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Resonant Microwave Irradiation Effect on the Emission Process of an Organic Electroluminescent Material

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Microwave irradiation to energized electroluminescent cells made of a copolymer of *p*-phenylenevinylene (PPV) derivatives under a resonant magnetic field resulted in a decrease in emission intensity. This is due to a reduction of singlet radical ion pairs by forced spin conversion into the triplet manifold. This microwave effect became 1.6 ± 0.1 and 2.3 ± 0.1 times larger after the "turn-off," the removal of the driving voltage of 8 and 10 V, respectively. Since the formation of radical ions terminates at turn-off, this increase cannot be attributed to the increase of radical ion pairs. The magnetic field effect on the emission intensity also increased from 1.09 ± 0.01 to 1.12 ± 0.03 after turn-off. These phenomena are ascribed to the decrease of the exchange interaction between radical ions in a pair by the removal of the electric field.

Organic electroluminescence (EL) devices, in other words, organic light emitting diodes (OLEDs), are one of the key components in constructing organic electric circuits, which are already available as consumer products.[1] The emission of EL material is ascribed to emission from the excited state of the component molecules. This excited state is created by charge-recombination reaction of organic cation and anion radicals generated by charge injection at the electrodes. Consequently, the emission process of the EL material is really a chemical reaction of radical ions in solid phase.

The charged organic radicals inside EL materials also carry electron spin. Therefore, the charge-recombination process is restricted by the spin multiplicity of the encountered radical ion pair (RIP), i.e. the object of spin chemistry. We have reported several results on the spin-chemical phenomena in liquid-phase reactions such as external magnetic field effects (MFEs), chemically induced dynamic electron polarizations (CIDEPs), and reaction yield detected magnetic resonance (RYDMR).[2,3] Recently, we reported the MFEs of the EL emission intensity of a small molecule, tris(8-hydroxyquinoline) aluminum (Alq_3), and of a poly(*p*-phenylenevinylene) (PPV) derivative.[4,5] Similar results are also reported by several groups.[6–9] Their MFE is based on the selection of the singlet spin state for emission at the charge recombination, the triplet–triplet annihilation, and the quenching of the triplet state by doublet species. The key process of the first is the spin conversion in RIPs. The observation of RYDMR supports this mechanism. A simple view of the MFE on the emission intensity of EL materials is described as above.

There remains one fundamental question. That is, why do typical EL materials show a large MFE. It may sound strange because we confirmed this fact by ourselves. In liquid-phase reactions, a larger MFE implies longer lifetime of RIP or radical pair (RP) in order to evolve spin dephasing.[2] If this scheme is applied to EL emission, it means that radical ions survive vainly to avoid the charge recombination. This seems inadequate for typical good EL materials. The difference of the circumstances in solution and solid may provide some clues. There are several differences between them, which are pointed out in our previous study.[5] They are summarized as follows; 1) In solid, radical ions do not move by themselves but the charge, and hence the spin, hops among molecules. 2) In electrochemical reactions, anion and cation radical ions are formed at different electrodes and no spin correlation exists between them. 3) In the emission process, the competition between the spin states is that between excited singlet and triplet states, implying that the recombination in the singlet state is more difficult. In usual reactions proceeding in liquid phase, the radical ions diffuse by themselves dephasing the spin coherence (singlet or triplet) given as a geminate pair, and recombination to the ground singlet state is much easier than that to the excited triplet state.

There are some findings in the previous studies and our parallel study with the present one.[4,5,10] They are as follows; a) The magnitude of the magnetic field effect (MFE) on the emission intensity is dependent on the driving voltage of EL cells.[4,5] b) The magnitude of the MFE increases at the initial aging process where the emission intensity also increases.[10] In liquid-phase reactions, there is no alternative for the former and the latter is undesirable and avoided as a deterioration of samples. To answer the questions about EL materials, the accumulated knowledge in liquid-phase spin chemistry is insufficient and the observation of the dynamic behavior of the spins in the EL emission process is required. This is, however, disturbed by one practical problem. Short pulse current experiments forming radical ions within a short period like laser photolysis give almost no emission. The slow rise of emission requires a current pulse of more than one hundred microseconds, which is not suitable to observe the dynamic process.

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In this study, we applied a pulsed emission detected magnetic resonance technique to observe the emission dynamics in an EL cell made of a PPV derivative. This technique provides not only RYDMR spectra of the RIP in EL but also dynamic properties of RIP. The resonant microwave (MW) field affects spin conversion processes as the external magnetic field does. We used a MW pulse shorter than 100 ns, which contributed an improvement of time resolution. We applied this technique to the light off process of the EL emission, where the current is turned off and no more radical ions are formed afterwards. The response of this process is much faster than the light on process that can exploit the quickness of MW response. We investigated response to microwave irradiation that should shed a light on the interaction between radical ions.

Experimental

The electroluminescent (EL) cells were constructed on 150-nm ITO glass. PEDOT was spin-coated 80 nm on ITO and the light-emitting polymer TNT2408, a copolymer of *p*-phenylenevinylene (PPV) derivatives containing 2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene (MEH-PPV) as an emitting material, was spin-coated 80 nm on it. As a cathode, calcium (5 nm) and then aluminum (100 nm) were deposited on it. Based on these parameters, the electric fields applied to the material were 0.63 and 0.5 MV cm^{-1} at 10 and 8 V, respectively.

