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Supporting Information *for*

The impact of chalcogen-substitution element and initial spectroscopic state on excited-state relaxation pathways in nucleobase photosensitizers: a combination of static and dynamic studies

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Table S1. Relative energies (eV) of different states at the optimized minima and crossing points in different level of theory. The LR-TD-ωB97XD/6-31G* calculated energies are based on MS-CASPT2 optimized geometries and given in italic. The oscillator strengths are given in parentheses.

Energy / Geometry		6TG		6SG	
		Based on MS-CASPT2(12,10)/ ANO-RCC-VDZP ptimized structures	MS-CASPT2//CASSCF (14,12)/ANO-L optimized structures (from Ref.45 in main text)	Based on MS-CASPT2(12,10)/ANO-RCC-VDZP optimized structures	MS-CASPT2//CASSCF(12,10)/cc-pVDZ optimized structures (from Ref.51 in main text)
S_0 minimum	S_0	0.0 *0.0*	0.0	0.0 *0.0*	0.0
	S_1	3.41 *3.38*	3.36	2.93 *2.94*	2.61
	S_2	4.0(0.50) *4.33*	4.05(0.54)	3.59(0.52) *4.0*	3.39(0.24)
	S_3	4.85 (0.11) *4.98*	4.90(0.144)	4.53 (0.05) *4.75*	
	T_1	3.03 *2.63*	3.10	2.68 *2.21*	2.40
	T_2	3.37 *3.08*	3.31	2.92 *2.65*	2.56
	T_3	4.20 *3.79*	4.24	4.07 *3.75*	
S_1 minimum	$S_1/T_2/T_1$	3.13/3.09/2.89 *3.23/2.89/2.49*	3.18	2.69/2.66/2.50 *2.93/2.59/2.09*	2.46
S_2 minimum	S_2	3.71 *4.23*	3.78	3.26 *3.89*	3.04
T_1 minimum	T_1	2.76 *2.44*	3.00	2.44 *2.03*	2.24
S_2/S_1	$S_2/S_1/T_2$	4.04/4.04/4.02 *4.42/4.15/3.93*	3.96	3.68/3.66/3.68 *4.28/3.94/3.74*	
T_1/S_0	T_1/S_0	3.06/3.06 *3.07/3.48*	3.16	2.73/2.73 *2.70/3.23*	2.35/2.22
$S_1(\pi_{45}\pi_{23}^*)/S_0$	S_1/S_0	4.73/4.71 *5.44/5.07*	3.90	4.28/4.27 *5.03/4.69*	
$S_1(n_{10}\pi_{610}^*)/S_0$	S_1/S_0	4.05/4.03	4.87	3.69/3.68	

Table S2. Spin-orbit coupling (SOC) magnitudes (cm^{-1}) between S_2 and T_2 at the S_2/S_1 points and between S_1 and T_2 at the S_1 minima of both molecules, calculated in different level of theory.

SOCs / Region	6TG		6SG	
	MS-CASPT2	LR-TDDFT	MS-CASPT2	LR-TDDFT
S_2/S_1	78.5	63.0	387.1	412.0
S_1 minimum	88.6	85.1	427.3	401.3

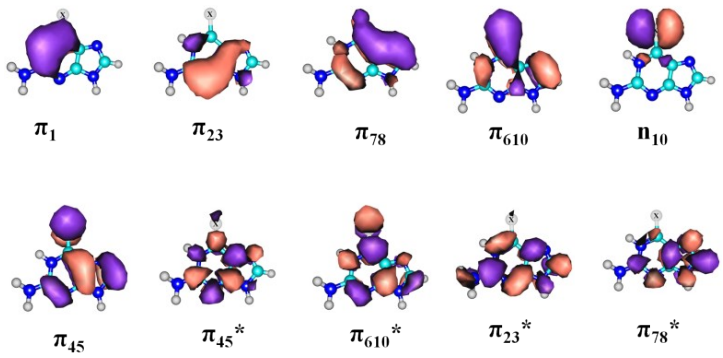

Figure S1. Molecular orbitals included in the active space. X=S or Se.

