Fractions of singlet and triplet excitons generated in organic light-emitting devices based on a polyphenylenevinylene derivative

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The effect of magnetic field on the intensity of electroluminescence from devices made of a poly-*p*-phenylenevinylene (PPV) copolymer was investigated. The emission intensity was enhanced by the application of magnetic field, and the magnitude of the increase depended on operational voltages. When the device was operated under application of low voltages, the intensity increased with magnetic field and reached an 8.5% increase at about 100 mT. With the increase of the operational voltage, the effect of magnetic field was lessened. In addition, when measured at high voltages with increasing magnetic field, the emission intensity started to decrease after passing a maximum, then leveled off. This saturation value was slightly higher than that observed in the absence of magnetic field. These findings suggest that two processes sensitive to magnetic field are included in the emission processes. They are assigned to the charge recombination (CR) of anion and cation radicals and triplet-triplet annihilation (TTA) processes. From the analysis of the effects of magnetic field on the emission intensity based on a kinetic model, we quantitatively determined the fractions of singlet and triplet excitons generated through the CR process to be 0.17 and 0.83, respectively. With the increase of the concentration of triplet excitons in the organic layer, production of singlet excitons through the TTA process was enhanced, and the total yield of the singlet excitons exceeded 0.5 under normal device operational conditions. We conclude that this high yield is responsible for the high emission efficiency observed in the light-emitting devices based on PPVs.

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I. INTRODUCTION

Organic light-emitting devices (OLEDs) have been attracting increasing interest as next-generation flat-panel displays. For the development of OLEDs that can compete with conventional displays, improvement in the quantum efficiency of electroluminescence (EL) is one of the most important requirements. OLEDs fabricated of poly-*p*-penylenevinylenes (PPVs) are known to be a kind of promising devices because of their high emission efficiency.[1,2] The high efficiency is partly attributed to the recombination of electron-hole pairs in a confined region near the transparent electrode.[3,4] The high efficiency has also been attributed to the high yield of singlet excitons that are generated from the charge recombination (CR) of electron-hole pairs.[5]

The combination of spins of electron and hole statistically results in one singlet and three triplet excitons for the CR process. However, Cao *et al.* have experimentally determined the fraction of singlet excitons formed in a PPV derivative to be about 0.5 from the comparison of quantum efficiencies of EL and photoluminescence.[6] Kim *et al.*[7] have estimated the lowest limit of the singlet exciton fraction to be 0.35 to 0.45 for two kinds of PPV derivatives on the basis of the observed angular distribution of EL intensity and its numerical simulation using a simple half-space optical model. Wohlgenannt *et al.*[8,9] have studied the cross-section ratios of singlet to triplet excitons formed in some conjugated polymers based on the magnetic resonance technique, and showed that the cross section for singlet excitons was larger than that for triplet excitons in the OLEDs; the singlet exciton fraction was estimated to be in a range from 0.37 to 0.57. Segal *et al.*[10] have determined the fractions of singlet excitons formed in poly[2-methoxy-5-(2-ethylhexyloxy)-*p*-phenylenevinylene] (MEH-PPV) and tris(8-hydroxyquinoline)aluminium (Alq_3) to be about 0.20 on the basis of the external quantum efficiency of EL. As seen in the literature, the values reported for the fractions of singlet excitons generated in the devices have large discrepancies.

The emission in OLEDs based on PPVs is generated through singlet excited states that are produced by the CR of an electron and a hole and also by the interaction between two triplet excitons. The latter process is called the triplet-triplet annihilation (TTA).[11,12] The yield of singlet excitons with efficiency higher than the statistical value of 0.25, as mentioned above, has been explained in terms of these processes. The explanations are that (1) the CR process to form a singlet exciton from a singlet radical pair (RP) is faster than that to form a triplet exciton from a triplet RP (Refs. 8 and 9) and/or (2) the TTA process boosts the yield of singlet exciton.[11,12] However, the contributions of the CR and TTA processes have not been quantitatively discussed yet.

The yield of the singlet excitons has sometimes been discussed on the basis of the experimental results of photolumi-

nescence. However, there is a marked difference in the production of excitons between photoexcitation and electroexcitation. Since photoexcitation usually produces negligible amounts of triplet excitons as the initial products, the contribution of the TTA process is much less in the photoexcited system than in the electroexcited system. Hence, for the analysis of the efficiency of EL, the quantitative study has to be done with the electroexcitation mode.

