

Study on spontaneous exciton dissociation in polar organic semiconductor solid-state films

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論 文 内 容 の 要 旨

Charge-transfer (CT) type excitons formed in an organic molecular system have been attracted in recent years because their excitonic characteristics play a critical role in a series of the photon-electron conversion processes. Recently, in organic light-emitting diodes (OLEDs), a thermally activated delayed fluorescence (TADF) molecule known as an emitter forming the intramolecular CT excited state is widely investigated since the emitter can realize nearly 100% internal electroluminescence (EL) quantum efficiency. The CT exciton, however, has relatively low Coulomb binding energy due to its larger exciton radius (i.e., electron-hole distance) compared to that of a locally excited molecule such as π -conjugated conventional emitters, resulting in the ease of an exciton dissociation inherently. This dissociation process is assumed to be a possible quenching path for photoluminescence (PL) characterization in a solid-state film composed of TADF emitters. Moreover, many polar emitters are prone to induce spontaneous orientation polarization (SOP) in their solid-state films, expected to facilitate the exciton dissociation. Although the exciton dissociation dynamics on the intramolecular CT excitons and their correlation with the SOP have not been discussed sufficiently so far, an understanding of the dissociation mechanism in CT excitons is essential for improving the performance of not only OLEDs but also other photo-receiving devices such as organic photovoltaics (OPVs). Thus, in this thesis, I focused on the exciton dissociation processes of organic polar emitters to unveil the dissociation dynamics of the intramolecular CT exciton in the solid-state films.

In Chapter 2, the exciton dissociation of a polar TADF emitter exhibiting a CT excitonic character was studied by using the method of a time-resolved PL (TRPL) measurement. I found that the CT exciton formed in a highly-doped host-guest film dissociates spontaneously due to an internal electric field induced by the molecular polarization, i.e., SOP. The charge carriers generated by exciton dissociation diffuse and slowly recombine in the solid-state film, which is observed as long-lived emission and the charge carriers can recombine forcibly by an external electric field modulation. In addition, I found that the spontaneous dissociation acts as an unignorable quenching process in the solid-state PL characterization for polar TADF emitters. While excitons of conventional emitters are generally believed to be stable because of their high exciton binding energies, this study clarified that the intramolecular CT excitons can dissociate free charge carriers spontaneously.

In Chapter 3, the role of the spin-triplet states in the organic molecules with a small energy offset between a singlet excited state (S_1) and a triplet excited state (T_1) for exciton dissociation was investigated. The exciton dissociation in 2,4,5,6-tetra(9Hcarbazol-9-yl)iso-phthalonitrile (4CzIPN) was evaluated by measuring TRPL characteristics in a solid-state host-guest film including the triplet activated host of 4'-bis(carbazol-9-yl)biphenyl (CBP) or a triplet scavenging host of 9,10-bis(2-naphthyl)anthracene (ADN). The exciton dissociation was clearly suppressed in the 4CzIPN:ADN co-deposited film, indicating that the excited spin-triplet state plays an important role in the exciton dissociation. Moreover, the result of an electric-field-modulated TRPL measurement in the 4CzIPN:CBP co-deposited film indicated that the exciton dissociation after the formation of the lowest energy states occurs selectively via the long-lived T_1 and the dissociation probability via S_1 is quite low. Further, the prolongation of charge carrier lifetime was also suggested in the 4CzIPN:CBP co-deposited film due to shutting off a Dexter energy transfer loss channel, which is equivalent to the back-electron transfer channel in OPVs. This study clarified that the excited spin-triplet state is advantageous for the exciton dissociation in the solid-state films.

In Chapter 4, a charge storage device using the principle of CT-exciton dissociation was explored. The lifetime of the charge carriers photogenerated in the device was characterized by visualizing recombination between the accumulated electrons and injected holes as pulsed electroluminescence (EL). The results indicated that the accumulated electrons survived over one month in the device due to interfacial pinning of accumulated electrons by SOP and the suppression of recombination probability by extracting counter holes in hold time. The charge carriers also retain spatial information over 1,000 seconds even though an active area in the device has no pixelized structure, suggesting that the electron diffusion is quite slow because the in-plane polarization of an emitter is expected to be significantly small. Furthermore, a linear relationship between photo-irradiation power and pulsed EL intensity was obtained in addition to the spatial retention. By assembling the charge storage ability, unique gray-scale imaging based on the exciton dissociation of organic semiconducting materials was demonstrated. This study highlighted that the charge carriers were stored stably in the device using the techniques of CT-exciton dissociation, and a multi-functional organic device combined light-receiving, memory, and emission was realized.

In Chapter 5, this thesis was summarized, and future perspectives were introduced. The findings related to the exciton dissociation not only contribute to elevating the performance of an organic photoelectric device, but also open up the possibilities for a novel multifunctional device with an organic semiconducting material exhibiting CT excitonic character in the future.