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for

How does Tetraphenylethylene Relax from its Excited States?

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Contents

1. Computational details

The excited state dynamics of TPE was investigated with Tully's fewest switches surface hopping method[1] with the decoherence correction (α=0.1).[2] Details of the implementation can be found in earlier publications.[3] A swarm of 60 trajectories was initiated in the first excited singlet state, S_1, and nonadiabatic couplings were computed between the ground and three lowest excited singlet states. Trajectories were propagated for a total time of 1.5 ps and a nuclear time step of 0.5 fs. However, as it was advocated earlier for single-reference methods, the trajectories were analyzed only prior to reaching the S_1/S_0 intersection (*i.e.,* up to the gap threshold value of 0.1 eV; see the dicussion in the review of Barbatti et al.[4]). The initial conditions (coordinates and velocities) for the excited state simulations were chosen randomly from the 20 ps ground state trajectory, equilibrated at 300K (NVT). The excited state simulations were performed in the NVE ensemble. The PBE[5]-D3[6]/def2-SVP[7] level was used for the ground state trajectory. The surface hopping dynamics was performed using the linear response TDDFT formalism,[8,9] within the Tamm-Dancoff approximation (TDA)[10] at the PBE0[11]/def2-SVP level. The ground state TPE geometries used for the single-point vertical excitation energies were optimized at the PBE0-D3/def2-SVP level. For comparison, the excitation energies of the lowest singlet and triplet states were computed at the TDA-TDDFT (PBE0/def2-SVP) and ADC(2)[12,13]/def2-TZVPD[14] levels. The ADC(2) computations use the resolution of identity and frozen core approximations. All DFT, TDDFT and ADC(2) computations were performed with the Turbomole 6.4 package,[15] whereas the surface hopping dynamics simulations were performed with an in-house code interfaced to Turbomole 6.4. Molecular structures and orbitals were visualized with the VMD 1.9.1 program package.[16]

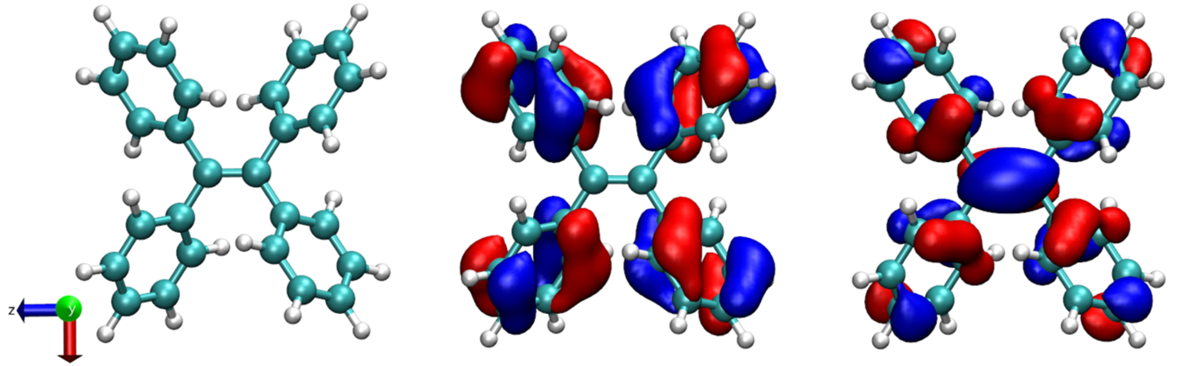
2. Method assessment

The PBE0/def2-SVP level was chosen for the excited state molecular dynamics simulations as a compromise between accuracy and computational efficiency. In Table S1, the excitation energies are compared to those obtained with ADC(2) (algebraic diagrammatic construction of second order), converged with the larger def2-TZVPD basis set (including diffuse functions). ADC(2) has proved to be a reliable reference for excitation energies[17,18] and excited state dynamics[19-21] of organic molecules. As shown in Table S1, the two methods give consistent trends for the lowest excited states of TPE despite the small but rather systematic shift in the excitation energies (which is within the method accuracy). The results for the lowest triplet transitions are also reported, although the spin-orbit effects are neglected.