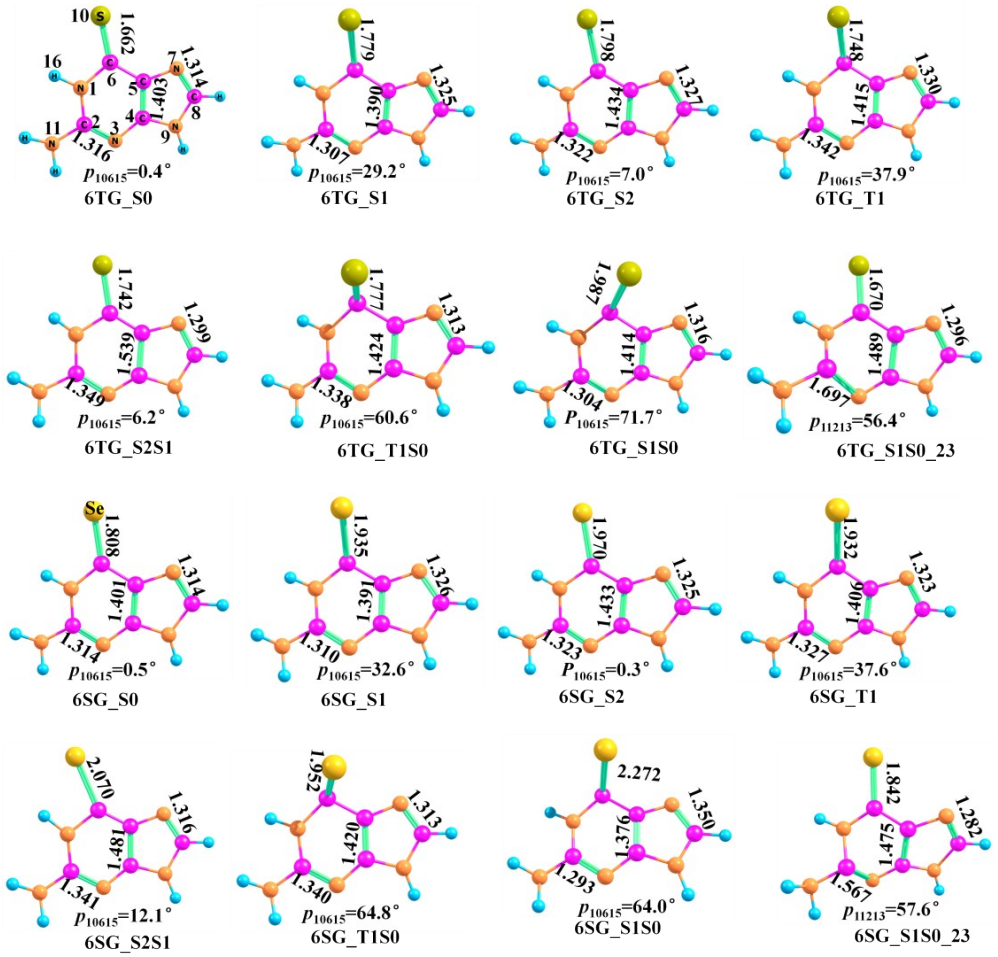

Figure S2. The MS-CASPT2(12,10)/ANO-RCC-VDZP optimized minimum and crossing structures, along with chosen geometrical parameters (bond-length in Å, and angle in °). The atom labels are given in the S_0 minimum of 6TG (6TG_S0). Minima in the $S_1(n_S\pi^*)$, $S_2(\pi\pi^*)$, $T_1(\pi\pi^*)$ states of 6TG are referred as 6TG_S1, 6TG_S2, and 6TG_T1, respectively, and crossing points between $S_2(\pi\pi^*)$ and $S_1(n_S\pi^*)$, between $T_1(\pi\pi^*)$ and S_0, between $S_1(n_S\pi^*)$ and S_0, and between $S_1(\pi\pi_{23}^*)$ and S_0 are referred as 6TG_S2S1, 6TG_T1S0, 6TG_S1S0, and 6TG_S1S0_23, respectively. For 6SG, minima in the S_0, $S_1(n_S\pi^*)$, $S_2(\pi_S\pi^*)$, $T_1(\pi\pi^*)$ states are referred as 6SG_S0, 6SG_S1, 6SG_S2, and 6SG_T1, respectively, and crossing points between $S_2(\pi\pi^*)$ and $S_1(n_S\pi^*)$, between $T_1(\pi\pi^*)$ and S_0, between $S_1(n_S\pi^*)$ and S_0, and between $S_1(\pi\pi_{23}^*)$

and S_0 are referred as 6SG_S2S1, 6SG_T1S0, 6SG_S1S0, and 6SG_S1S0_23, respectively.

