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Supplementary information to “Surface hopping excited-state dynamics study of the photoisomerization of a light-driven fluorene molecular rotary motor”

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Details of classical MD simulations

Following Ref. 1, the re-parametrized OPLS all-atom force field was used in the present MD-OPLS simulations of excited-state dynamics (see Ref. 1 for details of the force field parametrization). A time step of 1 fs was used to integrate the equations of nuclear motion. No cutoffs were applied for the non-bonded interactions. All classical MD-OPLS simulations in the excited state were initiated from equally spaced snapshots taken from a 1-ns ground state simulation that was equilibrated at -40°C (the temperature at which the photo-stationary state was experimentally measured). The system was first propagated on S_1 and, after the surface hop, evolved on the S_0 surface. These simulations were done in the NVE ensemble. Following Ref. 1, and similar in spirit to the approach of Groenhof *et al.*,² a surface hop back to the ground state was performed as soon as the molecule reached the vicinity of the conical intersection seam. This was monitored during the S_1 dynamics by computing the heavy-atom coordinate root-mean-square deviation (RMSD) from the OM2/GUGA-MRCI geometries of selected structures on the conical intersection seam. A surface hop was imposed as soon as the RMSD to any of the conical intersection seam structures dropped below a certain threshold value, which was chosen by taking into account the differences between the minimum-energy structures from OPLS and OM2/GUGA-MRCI calculations as well as finite-temperature effects. For the **1-P** conformation, the average heavy-atom RMSD during the equilibrium 1-ns ground-state classical MD simulation with respect to the OM2/GUGA-MRCI optimized geometry was $\langle \text{RMSD} \rangle = 0.14 \text{ \AA}$ with a standard deviation of $\sigma = 0.06 \text{ \AA}$. An RMSD threshold of $0.26 \text{ \AA}$ (obtained by adding 2σ to $\langle \text{RMSD} \rangle$) to any of the selected OM2/GUGA-MRCI conical intersection seam structures was chosen as a surface hopping criterion in the classical MD simulations.

Results of classical MD simulations

From equilibrated ground-state simulations of **1-P** or **1-M**, respectively, 1000 classical MD simulations were initiated. At time $t = 0$ a molecule is excited to the S_1 state, where it evolves until

the trajectory reaches the vicinity of the conical intersection seam. Previously, the seam was represented only by the two single minimum-energy conical intersection points **CI**₁ and **CI**₂, obtained from SA-REKS calculations.¹ In the present work, we used a number of points along the conical intersection seam. These points were found through OM2/GUGA-MRCI optimizations in which the torsion angle θ (see Scheme 2 in the main article) was constrained to a number of equally spaced values around the MECI geometry, **CI**₁ or **CI**₂, see Table 1 in the main article. We chose six points on the seam within an energy interval of 1 eV from each MECI (see Table 1). This energy interval covers the energetically accessible part of the CI seam (see Table 2 in the main article).

Table 1: Excited-state decay times τ_{S_1} , distribution of surface hops, and quantum yields of photoisomerization as obtained from 1000 classical MD-OPLS simulations initiated from **1-P** and **1-M**.

		1-P	1-M
τ_{S_1} (ps)		1.22	1.19
ϕ_{iso} (%)		75	49
SH ^a at CI ₁ (%)		86	84
	$\theta = 110^\circ$	53	46
	$\theta = 120^\circ$	8	14
	$\theta = 130^\circ$	3	13
seam near CI ₁ (%)	$\theta = 133^\circ$ ^b	1	13
	$\theta = 140^\circ$	2	11
	$\theta = 150^\circ$	33	3
SH at CI ₂ (%)		14	16
	$\theta = 30^\circ$	1	1
	$\theta = 40^\circ$	2	1
	$\theta = 50^\circ$	22	18
seam near CI ₂ (%)	$\theta = 56^\circ$ ^b	41	28
	$\theta = 60^\circ$	27	37
	$\theta = 70^\circ$	7	15
ϕ_{iso,CI_1} ^c (%)		77	52
ϕ_{iso,CI_2} (%)		62	38

^a SH: surface hop at the respective conical intersection seam; ^b MECI point; ^c quantum yield of photoisomerization at the respective point on the conical intersection seam.