The constructed device was set in the X-band ESR cavity of an ESR spectrometer (JEOL RSV2000). The direction of the current in the EL cell was set normal to that of the magnetic field. Its total emission was observed through the ITO layer and the basement glass and then it was transferred to the photomultiplier (Hamamatsu R5600U) using a small quartz prism and plastic optical fiber (radius = 2 mm). Output was recorded on a digitizing oscilloscope (Tektronix TDS7104). Magnetic field and MW pulse were applied by the ESR spectrometer. Data storage and control of the total system including the timing of MW irradiation was carried out by a home-made program executed on a personal computer and digital delay/pulse generators (SRS DG535). The details of the experimental set-up are similar to that described elsewhere.[3,4,11]

The driving voltage of the EL cell was supplied by a Tektronix AFG3102 arbitrary waveform generator. The applied waveform was basically an isosceles trapezoid whose rise and decay were usually 10 ns or 10 μs. The output was terminated by a 50 ohm resister in parallel to the EL cell plus 50 ohm input of the oscilloscope for current detection. Current detection is outside the scope of this study.

Results and Discussion

The emission of an organic EL cell is summarized as the charge-recombination reaction of electron carrier ($A^{-\bullet}$) and hole carrier ($D^{+\bullet}$), which can be illustrated as follows:

$$D \rightarrow D^{+\bullet} + e^- \quad (1)$$

$$A + e^- \rightarrow A^{-\bullet} \quad (2)$$

$$D^{+\bullet}\ D\ D \rightarrow\rightarrow D\ D\ D^{+\bullet} \quad (3)$$

$$A^{-\bullet}\ A\ A \rightarrow\rightarrow A\ A\ A^{-\bullet} \quad (4)$$

$$A^{-\bullet} + D^{+\bullet} \rightarrow {}^{1,3}(A^{-\bullet}\ D^{+\bullet}) \quad (5)$$

$${}^1(A^{-\bullet}\ D^{+\bullet}) \rightarrow A + {}^1D^* \quad (6)$$

$${}^3(A^{-\bullet}\ D^{+\bullet}) \rightarrow A + {}^3D^* \quad (7)$$

$${}^1(A^{-\bullet}\ D^{+\bullet}) \leftrightarrow {}^3(A^{-\bullet}\ D^{+\bullet}) \quad (8)$$

Here, A and D are molecules or units of polymer molecules that act as electron acceptors and donors, respectively. Reactions 1 and 2 occur at the anode and cathode, respectively. Other reactions proceed in solid without permanent displacement of molecules. Reactions 3 and 4 are charge hopping reactions that are alternatives of diffusion of the radical ions in liquid phase. Usually, only one of them is a major process, which depends on materials. Reaction 5 is the formation of radical ion pair (RIP). Since the spins of $A^{-\bullet}$ and $D^{+\bullet}$ have no correlation between them at their birth, the formation ratio of singlet and triplet RIP is 1:3, the same as the spin multiplicity. Reactions 6 and 7 are charge-recombination processes reserving total spin multiplicity. For fluorescence-type EL materials like the present study, reaction 6 gives emission. Here, recombination to the ground singlet state is neglected. Similarly, simple transits of charges to the opposite electrodes are eliminated although the energy efficiency depends on them. Reaction 8 is the spin-conversion process where the external magnetic field or the resonant MW field modifies its rate. There still remain many ambiguities in the above scheme, such as identity of A and D, major hopping processes,[7,12] discrimination of intra- and inter-chain hopping, etc. but it is enough as a starting point for considering the mechanism of MFEs. We can apply all possible mechanisms to reaction 8 that are developed to describe the MFEs of RIP or RP in liquid phase.[2,13]

Figure 1 shows the time profile of the emission intensity of the EL cell at two driving voltages, 8 and 10 V. The shape of applied voltage is almost rectangular. The voltage pulse starts from 0 V, and attains a plateau in 10 ns. The voltage at the plateau is referred to as the operating voltage. The voltage is then reduced to 0 V in 10 ns by 50 ohm termination. The biasing voltage that may accelerate the light on process was not applied. It was clearly observed that the rise of emission is much slower than the 10 ns rise of driving voltage and that the rise becomes faster with increasing driving voltage.[4] This is because the electron and hole must transit the EL layer to encounter each other for emission (i.e. reaction 3 and/or 4)

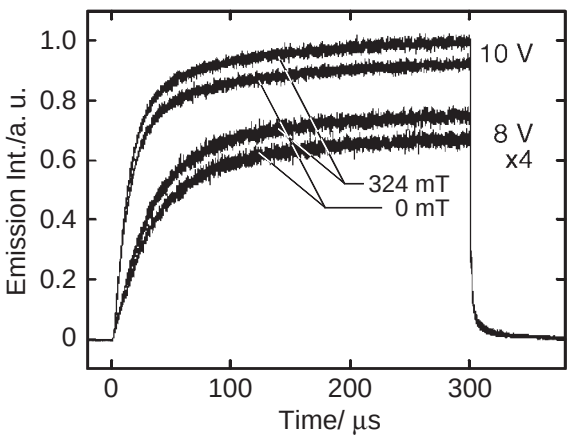

Figure 1. Time dependences of the emission intensity of the EL cell driven by 300 μs rectangular 8 and 10 V pulses. The signals at 8 V are multiplied by 4. In each set, the upper one is measured at 324 mT and the lower one at 0 mT, respectively.

and its rate is dependent on the driving voltage. The emission attains a stationary intensity in 150 or 100 μs after the application of electricity depending on the driving voltage of 8 or 10 V, respectively. Therefore, we can expect that the dynamics inside the EL cell attains a quasi-stationary state later than 150 μs. The remaining increase might be due to the rise in temperature, which is outside the scope of the present study. In a way, experiments using an electric pulse shorter than 100 μs are not suitable to describe the stationary EL emission. On the other hand, the light-off process shows quick response. When the driving voltage is turned off, the emission intensity decays immediately. Even if the decay of voltage takes 10 μs instead of 10 ns, the emission intensity decays immediately when the voltage starts to decrease.

