有機ＥＬ発光のスピン多重度と外部磁場効果

Spin multiplicities on organic electroluminescence and their external magnetic field effects

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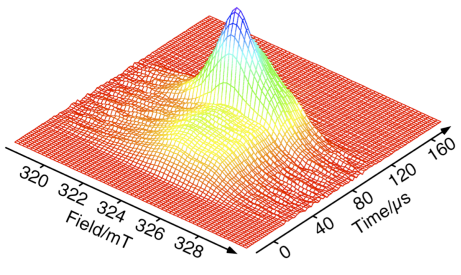
Organic electroluminescence (OEL) is exciton emission formed by the charge recombination in a thin organic film, where positive carriers are injected from one surface and negative carriers from another surface. It is also called organic light emitting diode (OLED) because the mobility of one carrier is much larger than the opposite one to prevent the carriers passing each other in vain. Both carriers have not only charges but also spins, but there is no spin correlation between them. The total spin multiplicity at the encounter in the charge recombination is stochastic, i.e., Singlet : Triplet = 1 : 3. Since the energy of the triplet exciton is lower than the singlet one, its yield can be 100% by the intersystem crossing (ISC) from the singlet one. This is the reason why triplet OELs became mainstream except for blue emitters. Although singlet OELs have higher energy and thus are suitable for blue emitters, it seems that the emission yield cannot exceed 25%. We can break this limitation by the magnetic field, which can change the emission efficiency by controlling the spin conversion. This technique is also applicable to elucidate the unexplored mechanisms of OEL.

The external magnetic field hardly modifies the ISC between singlet and triplet excitons, but usually blocks the ISC between singlet and triplet carrier pairs, the precursor of exciton. Polyphenylenevinylene (PPV) derivatives are noted fluorescent-type OEL materials. We found that the emission intensity of a certain PPV OEL cell was enhanced by the increase of the external magnetic field. Furthermore, the magnitude of the enhancement became large by lowering the driving voltage. The enhancement of singlet emission under the inhibition of the spin conversion between singlet and triplet carrier pairs implies that the conversion from singlet to triplet is more efficient than the opposite process. This means that the emission efficiency at low voltage drive is smaller than 25%. On the other hand, we found another magnetic field dependence at high voltage drive, which suggests the contribution of delayed fluorescence by triplet-triplet annihilation. This mechanism allows the singlet yield up to 55%.

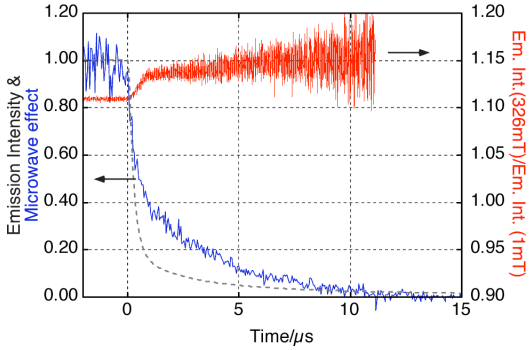


Reduction of emission intensity induced by microwave irradiation

In order to prove that the magnetic field manipulates charge carriers directly, we investigated the effect of rotating magnetic field by microwave. We observed that the emission intensity

decreased at the magnetic field corresponding to $g \approx 2.004$ suitable to organic carriers, indicating that the manipulation of the electron spin on carriers result in the variation of exciton yield. The decrease of emission intensity also suggests that the population of singlet carrier pair is larger than that of triplet, i.e. that the charge recombination of singlet carrier pair is more difficult than that of triplet. This is the same as that derived from the static magnetic field effects.

We obtained an interesting result when we applied this microwave irradiation to the shut-off process of the OEL cell. By the removal of driving voltage, the injection of the carriers is terminated and the decay of the emission is observed due to the charge recombination of remaining carriers. We found that the microwave effect after the shut-off is larger than that before that. Similarly, the static magnetic field effect became large at the shut-off process, being reminiscent of the larger effect at lower driving voltage. We concluded that the electric field increases the exchange interaction between carriers that prohibits their spin conversion by static or rotating magnetic field.



Microwave irradiation effect at the shut-off process and external magnetic field effect

An independent phenomenon is also explained by the exchange interaction. A fresh OEL starts to increase the emission intensity by its operation, attains a stationary intensity, and decreases the intensity slowly by degradation. The magnitude of the magnetic field effect also increases during and after the increase of emission intensity. The increase of the emission intensity is attributed to the enhancement of effective charge recombination. The emissive charge recombination is considered to occur at special emission centers with favorable conformation and/or circumstances. The observed aging variation is interpreted by the expansion of the trapping region of injected carriers toward the emission center, which induce the increase of distance between carriers, thus the decrease of exchange interaction and the increase of magnetic field effect.

To elucidate the spin dependence of OEL, the investigation of phosphorescence-type OEL is unavoidable. Usually, such type of OEL is composed of host materials and phosphorescent guests. Therefore we must discriminate the following three processes, 1. singlet energy transfer between host and guest followed by the ISC of guest, 2. ISC of host followed by the triplet energy transfer between host and guest, 3. charge recombination on the guest. We have started to investigate the OEL cells with polyvinylcarbazole as a host and iridium complex as a guest. We confirmed the increase of the emission intensity of host-only device by the magnetic field. We are also trying to measure the electric response of the devices.