

Spontaneous dissociation of charge-transfer type excitons in organic solid-state films

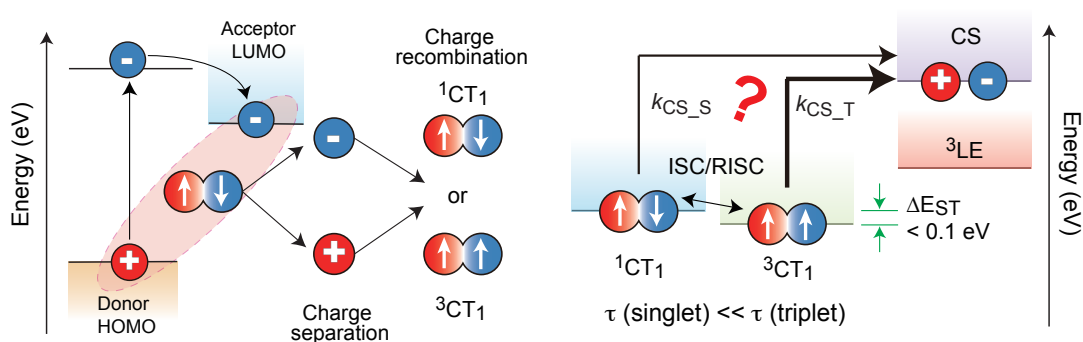
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Clarification of the role of the spin-state that initiates exciton dissociation is critical to attaining a fundamental understanding of the mechanism of organic optoelectronics devices. For example, the formation of low-energy triplet excitons *via* recombination of photogenerated carriers is generally considered a major energy-loss pathway in donor–acceptor (D–A) blend-type organic photovoltaics (1), leading to a low carrier extraction yield. Indeed, an excited spin-triplet state with an energy lower than that of excited spin-singlet state is disadvantageous in exciton dissociation. However, a small electron exchange integral results in small singlet-triplet energy splitting in some material systems (2). Therefore, if the energy level of an excited spin-triplet is nearly isoenergetically aligned with that of an excited spin-singlet, the question arises as to which excited spin state is advantageous for the dissociation events following the formation of the exciton (**Fig. 1**).

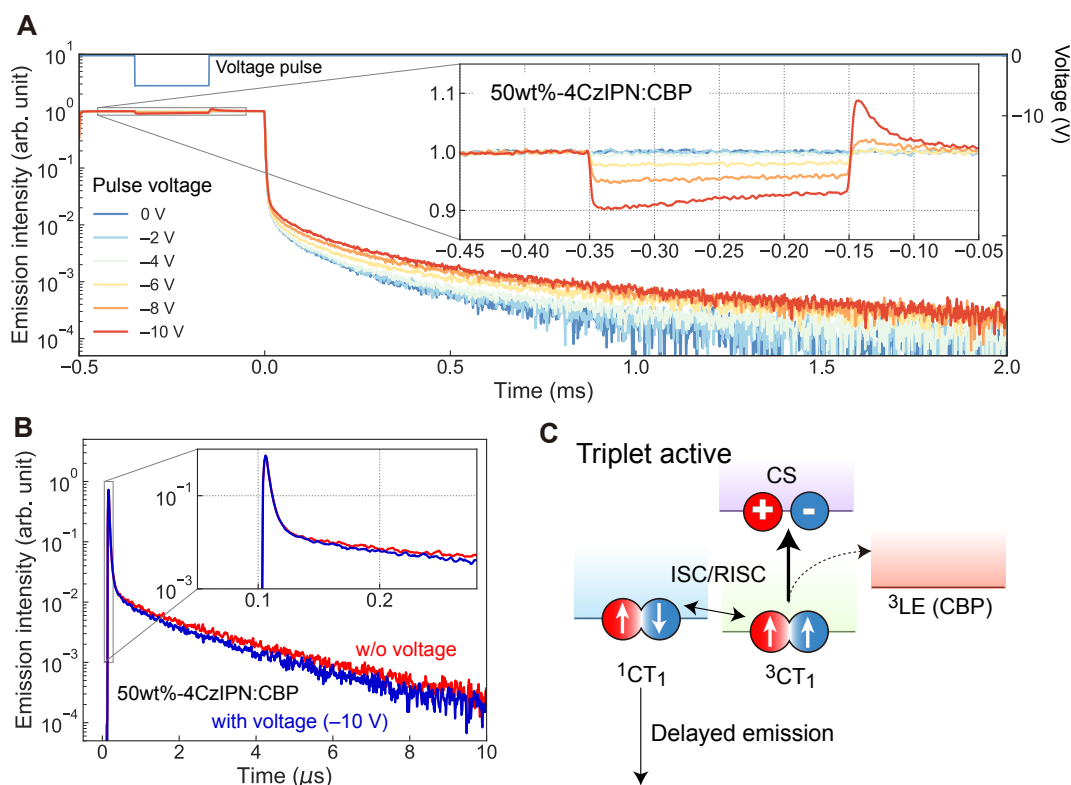
In this work, we therefore focused on the exciton dissociation dynamics of a highly-doped polar organic molecules exhibiting thermally-activated delayed fluorescence (TADF) in host molecules, *i.e.*, 2,4,5,6-tetra(9H-carbazol-9-yl)iso-phthalonitrile (4CzIPN) doped CBP film, because the excited spin-triplet is nearly isoenergetically aligned with that of an excited spin-singlet. **Figure 2a** shows the transient photoluminescence (TRPL) profiles for 4CzIPN:CBP film. After the photoexcitation light was turned off, two components in the emission decay were observed in the measurement time range of ~ 2 ms: an inherent radiative decay due to 4CzIPN and a long-lived emission decay arising from slow recombination of charge carriers dissociated from the 4CzIPN excitons (3). Notably, the excitons of 4CzIPN can also dissociate upon application of an external voltage to the films, and the long-lived emission intensity become stronger with increasing of the voltage,



indicating that the charge carriers generated by the dissociation of excitons can essentially maintain a stable state at least on the millisecond time scale in the film.

We then evaluated the electrical-field-modulated TRPL in the 50-wt%-4CzIPN:CBP film to directly confirm the spin-selective exciton dissociation. The delayed component (intrinsic delayed fluorescence lifetime *via* $^3\text{CT}_1$) in the 50-wt%-4CzIPN:CBP film with a negative voltage was appreciably attenuated compared with that of the device without an electric field, whereas the prompt decay component was unchanged (**Fig. 2b**). These results clearly suggest that the charge separation event after the formation of the excitonic states occurs selectively *via* the excited spin-triplet state and that the dissociation probability of the singlet excitons, contributing to the rapid radiative relaxation, is negligibly low (**Fig. 2c**). In fact, the relaxation time of the PL quenching after applying the external electric field is over several microseconds in the 4CzIPN:CBP film, indicating that the charge carriers are formed slowly (**Fig. 2a**).

We believe that our observations highlight that the charge separation following the exciton dissociation from the triplet CT states rather than the singlet CT states is inherently critical (4). In this presentation, we will discuss the experimental results in more detail.



1) T. M. Clarke, et al., *Chem. Rev.* **2010**, 110, 6736. 2) H. Nakanotani, et al., *Chem. Lett.* **2021**, 50, 938. 3) T. Yamanaka, et al., *Nat. Comm.* **2019**, 10, 5748. 4) T. Yamanaka, et al., (in press)