By application of an external magnetic field, emission intensity increases.[4] In Figure 1, the results at 0 and 324 mT are shown. The increase at 324 mT is 12 ± 3 and $8 \pm 2\%$ at 8 and 10 V, respectively. This is due to inhibition of spin conversion of the singlet RIP (S) to the triplet RIP (T, in detail T_{-1}, T_0, and T_{+1}). As stated in the reaction scheme, the ratio of S and T at their birth is 1:3. In the absence of a magnetic field, these four spin states are degenerate and the spin conversion among them by the hyperfine interaction is fast. This degeneracy is removed in the presence of a magnetic field due to the Zeeman interaction, and only the conversion between S and T_0 sublevel remains. The enhancement of emission at reduced coupling to the triplet states, as observed, indicates that this coupling is not a feeding but a leaking process of the singlet population. Consequently we can say that the singlet recombination (reaction 6) is slower than the triplet recombination (reaction 7).[4]

Prior to introducing Figure 2, we had better explain briefly the concept of reaction yield detected magnetic resonance (RYDMR). Spin inversion of one of the radicals in a pair by magnetic resonance induces a conversion of the total spin state of RP, and then changes subsequent reactions by RP. For example, RP with (α_1, β_2) spin configuration is converted to that with (β_1, β_2) one by the inversion of radical 1. The total spin state of the former RP is S or T_0 and the latter RP is T_{-1}. S and T_0 states are interchangeable by hyperfine interaction. This resonance also converts (β_1, β_2) RP into (α_1, β_2) RP, because the MW effect is bidirectional. Similarly, conversion between (α_1, α_2) RP and (β_1, α_2) RP proceeds under these conditions, too. Consequently, no resonance effect appears when the population of each state is the same. This excludes the contribution of isolated (i.e. escaped) radicals from the RYDMR spectrum because the difference in α and β spin states of isolated radicals is minimal by the thermal distribution. If the population of the RP in S and T_0 states is different from that in T_{+1} and T_{-1} ($T_{\pm1}$), a significant population transfer occurs between singlet and triplet states. Since the reaction paths of the singlet and triplet states are rather different from each other, the spin conversion induced by the magnetic resonance is reflected in the reaction yield of the RP concerned. In the present case, the EL emission intensity is a measure of the efficiency of the charge recombination of the singlet RIP. Therefore, we can derive the RYDMR spectrum using the emission intensity.

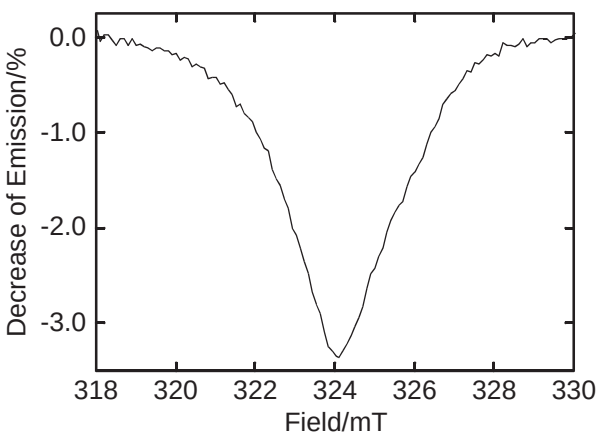

Figure 2. Emission detected magnetic resonance spectrum of the EL cell driven at 6 V. The resonant microwave transfers the singlet RIP into the triplet state, which results in the decrease of fluorescence.

Figure 2 shows the emission detected magnetic resonance spectrum of this EL material. Here, the 10 μs MW pulse was applied at 80 μs after the application of electricity of 6 V and emission intensity was integrated from 88 to 92 μs. The applied MW field strength at 9.0857 GHz is less than 1 mT. The emission intensity decreased at 324 mT ($g \approx 2.004$). Consequently, we can safely expect that the resonant species are ordinary radicals or radical ions that contribute the EL emission. On the other hand, this structureless spectrum does not allow us a definite assignment of the observed species.[14] The decrease of emission intensity indicates that the precursor of the emission, i.e. the singlet RIP is removed by the MW irradiation. The survival of singlet RIP over triplet indicates that the charge recombination of the singlet RIP (reaction 6) is slower than that of the triplet RIP (reaction 7), which is consistent with other experimental results. There remain several points to be discussed about this spectrum but the clear observation of the RYDMR spectrum is enough for the present study.

We have developed a method to measure dynamically the amount of RP or RIP,[15] which is based on RYDMR. When we observe a series of RYDMR spectra by a short MW pulse changing the irradiation time, the signal intensity reflects the population difference between S–T_0 states and $T_{\pm1}$ states at the moment of the MW pulse irradiation as described above. The plot of intensity at a certain fixed position in the spectrum gives the time dependence of this population difference. We refer to this method as "pulse shift" measurement. Since the standard optical and electron spin resonance methods do not discriminate the isolated radical from the same radical in a pair, this method is very helpful to determine the amount of RP or RIP directly.