The EL emissions via CR and TTA processes in OLEDs have different time responses against pulsed voltages due to the longer lifetimes of triplet excitons. They might be used for the quantitative analysis of these processes. However, the relatively large electrical time constant of thin-film devices makes their separation difficult. Another approach is the utilization of external magnetic field effects (MFEs), which make possible the separation of the two processes because they have different dependences on magnetic field.[13] In fact, MFEs have been utilized for the separation of chemical processes that take place via pairs of paramagnetic chemical intermediates such as a radical pair (RP) and a triplet-triplet pair (TTP).[13–20] These MFEs arise from spin-dependent reaction rates and also from the magnetic field-dependent efficiency of intersystem crossing. The latter effect is caused by the Zeeman interaction in the paramagnetic pairs. So far, MFEs have successfully been utilized in the analyses of photochemical processes in liquid media[13–19] and charge recombination and/or escape processes in photoconductive polymers.[20]

Several results have recently been reported on MFEs on the EL intensity of OLEDs, and the effects were attributed to the CR and TTA processes include in the EL processes.[12,21,22] In addition to these processes, MFE on current density, which affects the EL intensity, has been reported. Kalinowski *et al.*[21] reported that the application of magnetic field to the OLED based on Alq_3 increased current density, leading to enhanced EL intensity. They explained these MFEs in terms of the modulation of the concentration ratio of singlet electron-hole pairs to triplet electron-hole pairs by magnetic field. Mermer *et al.*[22] reported similar results for Alq_3-sandwiched devices. Davis and Bussmann[12] reported that the spin-flip transition between a singlet exciton and a triplet exciton was induced at low magnetic field, which resulted in enhanced current density and EL intensity. Besides the enhanced EL intensity by magnetic field, they observed weakened EL intensity under the application of high magnetic field. They attributed the latter effect to the TTA process because the observed magnetic field dependence was similar to that of the delayed fluorescence in anthracene crystals. Francis *et al.*[23] reported an increase in the current density by the application of magnetic field to the devices based on poly(9,9-dioctylfluorenyl-2,7-diyl). Since this MFE was observed in a hole-only device as well as in normal devices, they attributed the MFE to the hole transporting processes in the devices.

Most of these analyses of MFEs on OLEDs as mentioned above have been carried out qualitatively.[11,20–23] In contrast, detailed quantitative studies of MFEs have been reported in the field of photochemistry, especially for chemical reactions in solution.[12–19] In this paper, we quantitatively discuss the contributions of the CR and the TTA processes to the yields of singlet and triplet excitons in the OLEDs made of PPV as a light-emitting material, borrowing the method from the studies of photochemistry in solution. The theoretical background of the method is shown in the next section, in which the MFE due to the effect on current density is excluded because their contribution was small in our experiments, as discussed later.

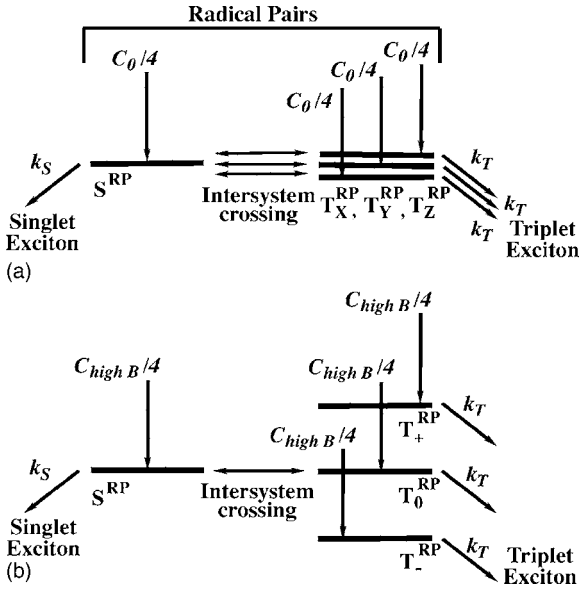

FIG. 1. Diagrams for recombination of radical pairs (a) in the absence of magnetic field and (b) in the presence of magnetic field. In the absence of magnetic field, the singlet state of a radical pair (S^{RP}) mixes with three triplet sublevels ($T_X^{RP}, T_Y^{RP}, T_Z^{RP}$), whereas, under high magnetic field, it mixes with only one triplet sublevel (T_0^{RP}).

II. THEORY

A. Mechanisms of generating singlet and triplet excitons and MFEs

When excitons are produced as a result of the recombination of anion radicals and cation radicals, singlet excitions and triplet excitons are generated from singlet RPs and triplet RPs, respectively, as shown in Fig. 1(a). In the absence of an external magnetic field, the intersystem crossing (ISC) between a singlet RP and a triplet RP is induced by the hyperfine interaction between electron spins and nuclear spins.[14–17] In this interaction, the singlet state of a RP can mix with the three triplet sublevels ($T_X^{RP}, T_Y^{RP}, T_Z^{RP}$) of a triplet RP. In the presence of external magnetic field, Zeeman interaction is induced, which is proportional to the intensity of external magnetic field. If the resultant Zeeman interaction becomes larger than the hyperfine interaction, the singlet RP can mix with only one sublevel (T_0^{RP}) of the triplet RP, as shown in Fig. 1(b).

