathode interface, as compared to SEs, which are susceptible to this quenching process.

## IV. SUMMARY AND CONCLUSIONS

In conclusion, an ELDMR study of 0, 1, 2.5, 6, and 20 wt. % PtOEP-doped Alq$_3$ phosphorescent OLEDs was described. In 1 wt. % PtOEP-doped devices, the ELDMR is very similar to that of undoped Alq$_3$ OLEDs, i.e., it includes a positive spin-$\frac{1}{2}$ ELDMR at $T\leqslant 60$ K, and a negative spin-$\frac{1}{2}$ ELDMR which emerges at 60 K and increases with increasing $T$. The ELDMR of the red guest phosphorescence and green host fluorescence are almost the same.

The low $T$ positive ELDMR decreases as the PtOEP concentration increases and disappears when the PtOEP concentration exceeds $\sim 6$ wt. %. The room temperature negative ELDMR decreases from $\sim 8\times 10^{-4}$ in 1 wt. % PtOEP device to $\sim 2\times 10^{-5}$ in the 6 wt. %-doped device. In the 20 wt. %-doped device, the negative ELDMR is observed from 20 K to 295 K. The amplitude and linewidth of the resonance both decrease as $T$ increases. The resonance is much less dependent on the current than in the other devices, indicating their different origin.

Due to its similarity to the positive spin-$\frac{1}{2}$ PLDMR, the enhancing ELDMR is attributed to magnetic resonance enhancement of polaron recombination and decay of host TEs, which reduces quenching of SEs by polarons and host TEs. As established recently by Lee *et al.*[37] and by Segal *et al.*,[38] *the interaction that is at the heart of the positive spin-*$\frac{1}{2}$ *and half-field spin-1 PLDMR and ELDMR is the polaron-host TE* *interaction*. This spin-dependent interaction annihilates the TE and excites the polaron, consequently enhancing its recombination. While the recent aforementioned studies[37,38] have established the significance of this interaction in the photoexcited films, and in retrospect, the previous study by Li *et al.*[35] establishes its importance in $\mathrm{Alq}_3$ OLEDs, this work establishes its importance in the forefront PtOEP phosphorescent OLEDs as well. *The recent*[35,37,38] *and present ODMR studies identify this interaction as one of the major interactions in photoexcited* π*-conjugated materials and OLEDs, since the steady-state populations of the polarons and TEs are usually much higher than that of the SEs.*

The quenching ELDMR for devices with $<6$ wt. % PtOEP is believed to result from magnetic resonance enhancement of the formation of dianions at the organic/cathode interface, and the effects of the enhanced dianion formation on the host SEs. *It is believed that the enhanced dianion formation generates the negative resonance due to its effect in enhancing the density of the sheet of charge at the organic-cathode interface. This enhanced charge density enhances the field-induced host SE dissociation rate.* At low PtOEP content, this field-induced quenching competes with the Förster energy transfer rate much more effectively than at high PtOEP content, where both the Förster and Dexter transfer rates are much higher. A rate equation model was developed to account for the behavior of the devices containing up to 6 wt. % PtOEP.

The abnormal negative spin-$\frac{1}{2}$ ELDMR in 20 wt. %-doped devices is not clear and may be due to magnetic resonance enhanced formation of dianions in the bulk of the doped layer.

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