Since we observed the RYDMR spectrum for this sample, the pulse shift measurement is applicable to it. In the case of the above emission detected spectrum, the current is maintained and hence the RIP is generated during the measurement. Consequently, analysis of the transient effect must evaluate the continuous supply of RIP during the observation. In the previous study, we analyzed it as a transition between two stationary states with and without a MW field.[5] The formation of RIP during the measurements of the dynamics of itself is undesir-

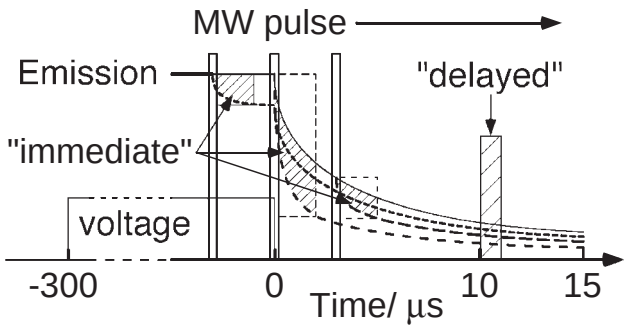

Figure 3. Timing chart of the measurement. The driving voltage for emission was applied from −300 to 0 μs. In each shot, a single 100 ns MW pulse was irradiated at a certain time between −3 and 15 μs. The emission decays are accumulated by digitizing oscilloscope changing the MW irradiation time. In the "delayed" type expression, the signal is observed at a fixed delay time. In the "immediate" type expression, the signal is observed by following the MW pulse.

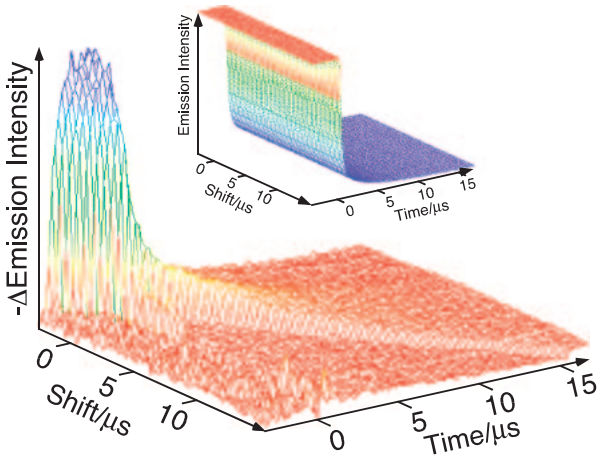

Figure 4. A 3D presentation of the result of pulse shift measurement of the EL cell driven at 10 V in the presence of a magnetic field of 324 mT. Insert: the original data before subtraction of the emission decay curve. The "delayed" type expression is obtained by observing the result between 10 and 11 μs at the "time" axis. The "immediate" type expression is obtained by following the peak diagonally in 2 μs window.

able. To avoid this problem, we first applied the pulse shift technique to the light off process, where no radical ions are formed after the removal of electricity. Hereafter, we refer to the removal of electricity as "turn-off."

Figure 3 shows the timing chart of the pulse shift measurement and Figure 4 shows the 3D presentation of the observed data and the extracted pulse shift signals at 10 V. The pulse shift signal is obtained by subtracting the decay profile without MW irradiation from the observed data. Here, the turn-off is set as time zero. The driving voltage was applied from −300 to 0 μs with 250 Hz repetition. In each shot, a 100 ns resonant MW pulse was irradiated at a certain time between −3 and 15 μs with 50 ns step. Then, emission intensity was accumulated between −3.4 to 16.6 μs shifting the MW irradiation time. It must be mentioned here that the appearance of RYDMR spectra requires a quantity of delay to convert the change in the spin state into that of the product yield,[15] such as the conversion of singlet RIP into the singlet excited state and its emission. There are two methods to take this delay into account. The first one is to observe the reaction at a fixed time of large enough delay to complete any transient effect.[16] Another is to observe the reaction with a fixed delay after MW pulse irradiation to equalize the transient effect.[8,17] Tentatively, we call the former "delayed" type, and the latter "immediate" type.

As shown in Figure 3, "delayed" expression plots the averaged emission intensity at a fixed delay time after turn-off, which was taken to be 10–11 μs in the present study. This expression corresponds to cutting the 3D figure along the "shift" axis. In the "immediate" expression, the difference of the emission intensity with and without MW irradiation is accumulated just after irradiation from 0 to 2 μs in our study. This expression corresponds to cutting the 3D diagonally along the "shift = time" line. We prefer the "delayed" type because the emission intensity without MW irradiation at a fixed time window is constant to all data and its subtraction is practically unnecessary for this expression. This reduces noise. The "immediate" type expression needs subtraction of the data at different time windows. The different sizes of the rectangle at the observation window in Figure 3 indicate this difference in the dynamics at each window. Therefore, it includes the noise of the signal in the absence of MW irradiation and the result must be interpreted to consider the background kinetics.

In Figure 4, the right side axis shows the time after turn off and the left axis shows the time of MW irradiation with reference to the turn-off. The vertical axis is the emission intensity. In this measurement, we irradiated a 100 ns MW pulse ($B_1 \approx 1$ mT) resonant to the spectrum center. Unfortunately, the effect of MW irradiation is very small and the decay of emission intensity is only observable in the original data. Since the MW effect appears as a decrease of emission intensity, the vertical axis of the signal is opposite to the original data. As clearly shown in the figure, the MW effect is running diagonally along the "shift = time" line. This is a simple confirmation that the observed signal is a response to the MW irradiation. This figure may be impressive but we should convert it to an interpretable form. As described above, there are two methods. The "delayed" presentation is given in Figure 6 and the "immediate" presentation is given in Figure 8.