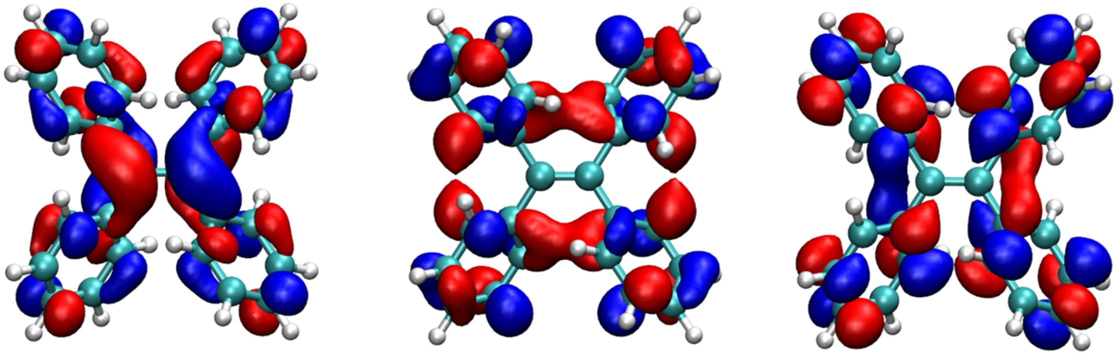
However owing to the absence of heavy atoms and the lack of experimental indications, we do not expect that intersystem crossing does play a major role in the fluorescence quenching of TPE. Figure S1 shows the relevant Kohn-Sham (PBE0/def2-SVP) orbitals involved in the lowest electronic transitions of TPE. The large delocalization on the phenyl rings illustrate that the "ethylene model" employed in earlier publications on TPE is not sufficient to fully interpret its photochemistry. Figure S2 shows that TDA-TDDFT (lines) and ADC(2) (points) are consistently further away from the Franck-Condon region (*i.e.,* along the computed trajectories). The D1 diagnostic parameter of MP2 measures the quality of the ground state wavefunction and also serves as a warning if the DFT+TDDFT is inappropriate (for example due to the radicaloid character of the ground state in the cases of distorted geometries). Values smaller than 0.04 indicate negligible multireference character. Values as high as 0.10 or 0.15 may sometimes be considered as acceptable.[22] As shown in Fig. S2, the D1 values along the trajectories are rather small, and get slightly larger close to the S_1/S_0 intersection. Due to the inherent problems of the employed DFT+TDDFT formalism in the vicinity of the S_1/S_0 intersection, the trajectories are analyzed only before reaching this crossing region.[4] While the information on the formed ground state photoproducts is thus missing, this analysis should should provide a sufficient picture of the nonradiative decay.

Table S1. Lowest singlet and triplet transitions of TPE computed at the PBE0/def2-SVP level and compared to ADC(2)/def2-TZVPD. Excitation energies are given in eV and the oscillator strengths are given in parentheses. All the computations correspond to the TPE structure optimized in the ground state at the PBE0-D3/def2-SVP level (D_2 point group).

stateirrep	character	PBE0/def2-SVP	ADC(2)/def2-TZVPD
singlets			
B_1	H→L	3.78 (0.463)	3.96 (0.452)
B_2	H→L +1, H-1→L	4.39 (0.002)	4.46 (0.001)
B_3	H→L +2	4.55 (0.148)	4.74 (0.091)
triplets			
B_1	H→L	2.58	2.92
B_3	H→L+2	3.70	4.00
B_2	H→L+1, H-1→L, H→L+3	3.71	4.00



TPE HOMO-1 HOMO



LUMO LUMO+1 LUMO+2

Fig. S1. Kohn-Sham orbitals (PBE0/def2-SVP) involved in the lowest singlet and triplet transitions of TPE (isovalue=0.03). Note that the main orbital features are independent from the level used.