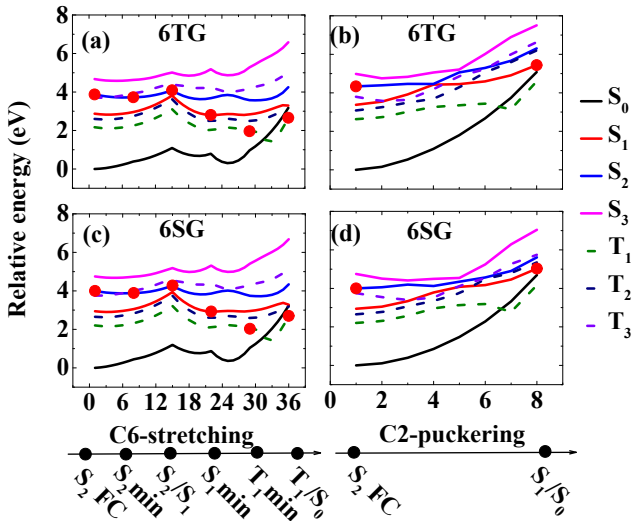

Figure S3. LIICs computed at the LR-TD-ωB97XD/6-31G* level of theory based on the MS-CASPT2(12,10)/ANO-RCC-VDZP optimized structures.

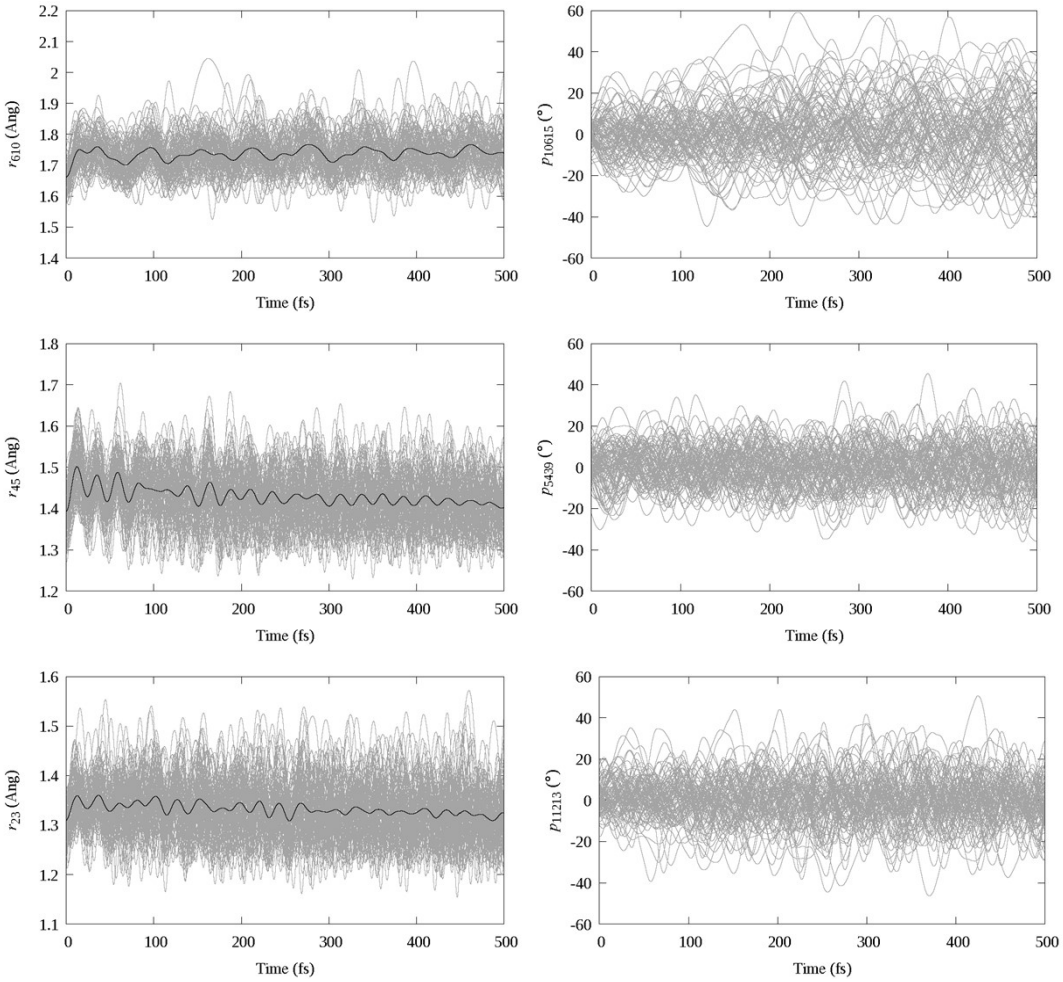

Figure S4. Time evolution of some chosen geometrical parameters from dynamics of the S_2 state of 6TG.