Figure 5 shows the immediate response of the MW irradiation, which is obtained by accumulating the results in Figure 4 shifting each data by 50 ns to overlap the MW irradiation time. In order to define the baseline, the accumulated data are limited to those from −3 to −2.5 μs before turn-off. The rise time was $(4.5 \pm 0.1) \times 10^2$ ns. Since the lifetime of the singlet excited state is estimated to be less than 1 ns,[18] this time is considered to be the recombination time of the singlet RIP during energization. It must be emphasized that this value may not hold after turn-off where the formation of radical ions is finished. From this behavior, we can estimate that most of the transient effect by the MW irradiation terminates in 2 μs.

Figure 6 shows the "delayed" expression of the pulse shift measurement. In this figure, the emission intensity from 10 to

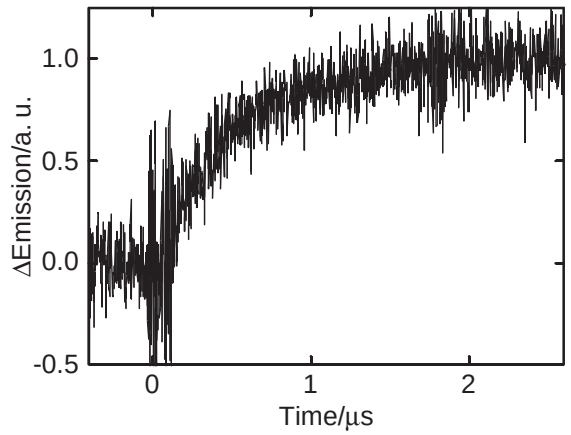

Figure 5. The transient response of emission intensity by a 100 ns resonant MW pulse. Its effect does not finish within the pulse width.

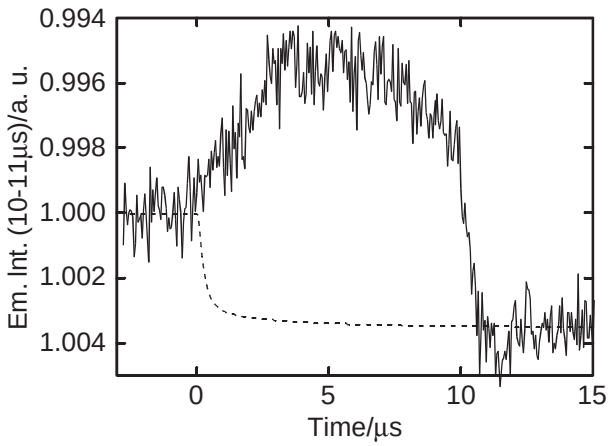

Figure 6. The MW irradiation effect on emission intensity of the EL cell driven at 10 V. The signal is averaged from 10 to 11 μs after turn-off. This is the "delayed" type expression of pulse shift measurement shown in Figure 4. The normalized decay profile of the emission intensity is also shown as dashed line.

11 μs after turn-off was integrated as a signal. The integrated intensity is shown upside down because the decrease in the emission intensity means an increase in the MW effect as is the case of Figure 2. Here, the decay of emission intensity is also presented. To gain the accuracy of the small variation of the vertical axis as indicated, we accumulated the signal more than a week. The signal is constant until turn-off and starts to decrease in value until 5 μs after turn-off. The signal then turns to increase and shows a steep increase in value from 10 to 11 μs. After that the signal is stable and 0.35% larger than the value before turn-off. The steep increase in value from 10 to 11 μs is due to the passing of the MW pulse through the observation window, which is not essential in the dynamics of electron spins. As expected from Figure 3, MW irradiation later than the observation window cannot be detected. If we shift the observation window, the steep increase in the signal moves accordingly.

The 0.35% increase of emission intensity later than 11 μs is evidence of the resonance. It says that the integrated emission

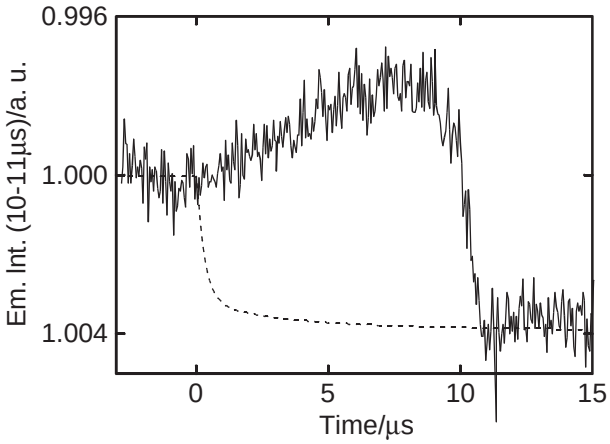

Figure 7. The MW irradiation effect on emission intensity of the EL cell driven at 8 V. The signal is averaged from 10 to 11 μs after turn-off. The normalized decay profile of emission intensity is also shown as a dashed line.

intensity at 10–11 μs without MW irradiation is 0.35% larger than that with MW irradiation at −3–0 μs before turn-off. The short MW pulse does really convert 0.35% of the singlet RIP to the triplet one. Since the applied MW pulse is one hundredth of that in Figure 2, we must accept this small variation to improve the time resolution. It assures at the same time that this MW effect is small enough to be treated as a small perturbation, which does not harm the spin dynamics of the light-off process. The increase of the intensity from 5 to 10 μs is partially ascribed the incompleteness of transient effect shown in Figure 5. When we shift the observation window, the starting point of the steep rise shifts accordingly.