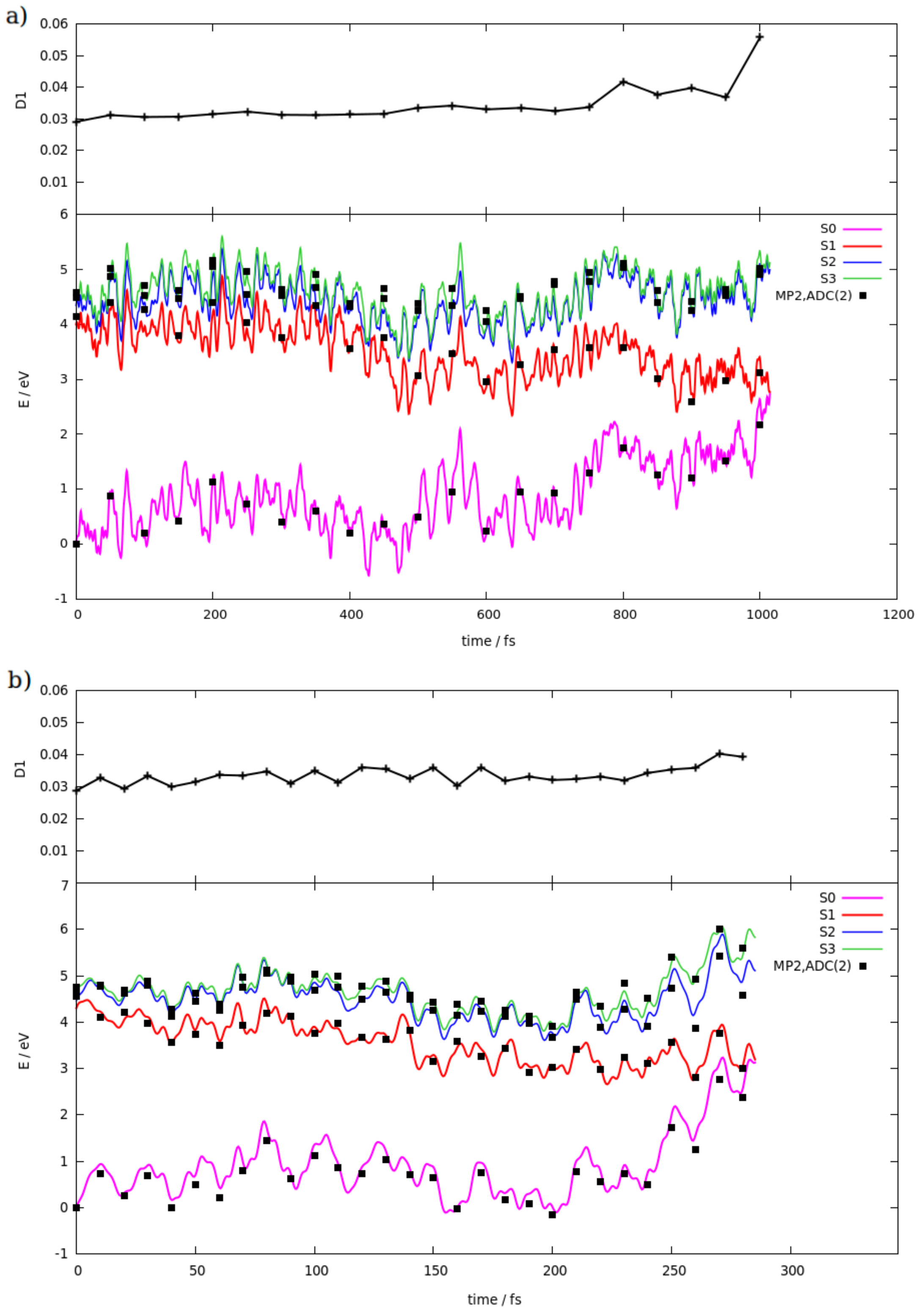


Fig. S2. Energy profiles for a) the ethylenic twist and b) the photocyclization trajectories (as given in Fig. 2 of the main text) computed at the PBE0/def2-SVP level (lines, lower panels) and compared to the MP2+ADC(2)/def2-TZVPD single points (black squares, lower panels). All the energies are relative to the initial (0 fs) S_0 energy which is set to 0 eV. The values for the D1 diagnostic of MP2 are plotted in the upper panels.

