Theoretical Analysis of Spin-Orbit Charge-Transfer Inter-System Crossing (SOCT-ISC) Mechanism in Donor-Acceptor

([1]*Graduate School of Science, Kyoto University*, [2]*CREST*, [3]*FOREST*)
○Maria Kosaka[1], Katsuki Miyokawa[1], Yuki Kurashige[1,2,3]

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Metal-free organic triplet photosensitizer is an attractive area of material science; in particular the use of a donor-acceptor linked chromophores is promising because its charge transfer (CT) state has a long lifetime and often exhibits efficient intersystem crossing owing to the spin-orbit coupling induced by charge transfer (SOCT-ISC). In the previous experimental study, it was reported that BDP-PXZ, a dyad of bodipy (BDP) as acceptor and phenoxazine (PXZ) as donor, exhibit a TR-EPR spectra consisting of two different transient species assigned to ^{3}CT (PXZ→BDP) and ^{3}BDP, while that of the methylated derivative TMBDP-PXZ is well explained by ^{3}BDP component alone. Most of the molecular mechanism of these processes has been still uncertain. Thus, in this theoretical study, we elucidated the detail of triplet formation process of TMBDP-PXZ and BDP-PXZ and the reason why the two different transient species coexist for the BDP-PXZ.

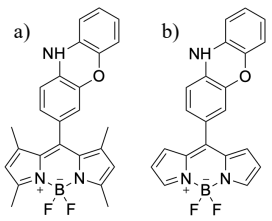

Figure 1. Structures of a)TMBDP-PXZ, b)BDP-PXZ

The potential energy curves along the dihedral angle between BDP and PXZ moieties were evaluated using the time-dependent density functional theory (TD-DFT) to reveal that the absence of the CH_3 moiety stabilizes ^{3}CT state of BDP-PXZ and allows the co-existence of two triplet states. We also investigated the spin orbit coupling (SOC) between ^{1}CT (PXZ→BDP) and each triplet state of BDP-PXZ nearby the crossing point, discovering that the ISC is spin selective and the generated triplets should be spin polarized to the component of the BDP's long axis (x-molecular axis). The calculation of zero-field splitting (ZFS) parameters on ^{3}CT and ^{3}BDP was performed with the CASSCF theory. These results well-reproduce the spectra of experimental TR-EPR, which strongly support the SOCT-ISC mechanism we propose.

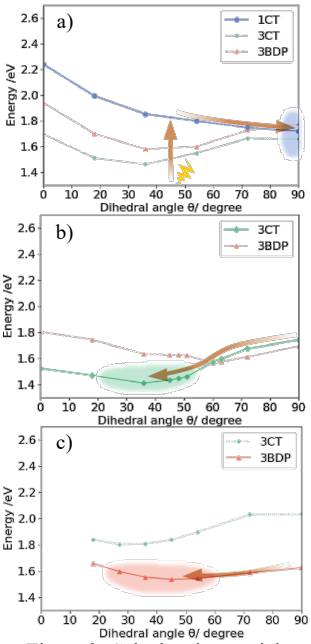

Figure 2. Calculated potential energy curves for BDP-PXZ along the geometry optimized for a)^{1}CT, b)^{3}CT, and c)^{3}BDP states.

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