The remarkable point of this time dependence is the decrease of the emission intensity when the MW pulse is irradiated after turn-off. This decrease of emission implies that the MW effect, that transfers the singlet RIP to the triplet ones, after turn-off occurs more efficiently than that before it. If we regard the average from 3 to 6 μs as the maximum MW effect, it is 2.3 ± 0.1 times larger than that before turn-off. Figure 7 shows the "delayed" expression of the pulse shift measurement of the same EL cell driven at 8 V. To accumulate this signal, it took more time than that for Figure 6. The signal became about half of that in Figure 6 but it is still significant. On the other hand, the increase after turn-off continued up to 9 μs near the averaging window, which is different from that in Figure 6. If we regard the average from 6 to 9 μs as the maximum MW effect, it is 1.6 ± 0.1 times larger than that before turn-off. This indicates that the increase of the MW effect after turn-off may be general but is dependent on the driving voltage. These magnitudes of the MW effect are observed using a small perturbation. Therefore, we can enhance this MW effect by increasing its power or irradiation time but the ratio of the effect before and after turn-off will vary (probably become smaller). The experiments at higher driving voltage lose reproducibility due to deterioration of the EL cell and those at lower voltage are very difficult owing to the accumulation time required to gain the acceptable S/N ratio.

This increase of the MW effect contradicts the expectation based on the quasi-stationary condition as described below.

This model described well our previous results.[4,5] After turn-off no radical ions are formed. These radical ions must make pairs to deactivate by emission. As shown in Figure 1, the emission intensity decays quickly after turn-off indicating the decrease of RIP, and hence radical ions. The first process that we must consider is the breakdown of the quasi-stationary condition by the decay of RIPs. In the presence of the magnetic field, the population of RIPs in $S–T_0$ and that in $T_{\pm1}$ decay with different rate constants. The RYDMR and the magnetic field dependence confirm that the latter rate constant is larger than the former. This means that the population difference, i.e. $[S–T_0] - [T_{\pm1}]$, might increase during the decay of total amount, $[S–T_0] + [T_{\pm1}]$, which may induce the observed effect. A similar phenomenon is observed in the RP dynamics in micellar solutions,[3,15] which originates from the vacancy of the population of the S state just after the formation of the triplet RP.

If we assume that the population of $T_{\pm1}$ states just before turn-off is near 50% as injected, the rise due to this process could be observed. Unlike the cases in micellar solution, the turn-off process starts from a quasi-stationary condition. If the population difference just before turn-off is induced by the difference in the decay rate constants from S and T states, the above population difference decays monotonically, as far as checked numerically. Therefore, it is hard to explain the observed rise with this process without another polarization mechanism to distort the population. Since the populating rate does not affect the dynamics of RIP within the reaction mechanism (reactions 1–8),[5] the difference between the observation at 8 and 10 V could not be observed with this process. Therefore, the present observation is unexplainable within the standard mechanisms.

Another plausible interpretation of these results is that the amount of RIP sensitive to the MW is enhanced by the turn-off irrespective of the decay of RIP that is measured by the emission intensity. This implies that the RIP is not a single entity. In the scheme shown in reactions 1–8, we did not introduce such discrimination in RIP for simplicity. We want to attribute this effect to the exchange interaction between the radical ions in a pair. Prior to discussing this point, we had better treat the experimental data in another way.

Figure 8 shows the "immediate" expression of the pulse shift measurement shown in Figure 4. The integration window from 0 to 2 μs corresponds to the fast changing part after MW irradiation as shown in Figure 5. As described earlier, the signal reflects strongly the original reaction dynamics, which requires some caution to interpret the results. In the present case, the observation window is moving in the light-off process and hence the signal decays with the decay of emission intensity. As clearly seen in this figure, the signal decays simply after turn-off but the tail part is much larger than the decay of emission intensity. This shape is also different from the moving average of emission intensity with 2 μs window, in which the tail part is not emphasized. If we fit the emission decay with two exponential components, it is split into components with a time constant of 0.25 and 3.2 μs with initial ratio of 85%:15%. The pulse shift data is similarly split into components with a time constant of 0.88 and 5.4 μs with initial ratio of 63%:37%. This analysis confirms that the enhancement of the tail part is real. If we compare the integrated intensity from 1 to 15 μs after turn-off, the MW effect is estimated to be 2.1 ± 0.1 times larger than that before turn-off. This value is in good agreement with the value (2.3 ± 0.1) derived from the "delayed" presentation.

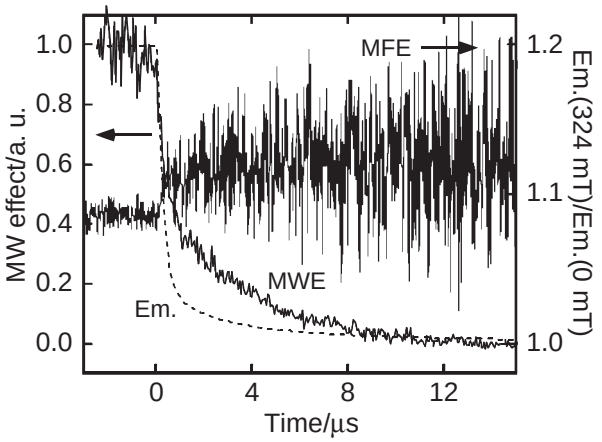

Figure 8. The microwave irradiation effect on emission intensity of the EL cell driven at 10 V (MWE, the left axis). The signal is integrated from 0 to 2 μs just after the MW irradiation. This is the "immediate" type expression of the pulse shift measurement shown in Figure 4. This figure also includes normalized emission intensity (Em., the left axis) as a dashed line and the magnetic field effect (MFE, the right axis) on the emission intensity at 324 mT divided by that at 0 mT.