3. Fulvene-like cyclization

Several trajectories (all of which were initiated in the S_1 state) include nonadiabatic transitions to the higher adiabatic singlet states. A trajectory in Fig. S3 shows a system evolving on the S_1 potential energy surface with a subsequent nonadiabatic transition to the higher excited states (S_2, S_3) and further relaxation towards the S_1/S_0 fulvene-like conical intersection (five-membered ring structure is highlighted in red).

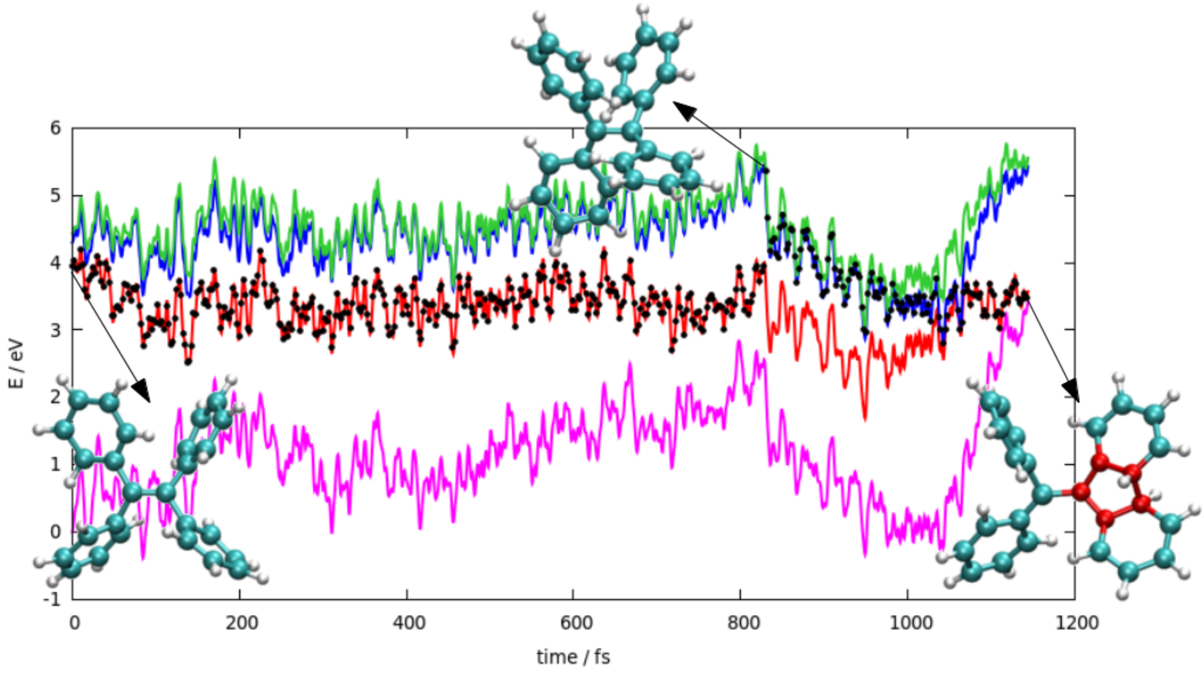


Fig. S3. The Electronic state potential energies as a function of time for the fulvene-like cyclization. Potential energies of $S_0/S_1/S_2/S_3$ are shown in magenta/red/blue/green, while the actual (running) electronic state is indicated in black. The energies are relative to the initial (0 fs) S_0 energy. The characteristic five-member cyclic structure close to the CI is highlighted in red. The trajectory is computed at the PBE0/def2-SVP level.

4. Opened and closed form of the TPE photoproducts

A key question is whether the allowed Woodward-Hoffmann photocyclization leads to the formation of a CC bond (biphenyl dihydrophenanthrene) or if the original TPE molecule is restored in the ground state. Our computations (including the coupling with the ground state) indicate that both situations are possible (Fig. S4). However, this should be taken with care, considering the well-known limitations of TDDFT in its standard approximations.[4] The dynamics in the close vicinity of conical intersection should be analyzed with highly correlated multireference methods that are beyond the scope of the present communication.