In order to discuss the CR process which generates excitons from RP, we introduce the rate constants for the recombination of RPs in the singlet and triplet states, which are denoted by k_S and k_T, respectively. In the absence of external magnetic field, if the rate constants for the ISC between the

singlet and triplet RPs is much larger than k_S and k_T, the yield of singlet exciton, α, is described by Eq. (1),

$$\alpha = \frac{k_S}{k_S + 3k_T}. \tag{1}$$

If k_S and k_T are the same, α will be 0.25. This will also be the case in the presence of magnetic field. However, in general, k_S is not the same as k_T, which makes the yield different from 0.25.[13–20] More specifically, if k_S is larger than k_T, α will be larger than 0.25 because the population of triplet RPs can be fed into singlet excitons via the intersystem crossing between the singlet and triplet RPs, as shown in Fig. 1(a). If magnetic field is applied to the system in which k_S is larger than k_T, the yield of singlet exciton will decrease because the mixable triplet sublevels of the RP decreases, as seen in Fig. 1(b). Therefore, EL (fluorescence) intensity decreases in the presence of an external magnetic field. Contrarily, if k_S is smaller than k_T, the discussion reverses, and EL intensity increases in the presence of a magnetic field. Consequently, the EL intensity of OLEDs can be strengthened or weakened by the application of magnetic field, depending on the relative magnitude of k_S and k_T. Such effects on the CR process by magnetic field are referred to as MFE by the radical pair mechanism (MFE-RPM) in the field of photochemistry.[14–17] In general, these effects level off at low magnetic field.[13–20]

Another type of MFE arises from the TTA process, which is represented by

$$T^* + T^* \leftrightarrow {}^{1,3,5}(T^* \cdots T^*) \rightarrow S^* + S_0. \tag{2}$$

This process is important at high density of triplet excitons, which allows two triplet excitons to encounter within their lifetimes. When a pair of triplet excitons is in close vicinity, it can possess nine spin combinations. Such a pair of triplet excitons is hereafter represented by TTP. Merrifield,[24] Johnson and Merrifield,[25] Suna,[26] and Avakian[27] theoretically discussed the MFE due to the TTA process in organic single crystals and concluded that this type of MFE occurs via the singlet character of TTP. At zero magnetic field, three out of the nine spin combinations of a TTP have the singlet character. In contrast, in the presence of low magnetic field, at which the Zeeman splitting is smaller than the zero-field splitting (ZFS) due to the dipole-dipole interaction, all the nine spin combinations posses the singlet character.[11,17,24–28] As a result, the TTA process is enhanced by the application of low magnetic field. When the magnetic field is increased to a certain level at which the Zeeman splitting is larger than ZFS, the number of spin combinations that gives the singlet character is either one or two.[11,16,24–28] This leads to decreased contribution of the TTA process under high magnetic field; the contribution becomes less than that at zero magnetic field. Hence, MFE can be positive or negative depending on the strength of magnetic field. In general, the absolute intensity of the positive MFE at low magnetic field is much smaller than that of the negative MFE at high magnetic field.[11,17,24–28] These MFEs relating to the TTA processes are hereafter denoted by MFE-TTPM.

To summarize the above discussion, we consider two kinds of MFEs: MFE-RPM and MFE-TTPM. They show different dependences on magnetic field as follows. MFE-RPM increases or decreases the formation of singlet excitons depending on the relative values of k_S and k_T. This effect, either positive or negative, appears at low magnetic field and soon levels off with the increase of magnetic field. On the other hand, MFE-TTPM increases the formation of singlet excitions at low magnetic field and decreases the formation under strong magnetic field. These behaviors of MFE-TTPM are irrespective of the relative values of k_S and k_T. These two kinds of MFEs should play important roles in MEFs in OLEDs. In order to discuss these effects quantitatively, we can utilize the fact that they show different dependence on the magnitude of magnetic field.

B. Concentrations of radical pairs

Using the above models of MFEs, we can discuss the concentrations of RPs formed in organic layers of OLEDs. The kinetics of exciton formation in OLEDs is characterized by the statistical spin combination under continuous formation of RPs. For its analysis we use the rate equations that have been used in the analysis of laser flash photolysis in liquid media.[13,15] Such approaches have been adopted to the phenomena in solid films by some groups,[9,21,29] and our method shown below is similar to that reported by Barford.[29] However, our method is different from his in that we consider the MFE-RPM on EL caused through both CR and TTA processes. In addition, our method differs from his in that we discuss the case where the rate constant of ISC rate in RPs is much faster than k_S and k_T, because the hyperfine interaction induced by nuclear spins and electron spins on organic radicals allows fast ISC.[14–17]

In the absence of magnetic field, the differential equation concerning the concentration of each level is given by

$$\frac{d[S^{RP}]_0}{dt} = \frac{d[T_X^{RP}]_0}{dt} = \frac{d[T_Y^{RP}]_0}{dt} = \frac{d[T_Z^{RP}]_0}{dt} = -\frac{k_S + 3k_T}{4}[S^{RP}]_0 + \frac{C_0}{4}, \tag{3}$$

where $[A]_0$ stands for the concentration of a species A at zero magnetic field, and C_0 is the rate of RP formation at zero magnetic field. Using the steady-state approximation, Eq. (3) yields

$$[S^{RP}]_0 = [T_X^{RP}]_0 = [T_Y^{RP}]_0 = [T_Z^{RP}]_0 = \frac{C_0}{k_S + 3k_T}. \tag{4}$$

