

Exchange Interaction in the Emission Process of Organic Electroluminescent Materials

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The emission in organic electroluminescent (EL) material originates from the charge recombination reaction between positive and negative charge carriers. These carriers are organic radical ions of a single molecule, such as tris (8-hydroxyquinoline) aluminum, Alq₃, or a unit of organic polymers, such as polyphenylenevinylene (PPV). Since these carriers have not only charges but also electron spins, the spin conservation must be hold in the charge recombination. Therefore, the modulation of their electron spins by static and alternating magnetic fields induces many effects on their emission dynamics. Such phenomena are called to be “spinchemical”.

The EL intensity of the PPV material is enhanced by the application of the external magnetic field (cf. Fig. 1). If the spin states of carriers are fixed at their injection, the yield of singlet emission should be 25 % and invariant. This observation indicates that the magnetic field can modify the spin state. The energy separation between singlet and triplet excitons is, however, too large to modify their population by magnetic fields, which was the classical argument against the external magnetic field effects. The origin of this separation is the exchange interaction between electron spins, which decreases exponentially with increasing the distance between spins. Therefore that between the separated doublet species is much smaller than those in excitons and it enables the modification of spin state by the magnetic fields. This is the concept of “radical ion pair” or “radical pair” in spinchemistry.

In liquid phase, the motion of radical is free and thus the distance between radicals is random. Consequently, the magnitude of the exchange interaction is negligible except for the chained radicals or confined radicals in a small region. On the other hand, even an amorphous solid has a relatively fixed distance between molecules or polymer units, which makes a series of the magnitudes of exchange interaction. Therefore, the contribution of exchange interaction in spinchemical phenomena is an interesting subject in solid.

The external magnetic field effect (MFE) on the EL intensity shown in Fig. 1 is induced by the blocking of the spin conversion in the presence of magnetic fields as observed in liquid phase reactions. Its operating voltage dependence has no parallel case in solution. Furthermore, the larger MFE in liquid phase implies a longer lifetime of the emission precursor. This slower charge recombination is an unwanted character for EL materials and is hardly acceptable as an interpretation for established EL materials.

The electron spin resonance (*i.e.* alternating magnetic field) reduces the EL intensity by converting the singlet radical ion pair to the triplet one. This microwave effect becomes larger when the operating voltage is removed from the device as shown in Fig. 2. The magnitude of the microwave effect shown as the blue line in Fig. 2 should be proportional to

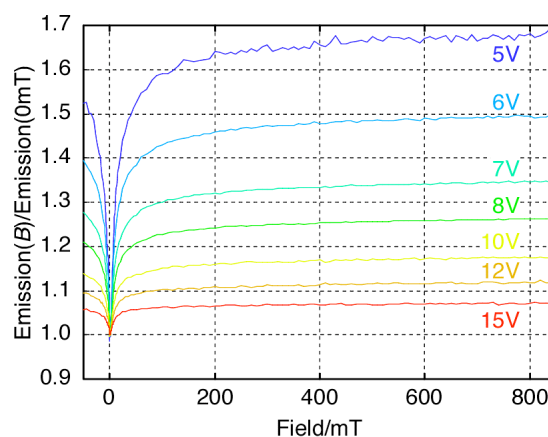


Fig. 1 Magnetic field effect on the EL intensity of PPV derivatives at several operating voltages.

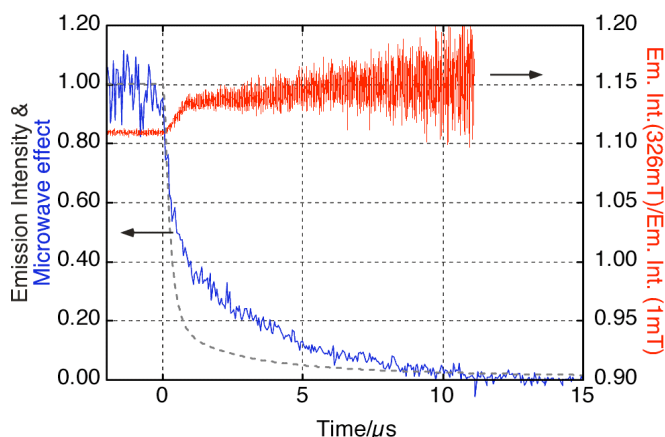


Fig. 2 Resonant microwave irradiation effect and MFE on the EL intensity of PPV derivative just after the removal of operating voltage.

the amount of the emission precursor and it must be the same to the decay of emission intensity shown as the dashed line. On the other hand, the MFE of EL intensity shown as the red line increases. These phenomena indicate that the circumstance of the emission precursor, the radical ion pair, changed by the removal of operating voltage. The most plausible interpretation is that the magnitude of exchange interaction increases with increasing the applied voltage. Thus the removal of the operating voltage enhances the microwave effect and MFE of EL as shown in Fig 2. This also explains the operating voltage dependence of MFE shown in Fig. 1. These results indicate the importance of exchange interaction in solids.

Fig. 3 shows the energization time dependence of the EL intensity and its MFE of a fresh device. In the early stage of the energization, the intensity increases with time and its MFE was found to increase more slowly. The retardation of charge recombination as an origin of the enhancement of

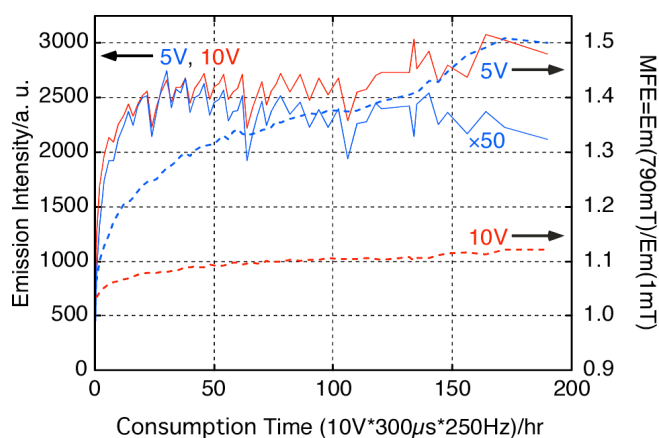


Fig. 3 Energization time dependence of the EL intensity of PPV derivative and its MFE measured at 5 and 10 V. Energization was 10 V by 110 hr and then was raised to 11 V.

MFE contradicts that of EL intensity because it promotes parallel quenching processes competing the charge recombination. The reduction of the exchange interaction explains this observation. The increase of the average distance of the charge recombination induces both the reduction of exchange interaction and the expansion of the recombination area of each reaction center. In this context, the increase of MFE and that of EL intensity are symbiotic.

The control of exchange interaction by the applied voltage will bring in fruitful information on conduction process in organic semiconductors.