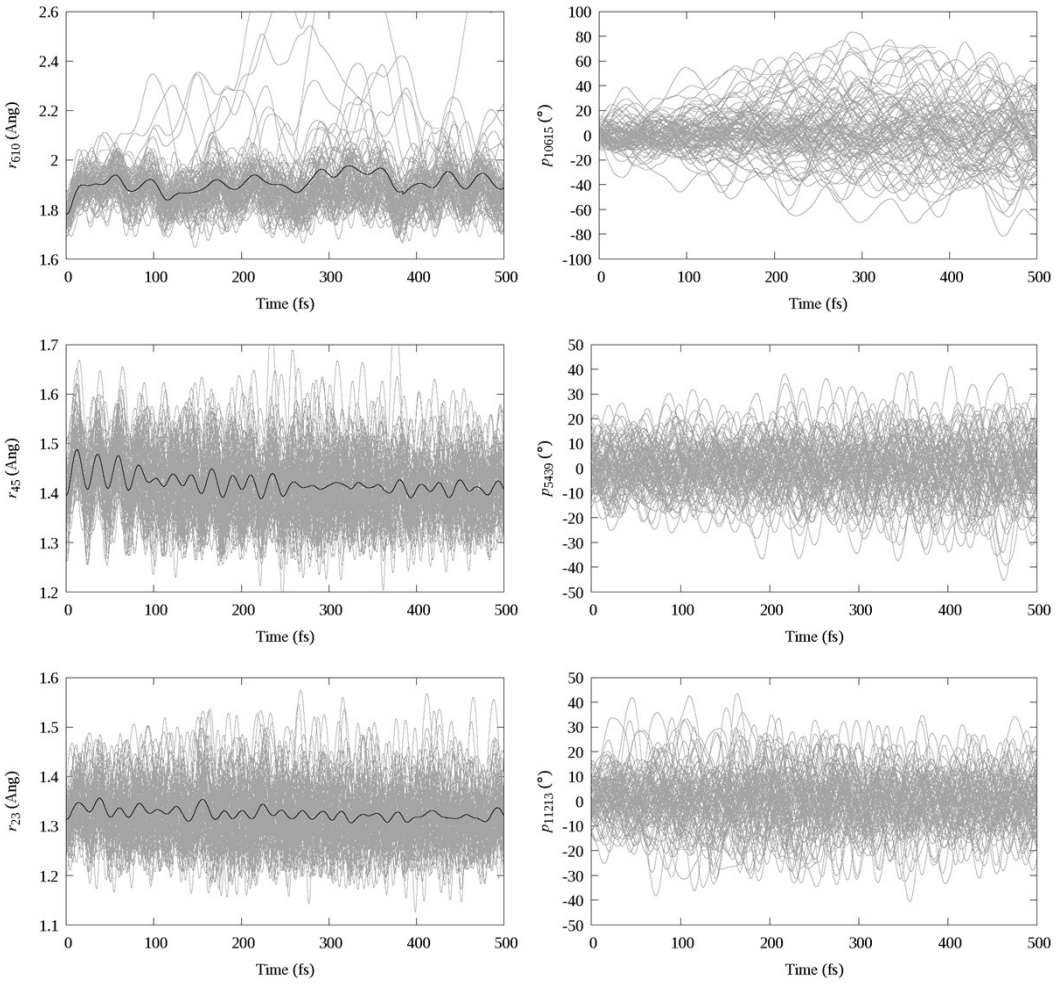

Figure S5. Time evolution of some chosen geometrical parameters from dynamics of the S_2 state of 6SG.

