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How does Tetraphenylethylene Relax from its Excited States?

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Tetraphenylethylene is a prototypical example of a molecule displaying aggregation-induced emission. Despite many studies on the optical properties of TPE and its derivatives, the origin of the non-emissive behavior in the gas phase or in dilute solutions has yet to be unravelled. Here, we identify the ultrafast deactivation mechanisms responsible for the fluoresence quenching in isolated TPE.

Aggregation-induced emission (AIE)[1-5] molecular systems are defined as having weak or non-emissive behaviour in dilute solutions or the gas phase while they emit strongly in aggregate solutions. These systems now receive considerable interest owing to their potential uses in organic light emitting diodes and in bio/chemosensing. Tetraphenylethylene (TPE) is a prototypical example of a system displaying AIE: its fluorescence depends upon the degree of conformational flexibility, with restricted conformers displaying higher fluorescence. Thus, a route to improve aggregation and emission properties is the addition of organic,[6-9] metal-organic,[10-12] ionic,[13,14] and other substituents onto the TPE frame. Despite a considerable amount of experimental research, reliable studies aiming to unravel the photochemistry of TPE are lacking. Here, we explore the ultrafast deactivation mechanisms responsible for fluorescence quenching in isolated TPE (*i.e.,* in gas phase).

The nonradiative decay of TPE has been interpreted in terms of an internal conversion associated with an ethylenic twist,[15-17] albeit several studies have hinted that phenyl ring torsions may also play a significant or even primary role.[18,19] However, no definitive geometry interpretation has been given for the decay process, yet this information would be quite beneficial for the rational design of novel TPE-based fluorophores. The present work seeks to gain atomic level insights into the excited state dynamics of TPE through the use of a mixed quantum-classical formalism[20] (see details in the computational section) based on trajectories that represent the motion of the molecular system upon photoexcitation. The same methodology has been previously employed[21-24] to identify radiationless decay mechanisms in organic molecules that yielded valuable insights for interpreting experimental data.

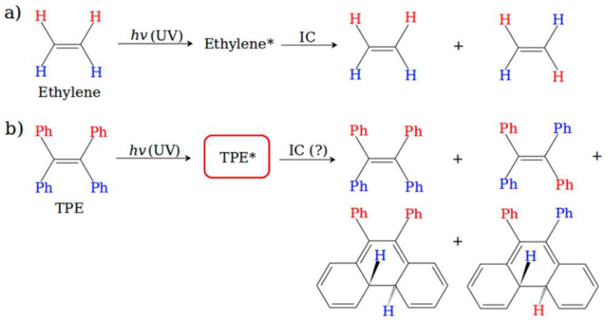

Fig.1 Photoexcitation and (assumed) photoproducts of (a) ethylene and (b) TPE upon internal conversion.

Despite an on-going debate,[25-27] the deactivation of ethylene from its first excited state (referred to here as an ethylenic twist) is a typical example of relaxation through a conical intersection (CI) seam.[28,29] Excitation to the S_1 state (HOMO→LUMO) causes a reduction in the C=C bond order, which initiates the twisting dynamics. This motion (along with the CH bond dynamics) stabilizes the first excited state (S_1) and destabilizes the ground state (S_0), ultimately causing the two states to become degenerate (i.e. the crossing referred to as CI). The dynamic process goes through (or in vicinity of) the CIs, which explains the ultrafast internal conversion from the excited to the ground state, as well as the subsequent cis-trans photoisomerization (see Fig. 1a). The excited state dynamics of TPE* (in the time interval between the Franck-Condon region and the S_1/S_0 CI, which is our primary focus) can be, in part, described by a similar picture (Fig. 1b). Indeed, the trajectory

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shown in Fig 2a confirms that TPE* can also deactivate via an ethylenic twist. The system, after initial excitation to the S_1 state (red curve, lower panel), evolves adiabatically on the same potential energy surface. Simultaneously, twisting of the central CC bond (upper panel) strongly destabilizes the ground state (magenta curve, lower panel). After ~1 ps the S_1 state becomes nearly degenerate with the ground state and eventually reaches the CI between the S_1 and S_0 states. The system then may undergo an ultrafast IC to the ground state. Surprisingly, only 3 out of 60 computed trajectories followed this specific deactivation channel that is considered to be the main pathway. Importantly, this implies that other, more efficient IC mechanisms exist that may involve phenyl ring dynamics.