In the presence of magnetic field, the sublevels of the triplet state of RP are split, and the levels are denoted by T_0^{RP}, T_+^{RP}, and T_-^{RP}. Under the application of magnetic field higher than 100 mT, the mixing between the S^{RP} level and the T_+^{RP} and T_-^{RP} sublevels are inhibited,[13–20] as shown in Fig. 1(b). In this case, the differential kinetic equations are given by

$$\frac{d[S^{RP}]_{high\ B}}{dt} = \frac{d[T_0^{RP}]_{high\ B}}{dt} = -\frac{k_S + k_T}{2}[S^{RP}]_{high\ B} + \frac{C_{high\ B}}{4}, \tag{5}$$

$$\frac{d[T_{\pm}^{RP}]_{high\ B}}{dt} = -k_T[T_{\pm}^{RP}]_{high\ B} + \frac{C_{high\ B}}{4}, \tag{6}$$

where $T_{\pm}^{RP}$ represents T_{+}^{RP} or T_{-}^{RP}, and $C_{high\ B}$ is the rate of RP formation at high magnetic field. Using the steady-state approximation, Eqs. (5) and (6) yield

$$[S^{RP}]_{high\ B} = [T_0^{RP}]_{high\ B} = \frac{C_{high\ B}}{2(k_S + k_T)} \tag{7}$$

and

$$[T_{+}^{RP}]_{high\ B} = [T_{-}^{RP}]_{high\ B} = \frac{C_{high\ B}}{4k_T}. \tag{8}$$

C. Concentrations of excitons

Singlet excitons are generated not only from singlet RPs but also from triplet RPs via the TTA process. Combining these two processes, we can write the differential equations for the concentrations of singlet and triplet excitons as

$$\frac{d[S^*]}{dt} = k_s[S^{RP}] + \frac{k_{TT}}{2}[T^*]^2 - (k_f + k_{nr})[S^*] \tag{9}$$

and $[S^*]$

$$\frac{d[T^*]}{dt} = k_T[T^{RP}] - (k_1 + k_{TT}[T^*])[T^*], \tag{10}$$

where and $[T^*]$ are the concentrations of singlet and triplet excitons, respectively, $[T^{RP}]$ is the total concentration of triplet RPs with different sublevels, and k_1, k_{TT}, k_f, and k_{nr} denote the rate constants for the first-order decay from triplet excitons, the TTA process, fluorescent and nonradiative decays from singlet excitons, respectively. Using the steady-state approximation, Eq. (10) yields

$$[T^*] = \frac{k_T[T^{RP}]}{k_1 + k_{TT}[T^*]}, \tag{11}$$

and Eq. (9) yields

$$[S^*] = \frac{2k_s[S^{RP}] + k_{TT}[T^*]}{2(k_f + k_{nr})} = \frac{k_s[S^{RP}] + \beta k_T[T^{RP}]}{(k_f + k_{nr})}. \tag{12}$$

The parameter β introduced into Eq. (12) stands for the probability of spin conversion from a triplet exciton to a singlet exciton via the TTA process and is expressed by

$$\beta = \frac{k_{TT}[T^*]}{2(k_1 + k_{TT}[T^*])}. \tag{13}$$

As seen from Eq. (13), the parameter β has a value in the range of 0 to 0.5 depending on the value of $[T^*]$.

Note that the total yield of singlet excitons is represented by $\alpha+(1-\alpha)\beta$ since the fraction of singlet excitons generated via the TTA process is given by $(1-\alpha)\beta$.

D. MFEs on EL intensity

In order to quantitatively discuss MFE on EL intensity, we define the magnitude of the effect as

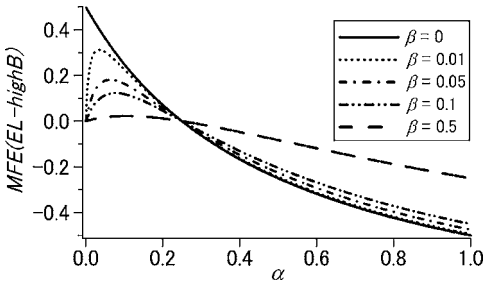

FIG. 2. *MFE*(*EL-high B*) vs α curves calculated from Eq. (16) for several α values.

$$MFE(EL) = \frac{I_{EL}(B) - I_{EL}(0)}{I_{EL}(0)}, \tag{14}$$

where $I_{EL}(B)$ and $I_{EL}(0)$ stand for the EL intensities observed with and without application of magnetic field, respectively. These $I_{EL}(B)$ and $I_{EL}(0)$ values are proportional to the concentrations of singlet excitons, i.e., $[S^*]_B$ and $[S^*]_0$, in the light-emitting layer. Hence, by combining Eqs. (12) and (14), we can write *MFE*(*EL*) as

$$MFE(EL) = \frac{[S^*]_B - [S^*]_0}{[S^*]_0} = \frac{k_S[S^{RP}]_B - \beta_B k_T[T^{RP}]_B}{k_S[S^{RP}]_0 - \beta_0 k_T[T^{RP}]_0} - 1, \tag{15}$$

where β_B and β_0 represent the β values for the cases with and without application of magnetic field, respectively. However, we will not differentiate them and use β for both of them because in our devices β_B was experimentally found to be nearly the same as β_0.[30] Let *MFE*(*EL-high B*) be *MFE*(*EL*) under the application of magnetic field higher than about 100 mT. Using Eqs. (1), (4), (7), (8), and (15), *MFE*(*EL-high B*) is written as

$$MFE(EL - high\ B) = \frac{3\alpha + (\alpha+2)\beta}{2(2\alpha+1)\{\alpha + (1-\alpha)\beta\}} \times \frac{C_{high\ B}}{C_0} - 1. \tag{16}$$