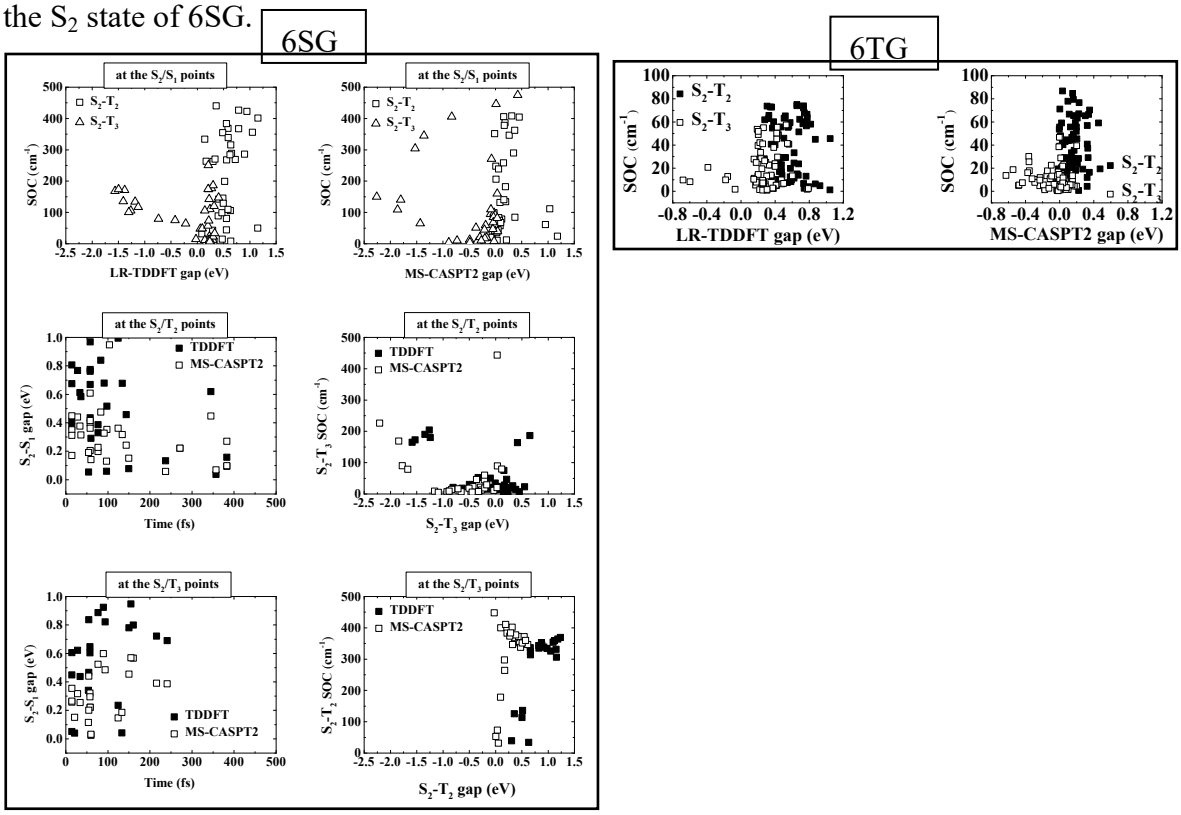

Figure S6. Additional calculations of the energy gaps and spin-orbit coupling (SOC) magnitudes at the S_2/S_1, S_2/T_2, and S_2/T_3 crossing points of 6SG, and the energy gaps and spin-orbit coupling magnitudes between S_2 and T_2 and between S_2 and T_3 at the S_2/S_1 hopping points of 6TG.

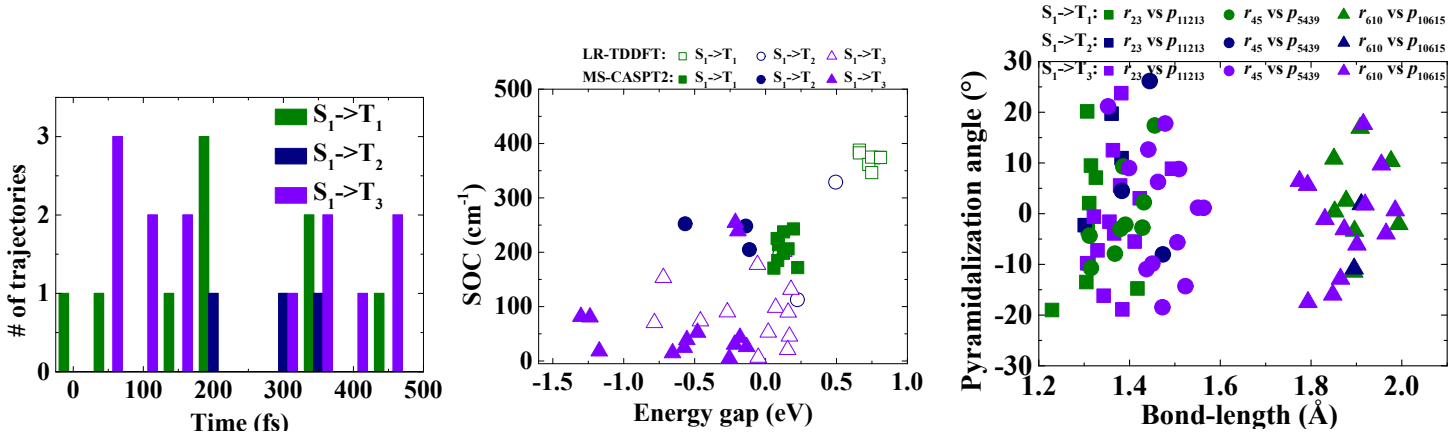

Figure S7. Distribution of crossing time, spin-orbit coupling (SOC) vs energy gap, and geometrical parameters for the S_1 → triplet crossings from dynamics of the S_2 state of 6SG.