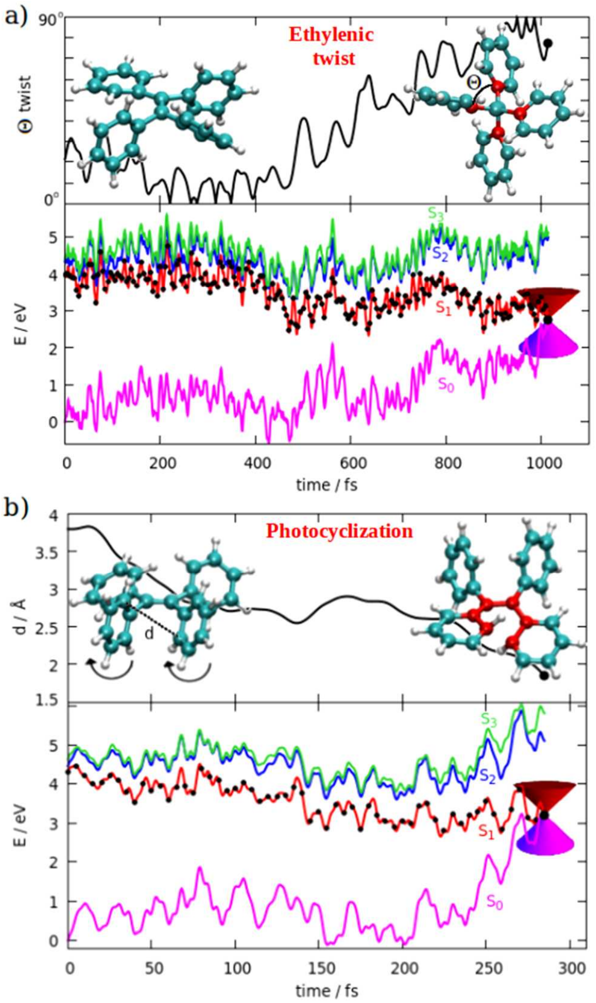

Fig. 2 Relevant geometrical parameters (upper panel) and electronic state potential energies (lower panel) as a function of time for two representative trajectories showing (a) the ethylenic twist and (b) the photocyclization process. The time evolution of the ethylenic twist is monitored by the torsional angle *Θ* (defined in the [0:90°] range), whereas for photocyclization is described by the suited CC distance. Potential energies of $S_0/S_1/S_2/S_3$ are shown in magenta/red/blue/green curves respectively, while the actual (running) electronic state is indicated in black. All the energies are relative to the initial (0 fs) S_0 energy. Initial (0 fs) and final (*i.e.*, close to CI) molecular structures are shown. The trajectories are computed at the PBE0/def2-SVP level (ESI for details).

A search for alternative mechanisms revealed that 75% of the trajectories (45/60) proceed through photocyclization (Fig. 2b). The fact that this particular mechanism has not been considered as a possible decay pathway is rather curious, particularly considering it verified existence in the structurally similar (cis-) stilbene[29-31] and the identification of biphenyl dihydrophenanthrene as a reaction intermediate in the photo-oxidative reaction of TPE.[32] Nonradiative decay via cyclization explains, for instance, why *ortho*- terpheny does not fluoresce, while the *meta*- and *para*- isomers do fluoresce.[33-35] Woodward-Hoffmann rules predict a conrotative electrocyclization of the excited 6*π*-electronic system for the photocyclization process. The phenyl-ring torsions bring the S_1 and S_0 close together (Fig. 2b, lower panel) leading the system to the CI (characteristic hexagonal arrangement of the C atoms highlighted in red). In contrast, restricting the torsional motion would, in principle, block the nonradiative decay and promote the radiative pathways. The extent to which various photoproducts are formed via nonradiative relaxation to the ground state (opened or closed ring TPE, as in figure 1b) essentially depends upon the precise CI topology encountered by the trajectory. If formed, experimental characterisation of the closed-ring TPE (*i.e.*, biphenyl dihydrophenanthrene) in its ground state would constitute definitive proof of photocyclization. Yet, the closed form is expected to be photochemically unstable (*i.e.*, in its excited state) and reopen in an ultrafast photoinduced process (see ESI) under visible light. Overall, the photodynamical cycle of TPE is rather complex but there is little doubt that photocyclization plays a key role.

Of the remaining trajectories: one followed the fulvene-like cyclization (ESI for details), representative of a minor deactivation channel, while the remainder (12/60) persist in the excited states with no change through the length of the simulation. Fig. 3 shows a time evolution of the twist angle *Θ* (as in Fig. 2a) for the ensemble of trajectories. Red/blue/green lines represent molecules in $S_1/S_2/S_3$, respectively, whereas S_1/S_0 crossing points are indicated by black dots. The cyclization dynamics is easily distinguished from the ethylenic twist by its modest *Θ* values. The phenyl rings are initially close to one another and cyclization dominates. As the twisting motion around the central CC bond proceeds, the cyclization becomes inaccessible and another decay channel (ethylenic twist) opens. The overall oscillatory nature of the dynamics shows that the interplay between both deactivation mechanisms (cyclization and twist) leads to the radiationless decay of TPE.

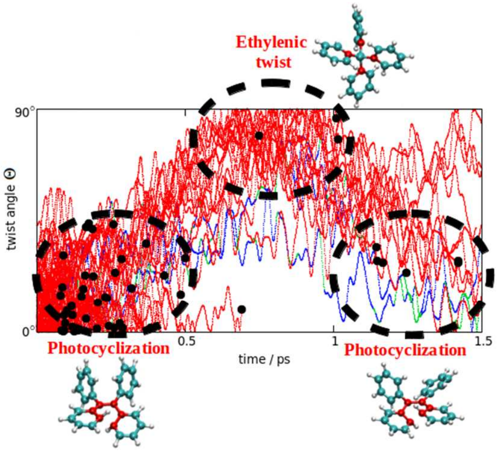

Fig. 3 Time evolution of the Θ twist angle (see Fig 2a) for 60 trajectories. The trajectories (lines) are colored according to the populated state (S_1/S_2/S_3 in red/blue/green) while the black dots indicate the S_1/S_0 crossings, i.e. the regions of population transfer from the excited to the ground state.