Note that the voltages applied to OLEDs affect *MFE*(*EL-high B*) because the concentration of triplet excitons is enhanced at high voltages; the parameter β increases from 0 to the maximum value of 0.5 with the applied voltage due to the enhanced TTA process. Figure 2 shows the relationships between *MFE*(*EL-high B*) and α, which are calculated from Eq. (16) for several β values between 0 and 0.5, under the condition of $C_{high\ B}/C_0=1$, which means that current density is independent of magnetic field. We chose this condition because the value of $C_{high\ B}/C_0$ experimentally obtained was close to 1, i.e., 1.0048, as shown later. Two important features are seen in Fig. 2. One is that *MFE*(*EL-high B*) is positive in the α region below 0.25, whereas it is negative in the α region above 0.25. Incidentally, the α value of 0.25 implies that k_S and k_T are the same and that the internal EL quantum efficiency of the device is 0.25 as long as the efficiency is determined only by the CR process. The other important feature is that the absolute value of *MFE*(*EL-high B*) decreases with increasing β. This

is because the increased formation of singlet excitons via the TTA process relatively lowers the contribution of MFE-RPM to *MFE*(*EL-high B*).

III. EXPERIMENTAL

The light-emitting material we used was a copolymer consisting of 98% 3-[4′(3,7-dimethyloctyloxy)phenylene]-*p*-phenylenevinylene (DMOP-PV) and 2% 2-methoxy-5-(2-ethylhexyloxy)-*p*-phenylenevinylene (MEH-PV).[3,4] This copolymer is an analogue of that reported in Ref. 7, in which the lowest limit of the singlet exciton fraction was reported to be 0.35-0.45. The polymer film was cast by spin coating from chloroform solution on a glass plate with indium-tin-oxide (ITO) stripe-electrodes, which had been cleaned by chemical and ultraviolet-ozone processes. The thickness of the polymer layer was about 70 nm. On the top of the polymer layer, a Ca (5 nm) layer as a cathode was deposited, which was protected by an Al overlayer (120 nm). Finally, the OLED was covered with a glass plate and sealed with a resin under an inert gas.

The measurements of MFE on the EL properties were carried in an *X*-band electron spin resonance (ESR) cavity. To minimize the deterioration of OLEDs during the measurements, they were operated by applying pulsed voltages for 19 μs and the EL intensity was obtained by integrating the emission over the 10–18 μs region after the voltage was turned on. The voltage was applied with a pulse generator (Hewlett Packard 214B). We also measured the MFE under dc operation and found that it showed essentially the same characteristics as those obtained under pulsed operation as long as the device was not deteriorated. The EL emission was introduced into a photomultiplier tube (Hamamatsu R636) via a plastic optical fiber, and the signal was transmitted to a digital oscilloscope (Tektronix TDS 540B), which was connected to a personal computer system for data processing. The coupling resistance of the digital oscilloscope was set at 50 Ω. For the observation of transient currents, the coupling resistance of 50 Ω was connected in series with the OLEDs. Magnetic field was applied in the direction perpendicular to the current flow using a set of electromagnets of the ESR apparatus, and was sequentially swept from −20 to 1000 mT and from 1000 to −20 mT. EL intensities measured in the two sweep directions were averaged and used for the evaluation of MFEs. All experiments were done at room temperature.

IV. RESULTS AND DISCUSSION

As shown in the inset of Fig. 3, the luminance/current-density efficiency, which is given by dividing EL intensity (I_{EL}) by current density (I), increases with applied voltage. The increased efficiency at higher voltages suggests that the contribution of TTA process to the generation of singlet excitons increases as the voltage becomes high, which will be discussed in more detail. The result that the luminance/current-density efficiency nearly levels off at about 10 V, at which the luminance is still increasing, suggests that the TTA process is almost saturated at this voltage.

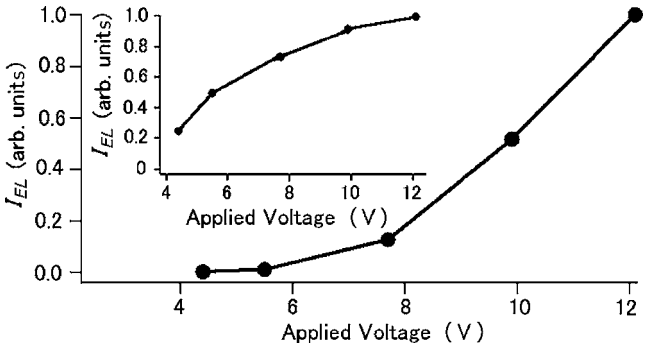

FIG. 3. Relationship between EL intensity and applied voltage for the device used for the study of MFE. The inset shows the luminescence/current-density efficiency as a function of applied voltage.