In Figure 8, the time dependence of the ratio of the emission intensity at 324 mT to that at 0 mT is also shown. This MFE value shows a transition from 1.09 ± 0.01 before turn-off to 1.12 ± 0.03 (average from 5 to 10 μs) after it in ca. 1 μs, although the value after turn-off shows a slight increase with time. The time region where the larger MFE is observed overlaps well to the region where the larger MW effect is observed. This fact implies that the enhancement of the MW effect and that of the MFE have a common origin. The "delayed" measurements indicates that such a change starts just after turn-off.

The enhancement of the MFE after turn-off might be ascribed to the elongation of RIP lifetime that enhances spin conversion, if we do not mention the MW effect. This implies the lifetime of RIP becomes longer with decreasing driving voltage. This is, however, opposite to the expectation based on the electric field induced delayed fluorescence discussed below.[19–21] As stated earlier, the magnitude of the MFE of the emission intensity becomes larger with decreasing the driving voltage. The denial of the longer lifetime of RIP at lower voltage requires another mechanism to interpret this observation. Furthermore, the longer RIP lifetime gives the RIP a chance to recover the population that is modified by the MW irradiation. Therefore, it reduces the MW effect after turn-off, which is opposite to the observation. Consequently, we can safely exclude the contribution of RIP lifetime.

To explain the MW effect and MFE of the EL emission simultaneously, we must go back to the basic mechanism of MFE and RYDMR. The classical argument against MFEs is that the exchange interaction among electron spins in a molecule is too large to control its reaction by the external magnetic

field. To avoid this problem, the radical pair mechanism replaces a molecule by a pair of radicals interacting weakly from afar. Therefore, the present results can be rationalized if the magnitude of the exchange interaction between radical ions in a pair is reduced by the removal of electric field. To consider the exchange interaction, discussion of experiments on electric field induced delayed fluorescence is helpful.[19–21] This phenomenon is described as follows. When an EL cell is illuminated in the presence of an electric field, a burst of the emission is observed after turn-off irrespective of the large delay compared to the lifetime of the excited singlet state (exciton). This is based on the field-assisted fission of the exciton into RIP. There are several interpretations of this phenomenon. One is that the bent potential surface induced by the electric field stabilizes the RIP state that regenerates the exciton after removal of the potential.[19] Here, the spin conversion in the RIP is secondary and is assumed to proceed freely. Another is that the electric field enhances the exchange interaction between the radical ions in a pair.[21] In this case, spin conversion is locked by the electric field. There is, however, another result insisting that there exists freedom of electron spin conversion under the electric field.[20] The discussion about the stabilization and thus the longer lifetime of the RIP in the presence of the electric field is common but the spin conversion in this process is still controversial.

Our observation becomes explainable by accepting the idea of the enhancement of the exchange interaction by the electric field.[21] The two-fold enhancement of the signal in both types of pulse-shift measurements after turn-off is explainable by the increase of the RIP with negligible exchange interaction that can undergo spin conversion by MW field. The reduced exchange interaction also enhances the spin conversion by the external magnetic field. This also explains the larger MFE in the emission at lower driving voltage if the spin conversion does not stop but decreases in the presence of larger electric field. During the application of electric field, the above RIP remained in place with larger exchange interaction. We cannot characterize the circumstance but an RIP that is accidentally arranged compressible along the electric field is assumed in the above article.[21]

Unfortunately, we cannot say much about the composition of the spin state of the locked RIP. If it is similar to that of the stationary condition, the MW effect will increase after turn-off as observed. The increase may correspond to the decrease of exchange interaction. If the spin state is kept as injected, the immediate effect is nothing but evolves with time. Therefore, we cannot analyze the kinetics of the observed rising process at the present stage. If the stabilization of the locked RIP is small enough to allow charge recombination, this composition can vary from full singlet to full triplet. Therefore, the MW effect at turn-off may depend on the EL material. There might be other mechanisms that can explain the present observation but the increase of exchange interaction by the electric field seems plausible to interpret the MW effect and MFE on the emission intensity simultaneously.

On the other hand, the same article reports the complete absence of spin conversion by the magnetic field in the presence of an electric field, which is ascribed to a large exchange interaction.[21] Since the EL material and the experimental conditions are not the same to ours, some difference in the conclusion might not be serious. In our case, the observation of the RYDMR spectrum during the energization clearly confirms the existence of RIP with negligible exchange interaction even in the presence of the electric field, which also assures the spin conversion by the external magnetic field under the same condition.

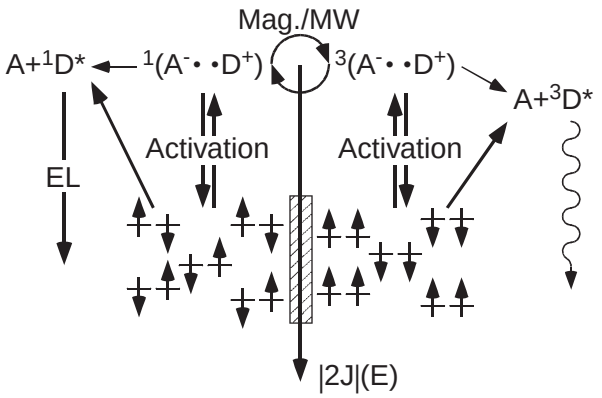

Figure 9. Proposed reaction scheme for the emission process of EL materials. The RIPs indicated by $^{1}(A^{-\bullet}\ D^{+\bullet})$ and $^{3}(A^{-\bullet}\ D^{+\bullet})$ represent remote RIPs that can change spin states by the external magnetic field or the resonant microwave field. The lower RIPs abbreviated by the pair of arrows represent close RIPs that are stabilized by the electric field and their spin conversions are blocked. The downward axis represents stabilization by the electric field and the increase of exchange interaction in a RIP. The formation of the singlet or triplet exciton proceeds from the charge recombination of close RIPs (inclined arrows) and from long-range charge recombination of remote RIPs.