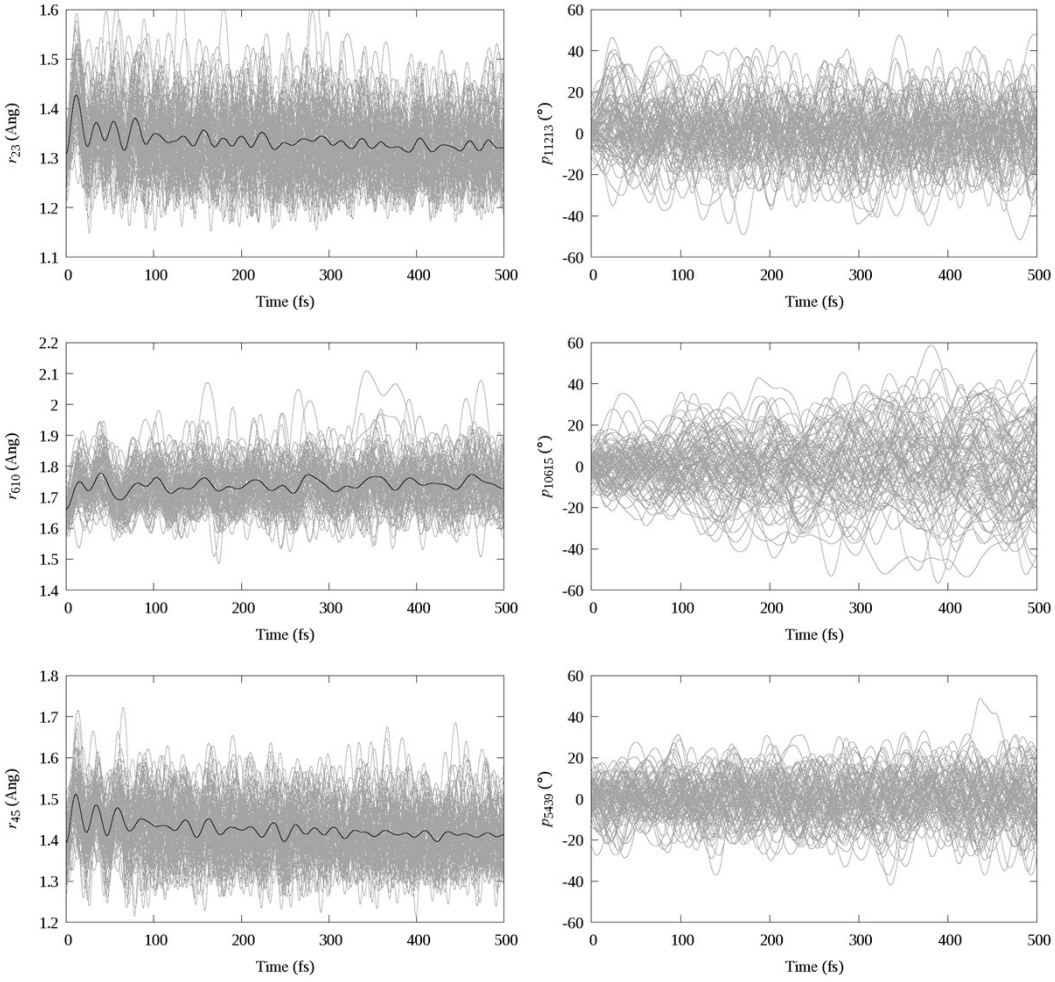

Figure S8. Time evolution of some chosen geometrical parameters from dynamics of

the S_3 state of 6TG.

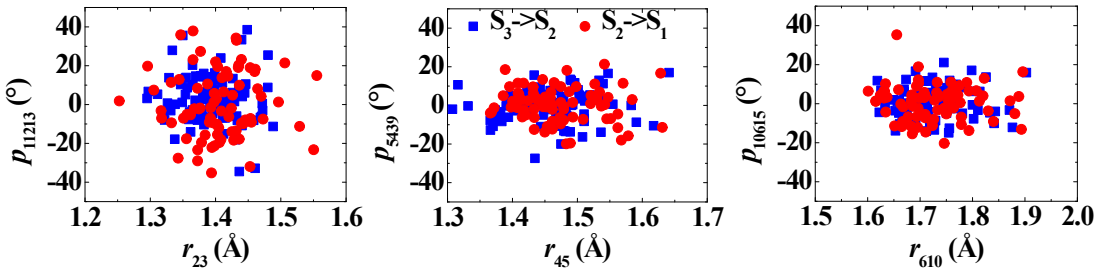

Figure S9. Geometrical parameters of hopping points involved in the $S_3 \rightarrow S_2 \rightarrow S_1$ internal conversion for 6TG.