Figure 4 represents the relationship between *MFE*(*EL-observed*) and magnetic field (B), which was obtained at different voltages. *MFE*(*EL-observed*) was always positive, which means that the EL intensity is enhanced by the application of magnetic field. It should be emphasized that *MFE*(*EL-observed*) depended on the applied voltages. At an applied voltage of 4.4 V, as seen in curve (a) in Fig. 4, *MFE*(*EL-observed*) reached the saturation value of 8.5% at about 100 mT, and the magnetic field at which the MFE becomes half the saturation value, $B_{1/2}$, was at about 8 mT.

In the field of photochemistry, besides MFE-RPM and MFE-TTPM, other mechanisms have been reported to cause the effect of magnetic field.[14–17] They include the Δg mechanism, the relaxation mechanism, the level crossing mechanism, and the triplet-doublet pair mechanism. However, MFE-RPM is most important because EL emission occurs as a result of electron transfer between radical pairs and the observed leveling off of the effect with increasing magnetic field is consistent with this mechanism.[14–17] In addition, the $B_{1/2}$ value of 8 mT meats the criterion of the value below about 10 mT that has been used for the confirmation of MFE-RPM for the phenomena occurring in solutions.[15] The validity of the criterion has been supported by theoretical works.[31,32] Despite these supporting facts, however, we consider that further evidence is necessary to conclude that the results observed in Fig. 4 are caused by MFE-RPM. This is because the criterion is applied to the phenomena in solu-

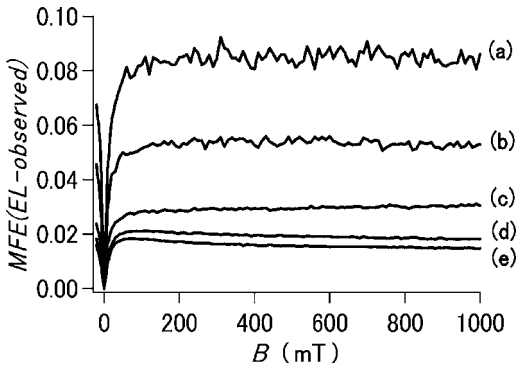

FIG. 4. *MFE*(*EL-observed*) measured at (a) 4.4 V, (b) 5.5 V, (c) 7.7 V, (d) 9.9 V, and (e) 12.1 V.

FIG. 5. ELDMR spectrum showing EL intensity under the irradiation of microwave (9.26097 GHz) as a function of magnetic field. The OLED was repeatedly irradiated with the microwave for 10 μs, and the EL intensity was obtained by collecting the EL signal 100 times. The EL intensity was normalized by the average value obtained at off-resonant magnetic fields; below 323 mT and above 336 mT.

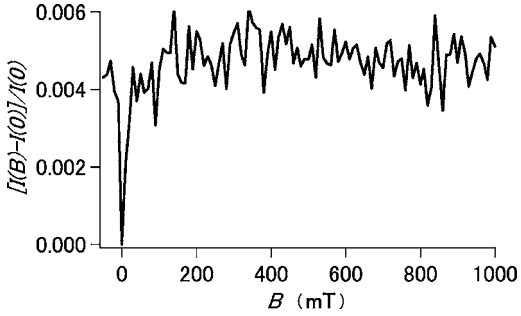

FIG. 6. MFE on current density, $[I(B)\text{-}I(0)]/I(0)$, measured at 11 V.

tions, but cannot be applied to the phenomena in solid state, where anisotropic hyperfine constants are important.

A useful method for analyzing the processes occurring via RP is the reaction-yield-detected magnetic resonance (RYDMR).[8,9,14–17,33–38] This method measures the changes in the yields, such as chemical products, chemiluminescence and transient absorption of intermediate species, under the application of the resonant microwave, which allows the transition between the sublevels of multiple spin states included in the reaction. If we apply this method to OLEDs, we can expect that the resonant microwave affects the magnitudes of MFE-RPM and EL intensity.[33] This effect on EL intensity will be denoted by ELDMR.

To measure ELDMR for our EL sample, we irradiated the sample with microwave at a frequency of 9.26097 GHz, and ELDMR thus obtained is shown in Fig. 5. The details of the measurements were almost same as that described elsewhere.[33,34] The result shows that EL intensity decreases by the application of the magnetic field, and the minimum appears at 328.3 mT. This magnetic field corresponds to the g value of 2.003, which is a typical g value of organic radicals. The half width at half maximum of the ELDMR spectrum, that is 1.9 mT, is also consistent with that the value of organic radical pairs.[8,9,11] Therefore, we can conclude that radical pairs are involved in the MFE; hence, it is MEF-RPM. The explanation for the observed ELDMR spectrum, based on the model shown in Fig. 1, is as follows: (1) The yield of singlet excitons by CR is below 0.25, i.e., k_S is smaller than k_T. (2) EL intensity is enhanced by the MFE-RPM process, which restricts ISC from singlet RP to the triple RP due to the splitting of the triplet sublevels. (3) This restriction is weakened by the application of resonant microwave because it induces the transition from T_0 to T_+ and T_- states, and the EL intensity is lowered.