Based on these observations, we present a model scheme for the EL emission in Figure 9. The upper side of the scheme is a standard radical pair mechanism in the absence of the exchange interaction, where spin conversion by the MW field and by the external magnetic field proceeds. The recombination of a singlet RIP generates an excited singlet state (exciton) and emits light but that of the triplet results simply in the dissipation of energy. The difference from the standard model is that the amount of such RIP (RP) is limited by the dispersion of exchange interaction, abbreviated by $|2J|$, which is assumed to be dependent on the electric field, E. This vertical axis may also be regarded as the axis of energy stabilization, because both Coulombic and exchange interactions become larger by decreasing the distance between component radical ions in a pair. Many RIPs shown as sets of two electron spins have significant exchange interactions that hinder spin conversion. The RIPs with smaller stabilization that have enough energy for exciton formation recombine their charges reserving their spin multiplicity. These processes are shown as the inclined arrows. They are activated to the negligible $|2J|$ condition to change their spin states. This process may be a hop of one component of RIP to a farther site. If this is the case, the upper RIP corresponds to the remote RIP in which several molecules are inserted between the component radical ions. At present we cannot say much about the efficiency of the charge recombina-

tion of remote and close RIPs. If the charge recombination from the close RIP is the main process, the time constant of 4.5×10^2 ns observed in Figure 5 may correspond to this.

With increasing electric field, the amount of RIP that is blocked from spin conversion is expected to increase (The dashed region in Figure 9 goes down.), which implies that the MW effect after turn-off will be larger at larger driving voltage. The difference in magnitude of the MW effect shown in Figures 6 and 7 (2.3 and 1.6) follows this expectation. If we assume that the emission includes the contribution of close pairs showing no MFE, its amount becomes 97% of the emission intensity at 0 mT and 10 V based on the MW effect. This implies the real MFE will be 4 instead of 1.09 at 324 mT, which seems too large. Probably, the bisection of RIP into no and free spin conversion is inadequate and the dispersion in the exchange interaction as shown in Figure 9 seems better.

The simple check for the existence of the exchange interaction is the observation of $S–T_{-1}$ or $S–T_{+1}$ level crossing mechanisms on the MFE.[22] In this mechanism, the spin conversion of RIP is enhanced at a special magnetic field where the Zeeman splitting of the T_{-1} or T_{+1} state becomes degenerate with the S state compensating the exchange interaction between them. We reported this type of behavior in the decay process of the RIP of photosynthesis model compounds.[23] In the solid state, the MFE on the charge-transfer fluorescence of a poly(*N*-vinylcarbazole) (PVCz) film doped with 1,2,4,5-tetracyanobenzene (TCNB) is reported.[24,25] PVCz is a well-known organic photoconductor. The emission intensity increases from 0 to 5 mT, decreases around 30 mT, then increases again until 80 mT, and becomes constant above it. The center of dip in the MFE was observed at 46 mT. The appearance of this dip is attributed to the level crossing mechanism. Unfortunately, we have not yet found such a dip in the emission intensity of our material.[4] This may be attributed to the absence of regular structure in our material. PVCz is composed of a single unit and TCNB is doped in the array of carbazoles (C's). Its photoexcitation forms a RIP consisting of carbazole cation radical ($C^{+\bullet}$) and TCNB anion radical ($B^{-\bullet}$). Consequently, the RIP has a rather fixed structure such as a close pair, $C^{+\bullet}/B^{-\bullet}$, a pair separated by one unit, $C^{+\bullet}/C/B^{-\bullet}$, and so on. On the other hand, our material is a copolymer of PPV derivatives implying that the neighboring molecules around the cation radical are random. Furthermore, we cannot indicate the character of anion radical beyond a broad RYDMR spectrum shown in Figure 2. Therefore, the exchange interactions of our sample may be too widespread (as shown in Figure 9) to give a significant dip in the MFE. A single component polymer such as poly(MEH-PPV) might alleviate the first problem but the shortening of cell lifetime invokes another problem.

Conclusion

MW irradiation of electroluminescent cells made of a copolymer of *p*-phenylenevinylene derivatives under resonant magnetic field was carried out to investigate the spin dynamics in charge recombination. The irradiation induced the spin conversion of singlet radical ion pair into the triplet manifold, which induces a decrease in emission intensity. This MW effect became 1.6 and 2.3 times larger after removal of the driving voltage of 8 and 10 V, respectively. The MFE on the emission intensity also increased from 1.09 to 1.12 after turn-off. These phenomena are interpreted by the decrease of the exchange interaction between radical ions in a pair after the removal of the electric field. The contribution of the exchange interaction may be the answer of the question presented at the introduction. Probably, good EL materials afford long-range charge recombination of RIPs where the exchange interaction is small. Or such a spin conversion is not wasted in good EL materials. In this case, the enhancement of the magnetic field effect of the emission intensity contributes positively to the enhancement of emission efficiency. Control of the exchange interaction between radical ions by the electric field may be a key mechanism to develop new electric devices made of organic semiconductors.

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