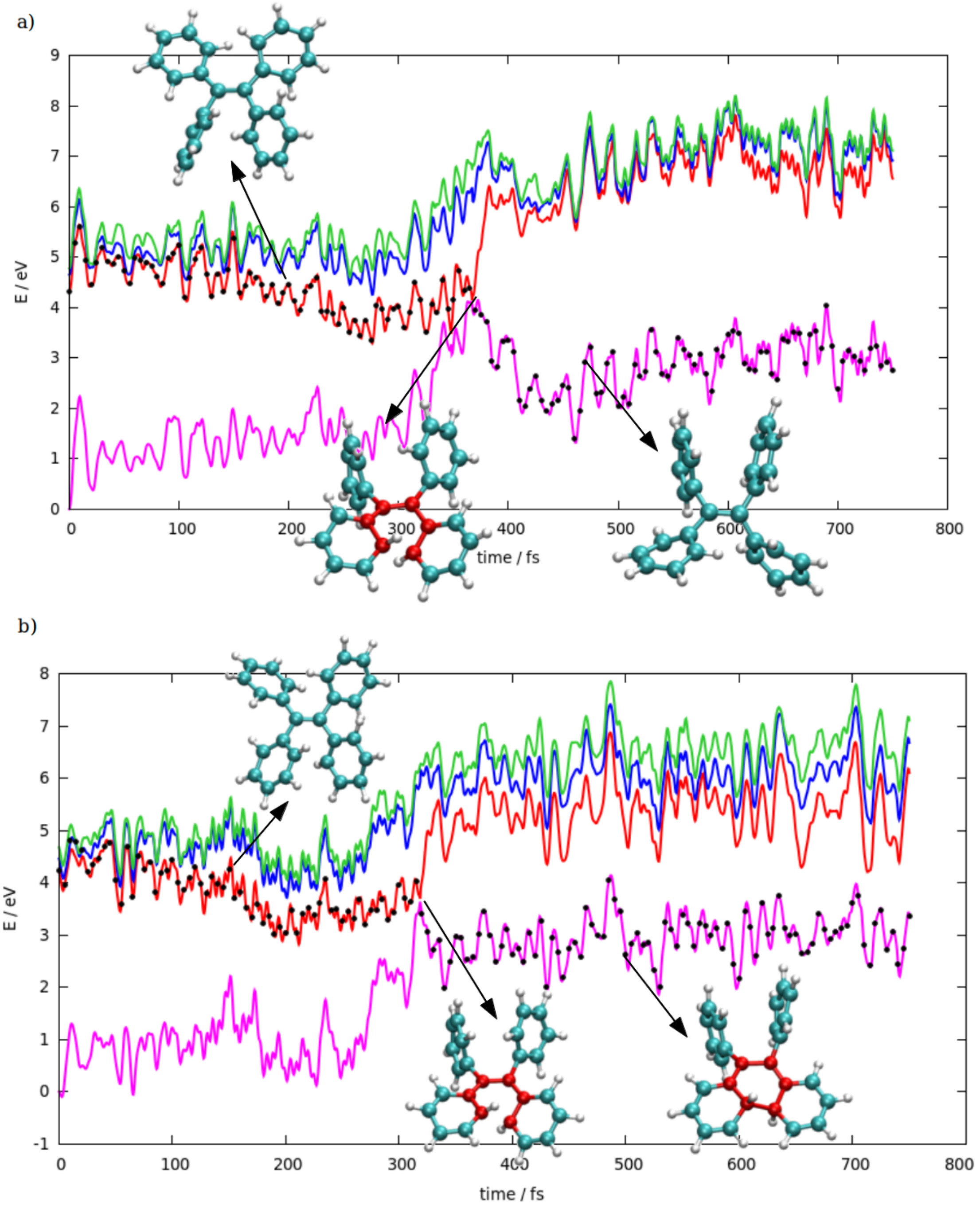


Fig. S4. The electronic state potential energies as a function of time for two cyclization trajectories leading to the distinct photoproducts: a) the opened (*i.e.,* TPE) and b) closed forms (*i.e.*, biphenyl dihydrophenanthrene). Potential energies of $S_0/S_1/S_2/S_3$ are shown in magenta/red/blue/green, while the actual (running) electronic state is indicated in black. The energies are relative to the initial (0 fs) S_0 energy. Trajectories are computed at the PBE0/def2-SVP level.