The fact that k_S is smaller than k_T, which is deduced from the above discussion, is especially important because it denies the possibility that the high EL efficiency of the PPV copolymer-based device is due to the high yield of singlet exciton at the CR process. Instead of this explanation, the following results suggest that the TTA process is responsible for the high EL efficiency of these OLEDs.

The result observed in Fig. 4 showed that MFE becomes smaller with the increase of applied voltage. In addition, *MFE*(*EL-observed*) at high voltages starts to decrease with increasing magnetic field, after passing a maximum, as seen in the curves (d) and (e) in Fig. 4. These properties are related to the properties of the TTA process. This is because the TTA process becomes important at high voltages as the concentration of the triplet excitons increases, and the generation of a large number of singlet excitons via the TTA process relatively lowers the contribution from of the CR process that is sensitive to magnetic field. In addition, as discussed in the Sec. II, MFE-TTPM has a negative effect at high magnetic field and is less sensitive to magnetic field than MFE-RPM. This is consistent with the gradual decrease in *MFE*(*EL-observed*) with increasing magnetic field, as seen in the curves (d) and (e) in Fig. 4.

Alternative possible explanation for MFE on the EL intensity may be that the current density is affected by magnetic field, as has been reported by Kalinowski *et al.*[21] We observed an increase in the current density by the application of magnetic field, as shown in Fig. 6. However, since the largest increase in the current density was only about 0.48%, it has only small effect on the EL intensity.

In order to quantitatively analyze the contributions of CR and TTA processes to the EL intensity using Eq. (16), MFE on the TTA process has to be quantified. To quantify the effect, we assumed that *MFE*(*EL-observed*) value at 4.4 V in Fig. 4 was not influenced by MFE-TTPM because MFE-TTPM appears only at high magnetic field. We also assumed that MFE at 50 mT was free from MFE-TTPM for all operational voltages. On these assumptions, we estimated MFE free from MFE-TTPM by dividing *MFE*(*EL-observed*) at 50 mT by 0.92, which is the ratio of *MFE*(*EL-observed*) obtained at 4.4 V under operation at 50 mT to the saturated value at high magnetic field. We hereafter call the values thus obtained *MFE*(*EL-corrected*). As seen in Fig. 7, the magnitude of *MFE*(*EL-corrected*) decreased with increasing voltage. We attribute this decrease to the increased contribution of the TTA process to EL. On the basis of this understanding, we can analyze *MFE*(*EL-corrected*) using Eq. (16), which involves two parameters α and β.

For the analysis of *MFE*(*EL-corrected*) shown in Fig. 7, we consider two cases. In the first case, the current density is low, and the TTA process does not contribute to EL, i.e., β is zero. We tentatively assume that this condition is met when the device is operated at 4.4 V. By using 0.085, which is

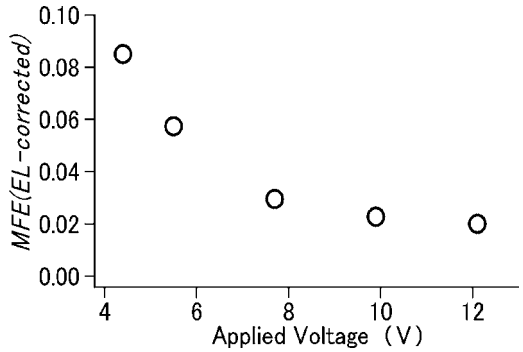

FIG. 7. Relationship between applied voltage and *MFE*(*EL-corrected*), which was estimated from the results shown in Fig. 4.

read at 4.4 V in Fig. 4, for *MFE*(*EL-corrected*), and 1 for C_{highB}/C_0 in Eq. (16), we obtained α of 0.19. Using this α value, β values are determined from the values of *MFE*(*EL-corrected*) at different voltages. For example, the β value at 12.1 V is determined to be 0.39. In the second case, we consider that the contribution from the TTA process becomes at the maximum, i.e., β is 0.5. We assume that this condition is met at 12.1 V in Fig. 7 because the *MEF*(*EL-corrected*) almost levels off at this voltage. On this assumption, the α value was determined to be 0.065 or 0.15 from Eq. (16), which gives two solutions because it is a second-order function. Judging from the physical meaning of the α value, which is defined by Eq. (16), we choose α of 0.15. This value, in turn, gives β of 0.11 at 4.4 V.

It should be noted that the above two cases give close values for α as well as for β. Since these two cases are extremes, the true α and β values are expected to fall between the values estimated; true α is between 0.15 and 0.19, and true β at 4.4 V is between 0 and 0.11 and true β at 12.1 V is between 0.39 and 0.50. By using the mean values of α, 0.17, and the *MFE*(*EL-corrected*) values shown in Fig. 7, we plotted the β value as a function of the operational voltage by the dotted line in Fig. 8. The total yield of singlet excitons generated via the CR and TTA processes, which is given by $\alpha+(1-\alpha)\beta$, is also plotted by the thick solid line in Fig. 8. The circles in the figure represent the voltage dependence of the experimental luminance-current efficiencies, which are normalized to show a good fit to the $\alpha+(1-\alpha)\beta$ curve. The good fit of the plots to the curve supports our arguments.