Figure 1: Populations of the S_0 (blue) and S_1 (red) states as a function of time for the $\mathbf{1-P} \rightarrow \mathbf{1-M}$ (left panel) and $\mathbf{1-M} \rightarrow \mathbf{1-P}$ (right panel) photoisomerization reactions, as obtained from the classical MD-OPLS simulations.

The results of classical MD-OPLS simulations are summarized in Table 1 and Figures 1 to 3. The time evolution of the total population of the S_0 and the S_1 states is shown in Figure 1 for the two reactions. The rate of the S_1 decay was determined from an exponential fit of the data in Figure 1. Single exponential decay with $\tau_{S_1} = 1.22$ ps was observed in the $\mathbf{1-P} \rightarrow \mathbf{1-M}$ photoisomerization, whereas the inverse reaction followed a biexponential decay: 15 % of the trajectories decay with $\tau_{S_1} = 0.18$ ps and 85 % with $\tau_{S_1} = 1.19$ ps. A similar biexponential decay of the S_1 state was also obtained in Ref. 1 for the $\mathbf{1-M} \rightarrow \mathbf{1-P}$ reaction, where 15 % of the trajectories were found to decay with $\tau_{S_1} = 0.2$ ps. Closer analysis of the lifetime distributions at the individual points on the conical intersection seam reveals that this ultra-fast decay component originates almost exclusively from surface hops at $\theta = 110^\circ$ point near the $\mathbf{CI}_1$ structure (see Table 1). Inspection of the S_1 PES in Figures 1 and 2 of the main article suggests that this part of the seam should be easily accessible when starting an MD trajectory from the $\mathbf{1-M}$ FC point with a suitably oriented initial momentum.

Generally, the results of the present classical MD-OPLS simulations, such as the S_1 lifetimes, the distribution of surface hops, and the isomerization quantum yields, are consistent with those reported previously.¹ The main distinction between the previous¹ and present MD-OPLS simu-

lation is that the hopping region around each conical intersection is no longer represented by a single point, but by several points on the seam. As expected, this extended representation leads to a somewhat faster S_1 decay: τ_{S_1} is reduced by *ca.* 0.2 ps and 0.6 ps for the **1-P** $\rightarrow$ **1-M** and **1-M** $\rightarrow$ **1-P** reactions, respectively.

Figure 2: Time evolution of the populations of **1-P** and **1-M** structures in the ground S_0 and excited S_1 states as obtained from the classical MD-OPLS simulations of the **1-P** $\rightarrow$ **1-M** (upper panel) and **1-M** $\rightarrow$ **1-P** (lower panel) photoisomerization reactions. For definition of different species, see Figure 7 in the main article.

The time evolution of the populations of the P, M, and X molecular structures (for definitions, see Figure 7 in the main article) in the S_0 and S_1 states is shown in Figure 2. Despite the use of

different approaches for calculating the S_0 and S_1 energies and different surface hopping criteria in the TSH-OM2 and MD-OPLS simulations, the time-dependent plots of these populations in Figure 7 of the main article and those in Figure 2 are strikingly similar. The MD-OPLS populations reach their equilibrium values after *ca.* 2.5 ps. Using the computed quantum yields of the two photoisomerization reactions, see Figure 3, the PSS ratio of the **1-M** and **1-P** conformers is evaluated as 2.4:1, in reasonable agreement with the TSH-OM2 simulations (2.7:1) and the experimental data (3:1).³ The PSS curve in Figure 3 shows that the PSS value at *ca.* 1.5 ps is not very different from the equilibrium value, which justifies the approach used to calculate the PSS ratio from the results of the TSH-OM2 simulations, see Figure 8 in the main article.

Figure 3: Quantum yields of the **1-P** $\rightarrow$ **1-M** (blue) and **1-M** $\rightarrow$ **1-P** (red) photoisomerization reactions and photo-stationary state ratio (gray) of the **1-P** $\rightleftharpoons$ **1-M** photoisomerization reaction as obtained in the classical MD-OPLS simulations.

The results of the classical MD-OPLS simulations in Table 1 confirm that the MECI structure does not always play the most important role in the dynamics. The majority of surface hops occur around geometries with $\theta = 110^\circ$ in the seam near CI_1 . In general, the seam near CI_1 plays a more important role in the photoisomerization dynamics than the seam near CI_2 . During both reactions, in *ca.* 84–86 % of cases, surface hops occur via the seam close to CI_1 . In this respect, the classical

MD-OPLS simulations are fully consistent with the TSH-OM2 results.

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