5. Ring opening of biphenyl dihydrophenanthrene

A 10 ps ground state trajectory (PBE+D3/def2-SVP; 300 K) was run in order to assess the viability of the biphenyl dihydrophenanthrene (BP-DHP) in its ground state. Since the covalent bond between the two rings shows no tendency to break in the ground state, we conclude that BP-DHP is a long-lived compound. If formed via the nonradiative decay of TPE, BP-DHP could therefore be identified by spectroscopy. We demonstrate however that BP-DHP is not stable in its first excited state and follows a conrotative ring opening motion (in line with the Woodward-Hoffmann rules) similar to the TPE ring closure. Fig. S5 shows the ultrafast photoinduced ring opening of BP-DHP. Note that the structure in the vicinity of the CI is similar to that of the TPE cyclization. The S_1 state of BP-DHP falls into the visible region of the spectrum (bright S_1 state around 2.5 eV), while the S_1 state of TPE corresponds to the ultraviolet range (lowest absorption maximum around 4eV; UV). BP-DHP may also be excited to the higher energy excited state manifold with subsequent relaxation to the S_1 state and ring opening from S_1.

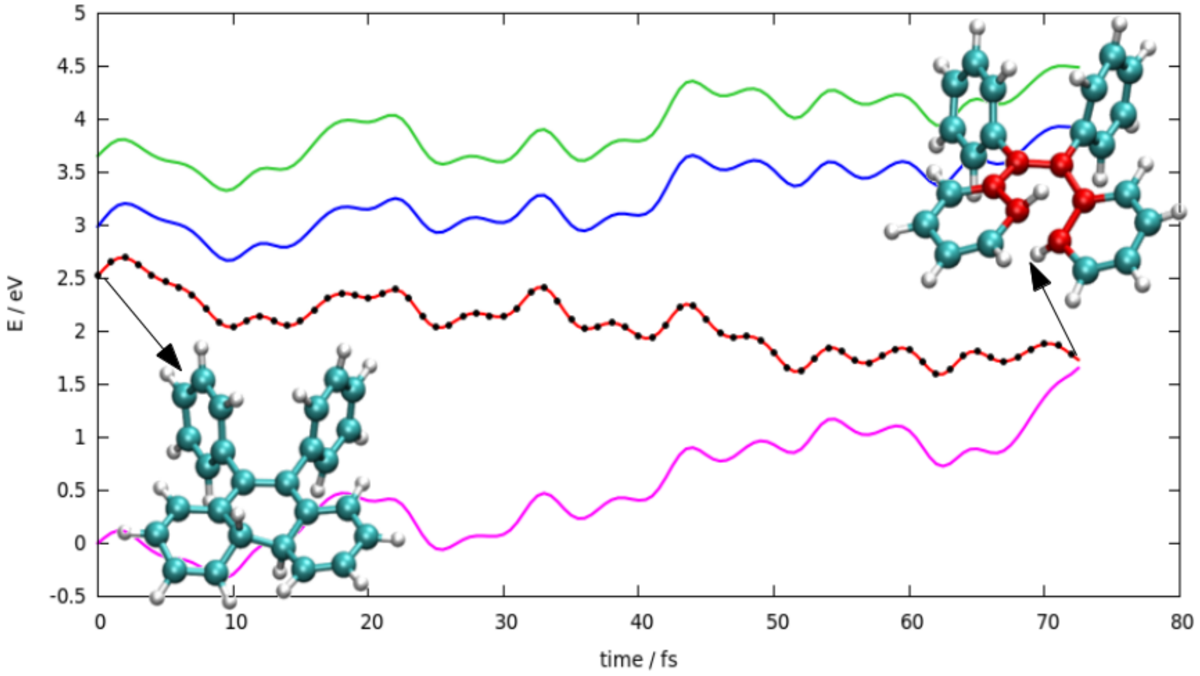


Fig. S5. The electronic state potential energies as a function of time for the ring opening of BP-DHP. Potential energies of S_0/S_1/S_2/S_3 are shown in magenta/red/blue/green, while the actual (running) electronic state is indicated in black. The energies are relative to the initial (0 fs) S_0 energy. The trajectory is computed at the PBE0/def2-SVP level.

6. References

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