As mentioned before, the result that the α value thus determined is less than 0.25 is of importance for discussing the efficiency of OLEDs and the exciton generation processes. It has been known that OLEDs based on PPVs show high efficiency, and the high efficiency has often been attributed to the high yield of singlet excitons produced by the CR process.[6–9] However, the determined α value below 0.25 is not consistent with this explanation. Instead, it suggests that the high EL efficiency is mostly due to the TTA process, whose contribution is represented by $(1-\alpha)\beta$. The contribution from the TTA process increases with applied voltage because the concentration of triplet exciton increases with current. The presence of the TTA process in the related materials have been suggested by the observation of delayed

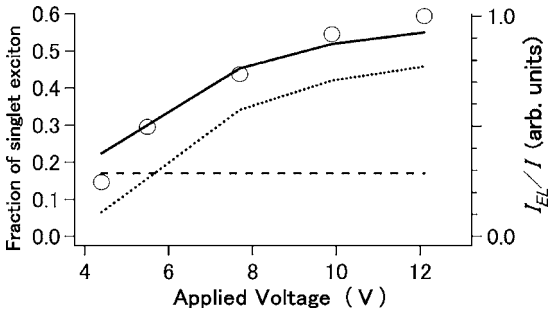

FIG. 8. Fractions of singlet excitons generated via the CR process (α, broken line) and via the TTA process $[(1-\alpha)\beta$, dotted line] and the total fraction of singlet excitons generated from electron-hole pairs $[\alpha+(1-\alpha)\beta$, solid line] against applied voltage in the case of no magnetic dependence of the formation rate for RPs. The experimental luminescence/current-density efficiency, which is the same as that shown in the inset of Fig. 3, is superimposed with opened circles, after being normalized to best fit the total fraction of singlet excitons.

photoluminescence.[39,40] The total yield of singlet excitons generated via the two processes, i.e., $\alpha+(1-\alpha)\beta$, falls in the range of 0.40 and 0.50 under the normal operational conditions, as seen in Fig. 8. This value is in good agreement with the value reported by Kim *et al.* for the devices made of a similar polymer material, i.e., above 0.35-0.45.

Finally, we discuss the effect of the magnetic-field-induced change in current density on the above discussion. In the above discussion, we have employed the C_{highB}/C_0 value of 1 for the analysis of MFE using Eq. (16), although the experimental value was 1.0048 at 11 V. If we use C_{highB}/C_0 value of 1.0048, together with the experimental value of *MFE*(*EL-corrected*) at 12.1 V, which is shown in Fig. 7, and the β value of 0.5, Eq. (16) gives the α value of 0.19, which is almost the same as that obtained using the assumption that C_{highB}/C_0 equals 1. This indicates that chief reason for MEF observed in the EL intensity is not by the change in the current density but by the magnetic effect on the processes of recombination between anion and cation radicals. More precisely, we attribute the effect to the splitting of the energy levels of triplet RPs by magnetic field, which then affects the contribution of the triplet RPs to the formation of singlet excitons, as shown Fig. 1.

We believe that our discussion is consistent with our experimental results. However, it should be fair to note that there have been different explanations on the similar phenomena of OLEDs, as discussed in Refs. 12, 21, 22, and 41. In order to further confirm the validity of our discussion and elucidate the mechanisms in more details, the pulsed resonant microwave method seems to be promising,[33–38] and the study using the method is now in progress.

V. CONCLUSIONS

Using OLEDs made of a PPV copolymer, we determined the fractions of singlet and triplet excitons generated as a result of the electron-hole recombination to be about 0.17 and 0.83, respectively. Although the yield of singlet excitons

generated in this process is not high, the total yield of the singlet excitons exceeded 0.5 under normal device operational conditions because of the large contribution from the TTA mechanism. Our method for determining the fractions of singlet and triplet excitons in OLEDs is advantageous over the conventional methods in that (1) it can be directly applied to EL from OLEDs with any materials, (2) magnetic field can be applied to OLEDs under their normal operational conditions, and (3) the singlet exciton fractions due to CR and TTA processes are determined quantitatively without making assumptions about the light-extraction efficiency from OLEDs. This method can quantitatively determine the contributions of CR and TTA process to the yield of singlet excitons in OLEDs.

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[30] In a strict sense, β depends on magnetic field because β is a function of $[T^*]$, which is affected by magnetic field, as seen from Eqs. (4), (7), (8), and (11). The effect of magnetic field becomes the maximum under the condition of $k_1 \gg k_{TT}[T^*]$, as expected from Eq. (13). In such a case, the ratio of β (or $[T^*]$) under strong magnetic field to that without magnetic field is represented by $(2+\alpha)/[2(1-\alpha)(1+2\alpha)]$, which is derived from Eqs. (1), (4), (7), and (8). By using α of 0.17, which was obtained experimentally as discussed later, the ratio of β under strong magnetic field to that without magnetic field is determined to be 0.98, indicating that the change in β by application of magnetic field can be neglected.
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