

## Theoretical Analyses on Triplet-triplet Annihilation Processes of 9,10-diphenylanthracene and derivatives in solution

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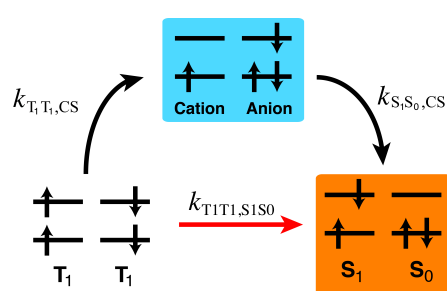
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Recently, the triplet-triplet annihilation (TTA) based photon up-conversion (UC) process has been extensively studied as a possible device that utilizes solar power because TTA-UC generates high-energy photon emission from absorptions of lower energy photons. One of the most remarkable advantages of TTA-UC over the other UC processes using multiphoton absorptions, f-f transitions of rare-earth elements, and so on, is that TTA-UC occurs even with the solar light intensity ( $\sim 100$  mW/cm<sup>2</sup>). Thus, the investigation into design principles for developing robust TTA materials is of great importance. However, TTA-UC process is quite complicated. Thus, one should analyze a series of these processes in parallel to deeply understand the mechanism of TTA-UC. In many experiments, platinum or palladium octaethyl porphyrin (PtOEP or PdOEP) and 9,10-diphenylanthracene (DPA) have been selected as the sensitizer and emitter, respectively and achieved the high TTA-UC quantum yield (QY) (26%) in solution. However, in theoretical analysis, there are many studies for the TTET processes, but not for the TTA processes. Thus, the present study focuses on the clarification of TTA processes using theoretical method.

TTA is driven by an electron exchange mechanism generated charge separation between two triplet emitters as shown in Figure 1. For each step in Figure 1, the electron transfer (ET) rate can be estimated by the Marcus formula. To evaluate electron coupling matrix element,  $T_{DA}$ , for the TTA, we have adopted the fragment molecular orbital (FMO) method and FMO-linear combination molecular orbital (FMO-LCAO) methods [1]. Then, we perform results from molecular dynamics (MD) simulation to estimate a diffusion constant of the emitters to estimate a kinetic constant for the encounter of two emitters. Finally, we discuss the mechanism of TTA from all the results.

In the TTA process, a series of the ET processes are just reversal processes found in the singlet fission (SF) processes. Thus, the kinetic constant of the TTA processes is approximately estimated by a method used for the SF processes, which is modified for the TTA processes,  $k_{TTA}$ , as  $k_{TTA} = k_{T_1T_1,CS}k_{S_1S_0,CS} / (k_{S_1S_0,CS} + k_{back})$  where  $k_{X,Y}$  (X and Y =  $T_1T_1$ , CS, and  $S_0S_1$ ) are rate constants for intermediate ET processes and  $k_{back}$  is that for the backward ET from the CS to the  $T_1T_1$  state. In the CS state, one molecule is oxidized, while the other is reduced, so that we assume one emitter becomes a cationic state and the other an anionic state in calculating  $k_{TTA}$  of each process. For these calculations, GAUSSIAN 09. D01 program suite was used [2]. We also performed molecular dynamics (MD) simulations of DPA in DMSO. Force field parameters of DPA and DMSO were created using Gaussian 09 and AMBER



**Figure 1** An electron exchange mechanism for the triplet-triplet annihilation processes. First step is the electron transfer in a triple pair ( $T_1$ - $T_1$ ) state, resulting in a charge separated (CS) state. The second step is the electron transfer from the CS state, resulting in a pair of one singlet excited state and one ground state ( $S_1$ - $S_0$  state).

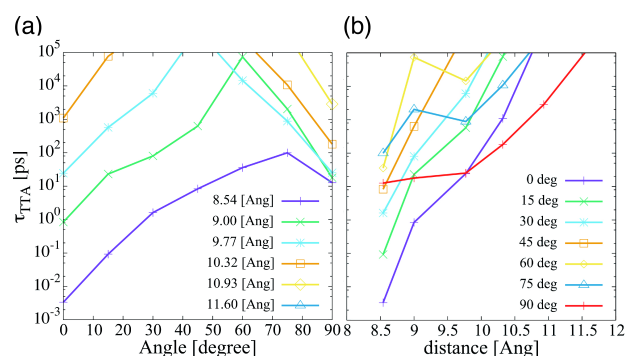
program package [3]. DPA and DMSO molecules in a unit cell were 2 and 864. In production runs, a total simulation time was set to 500 ns, and NPT ensemble was adopted with a constant temperature,  $T=300\text{K}$ , and pressure,  $P=1\text{ atm}$ .

Figure 2 plots the reaction time of the TTA,  $t_{\text{TTA}}=1/k_{\text{TTA}}$ , calculated for model dimer structures. Maximum values of  $k_{\text{TTA}}$  at a molecular orientation angle,  $\theta$ , of 90 deg. were found with the distance between centers of two monomers ( $d$ ) larger than 9.5 Å, while those at 0 deg. with  $d$  smaller than 9.5 Å. The TTA reactions occur very fast for all the molecular orientations (0.001 – 100 ps order) at  $d = 8.5$  Å. With  $d = 8.5$  to 9.5 Å,  $t_{\text{TTA}}$  is an order of 100 ps. On the other hand, With  $d > 10$  Å,  $t_{\text{TTA}}$  rapidly increases, exceeding 1 ns except for  $\theta = 90$  deg., where it moderately increases. It is thus indicated that the TTA process is likely to occur for distant  $d$  only when  $\theta$  is 90 deg., while TTA occurs quite fast at the short distance. Since the rotational relaxation time of DPA is 110 ps in *n*-propanol,<sup>34</sup> which has a similar viscosity to DMSO, the rate limiting step in the TTA process for large  $d$  might be diffusion process to orient two emitters at a proper molecular orientation angle, which was shown to be 90 deg. According to these results, we will next know how fast DPAs diffuses and how often two DPAs encounter in solution.

From the results obtained by MD simulations, the diffusion coefficient of DPA in DMSO was estimated to be  $D_{\text{dif}} = 1.77 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$ . Assuming no orientation dependence and an effective range of TTA reaction being  $d_{\text{eff}} = 10$  Å, the diffusion-limited rate constant in solution ( $k_{\text{dif}} = 8\pi N_{\text{A}} d_{\text{eff}} D_{\text{dif}}$ ) was  $k_{\text{dif}} = 2.68 \times 10^9 \text{ s}^{-1} \cdot \text{dm}^3 \cdot \text{mol}^{-1}$ . Thus, the corresponding reaction time for a typical experimental concentration,  $c_{\text{exp}} = 1\text{mM}$ , becomes 37 ms. This reaction time is obviously longer than that for TTA within 10 Å. Moreover, it should be stressed here that the real diffusion-limited rate constant may be lower than the present estimation, because in reality all the emitters do not always exist in the triplet state. This result indicates that, once the DPA enters an effective region in which the TTA might occur, it is possible for two DPAs to form a profitable conformation for TTA due to shorter time-scales of energy transfer and rotational relaxation.

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**Figure 2.** The reaction time of the TTA process in the model dimers (a) as a function of molecular orientation for each center-to-center distance and (b) as a function of the center-to-center distance for each molecular orientation.

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