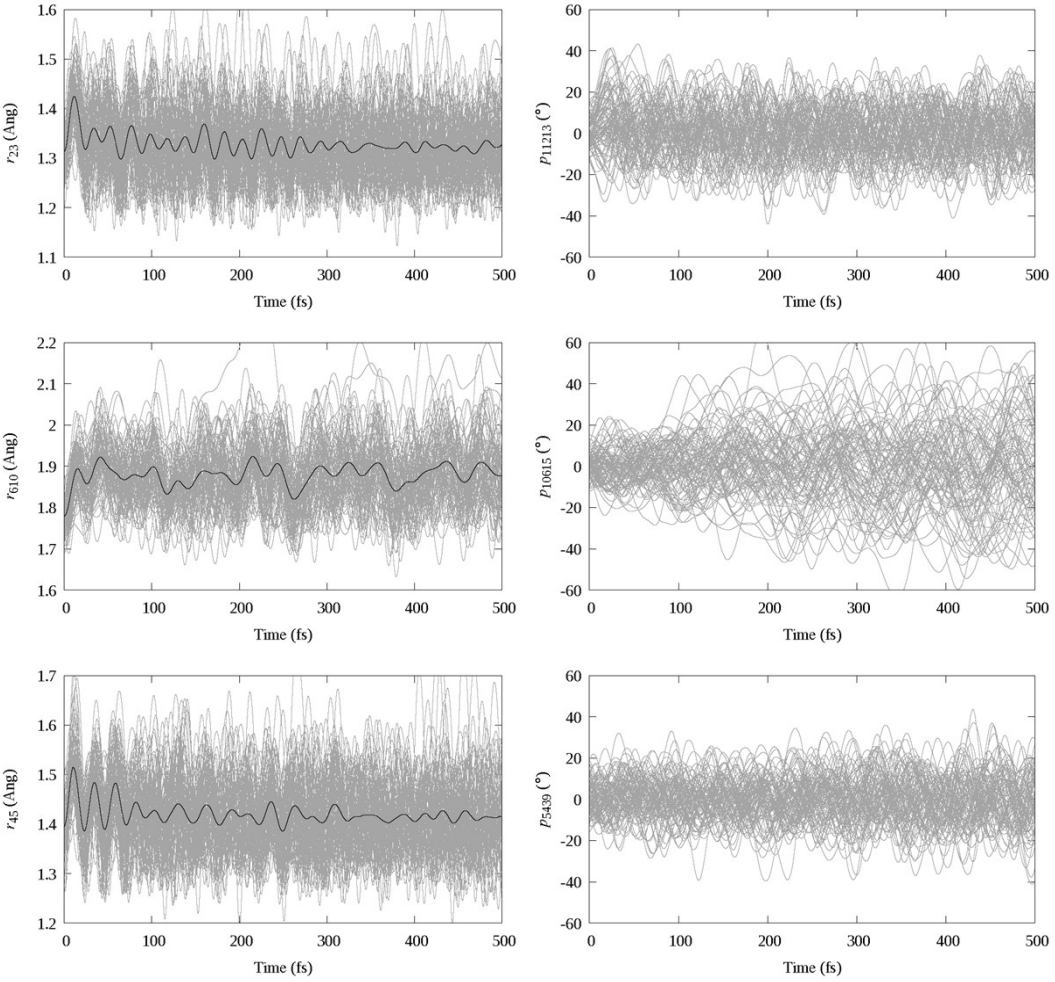

Figure S10. Time evolution of some chosen geometrical parameters from dynamics of the S_3 state of 6SG.

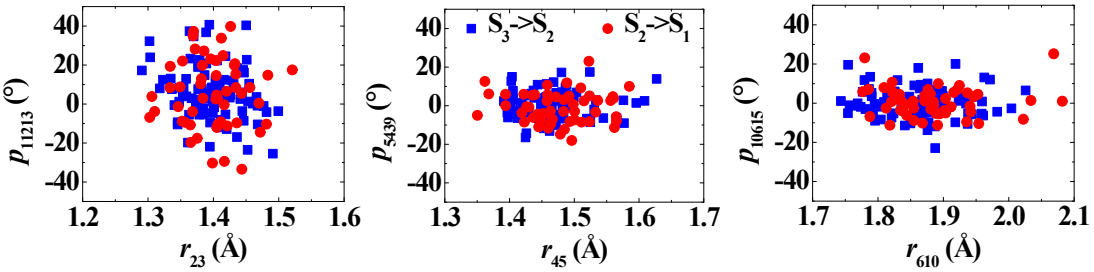

Figure S11. Geometrical parameters of hopping points involved in the $S_3 \rightarrow S_2 \rightarrow S_1$

internal conversion for 6SG.