From the general perspective of aggregation-induced emission, the fluorescence quenching in various fluorophores has traditionally been assigned to the photophysical energy dissipation caused by propeller-like rotations of the side groups, rather than to photochemical decay as shown here. Restricted intramolecular rotations (RIR) in the aggregate were invoked as an explanation for the observed induced emission.[3-5] However, very recently this picture has been challenged,[36,37] at least for systems possessing accessible conical intersections. Static QM/MM investigation of the CIs of a related molecule (*i.e.*, diphenyldibenzofulvene) in the crystal phase has shown that induced emission can be explained by the inaccessibility of the CI seam. Although we did not accounted for the effects of aggregation, we have clearly demonstrated that CIs play a key role in the photochemistry of the prototypical TPE (though the accessibility of the CIs is indeed related to the intramolecular rotations). The present findings will be of considerable value for future interpretation and understanding of the AIE properties.

Computational Details. Full details can be found in the ESI. We used a mixed quantum-classical trajectory surface hopping method based on Tully's fewest switches scheme[20] (for implementation details see Ref. 38). 60 trajectories were computed with the initial conditions taken from the Boltzmann ensemble at 300K and assuming the vertical excitations to the first excited singlet state, S_1. The electronic structure was described using linear response time dependent density functional theory (TDDFT) within the Tamm-Dancoff approximation.[39-41] Despite the typical challenges associated with the description of the excited states of conjugated organic molecules,[42-44] earlier benchmark studies have shown that TDDFT can describe both photoisomerization and photocyclization qualitatively well.[45] Consequently, we intentionally do not deliver a detailed quantitative interpretation (e.g., yields, lifetimes) but rather focus on the qualitative TDDFT picture. Note also that in the realistic environment (*i.e.,* in solution) these quantities will be influenced by the viscosity and polarity of the specific solvent.

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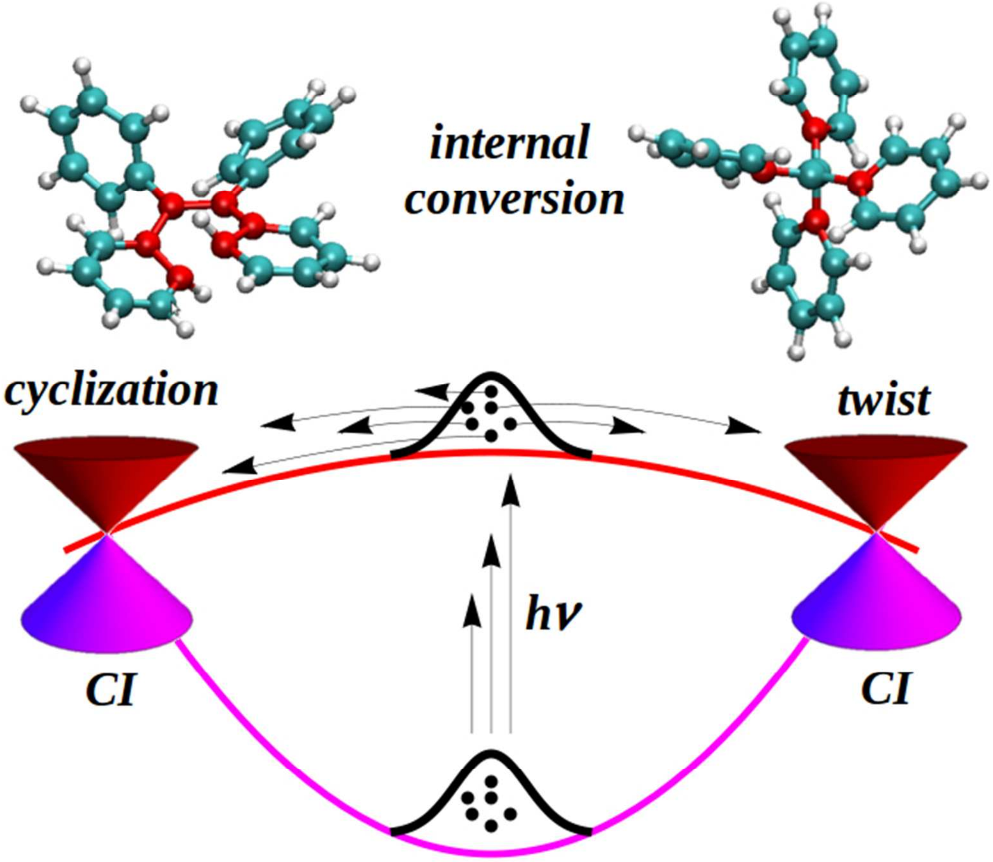

Abstract Figure