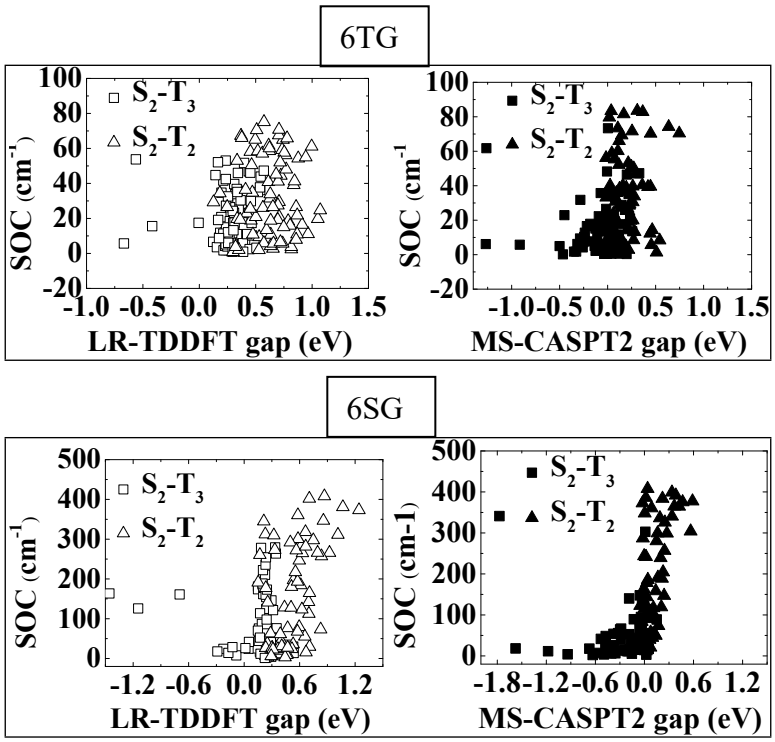

Figure S12. Spin-orbit coupling (SOC) vs energy gap for those between S_2 and T_2 and between S_2 and T_3 at the $S_2 \rightarrow S_1$ and $S_2 \rightarrow T_{2,3}$ crossing points from dynamics of the S_3 state of both molecules, calculated in different level of theory.

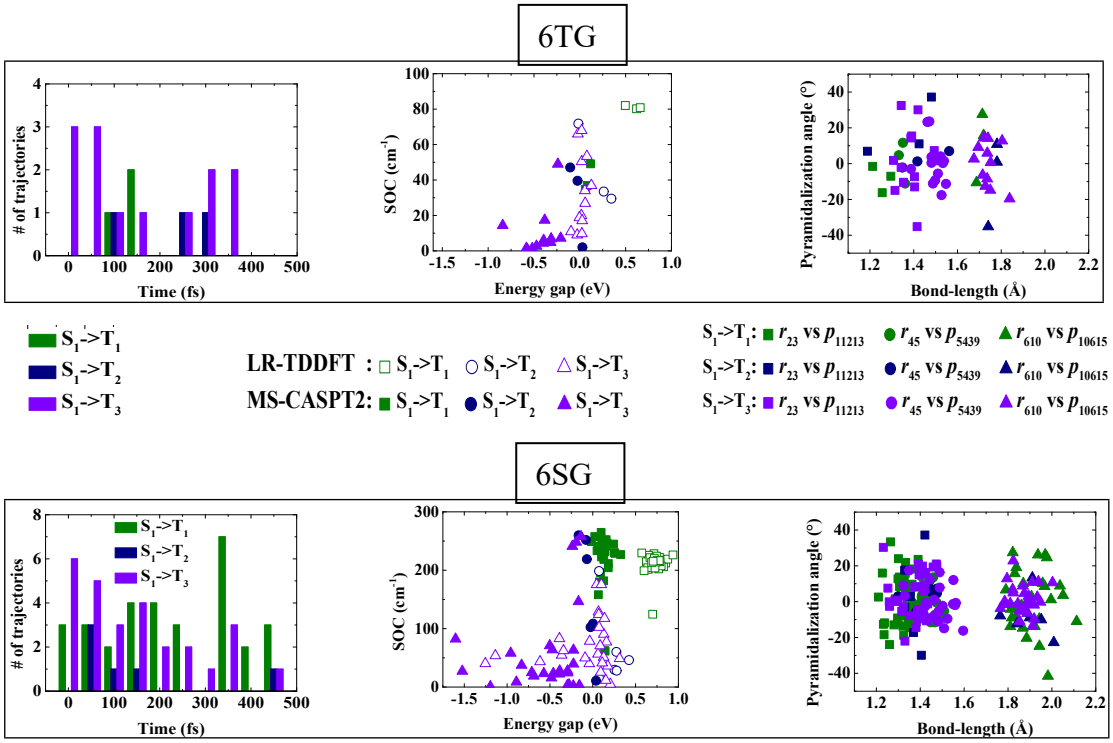

Figure S13. Distribution of crossing time, spin-orbit coupling (SOC) vs energy gap, and geometrical parameters for the $S_1 \rightarrow$ triplet crossings from dynamics of the S_3 state of both molecules.