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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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The substitution of oxygen with chalcogen in carbonyl group(s) of canonical nucleobases gives an impressive triplet generation, enabling their promising applications in medicine and other emerging techniques. The excited-state relaxation $S_2(\pi\pi^*) \rightarrow S_1(\pi\pi^*) \rightarrow T_1(\pi\pi^*)$ has been considered the preferred path for triplet generation in these nucleobase derivatives. Here, we demonstrate an enhanced quantum efficiency of direct intersystem crossing from $S_2$ to triplet manifolds upon substitution with heavier chalcogen element. The excited-state relaxation dynamics of sulfur/selenium substituted guanines in vacuum is investigated using a combination of static quantum chemical calculations and on-the-fly excited-state molecular dynamic simulations. We find that in sulfur-substitution the $S_2$ state predominantly decays to the $S_1$ state, while upon selenium-substitution the $S_2$ state deactivation leads to simultaneous population of the $S_1$ and $T_{2,3}$ states in the same time scale and multi-state quasi-degeneracy region $S_2/S_1/T_{2,3}$. Interestingly, the spectroscopic $S_3$ state of both studied molecules ultrafastly deactivates to the $S_1$ state through a successive $S_3 \rightarrow S_2 \rightarrow S_1$ path involving a multi-state quasi-degeneracy $S_3/S_2/S_1$. The populated...
S\(_1\) and T\(_2\) states will cross the lowest triplet state, and the S\(_1\) → T intersystem crossing happens in a multi-state quasi-degeneracy region S\(_1\)/T\(_{2,3}\)/T\(_1\) and is accelerated by selenium-substitution. The present study reveals the influences of both chalcogen-substitution element and initial spectroscopic state on excited-state relaxation mechanism of nucleobase photosensitizers and also highlights an important role of multi-state quasi-degeneracy in mediating the complex relaxation process. These theoretical results provide additional insights into the intrinsic photophysics of nucleobase-based photosensitizers and are helpful for designing novel photo-sensitizers for real applications.

1. Introduction

Substitution of carbonyl oxygen atom(s) in canonical nucleobases with sulfur atom(s) substantially influences their photophysical and photochemical properties, such as red-shifted UV absorption spectra and a high yield of triplet generation.\(^{[1-12]}\)

These properties are crucial for their promising applications in drugs and other novel techniques. Elucidating the excited-state relaxation pathways, especially the underlying physical mechanisms of the lowest triplet state formation, and their timescales in sulfur-substituted nucleobases is the focus of many spectroscopic\(^{[3-5, 10, 12-35]}\) and theoretical\(^{[14, 16, 34, 36-45]}\) studies in the past few years. These studies have reported the following three most probable pathways for triplet formation: (1) Path I: S\(_2\) → S\(_1\) → T\(_1\); (2) Path II: S\(_2\) → S\(_1\) → T\(_2\) → T\(_1\); (3) Path III: S\(_2\) → T\(_2\) → T\(_1\). Among them, Paths I and II satisfy the Kasha’s rule\(^{[46]}\) and have been proposed the predominant pathways for the lowest triplet (T\(_1\)) formation based on the static and/or dynamic simulations. Sub-30 fs broadband transient absorption spectroscopy combined with quantum chemical calculations of 4-thiouracil in aqueous solution\(^{[23]}\) and time-resolved photoelectron spectroscopy for 2,4-dithiouracil\(^{[47]}\) and 6-thioguanine (6TG)\(^{[48]}\) supported the involvement of the S\(_1\)(n\(_S\)π*) state in triplet
generation. Path III has been reported to play a minor role in triplet generation. In Path III the intersystem crossing occurs before any other non-radiative processes, and triplet population from this direct path was reported <25% in dynamic simulation of 4-thiothymine and thionated uracils,[14, 16, 42] although a sub-20 fs broadband transient absorption measurement of water solvated thiouracils[49] indicated that the direct intersystem crossing happen on a same timescale (ca. 100 fs) as that for S2 → S1 internal conversion.[23, 27]

When substitution of sulfur with selenium in 6-thioguanine, 6-selenoguanine (6SG) was found to have a further red-shifted maximum absorption (357 vs 341 nm) and a much faster triplet generation (130 vs 350 fs) and decay (1.7 vs 1420 ns) than its thio-analogs in pH 7.4 phosphate buffer saline (PBS) at room temperature.[50] These authors supposed that intersystem crossing of 6SeG starts from the intermediate S1 state of nSeπ* character on the analogy of the similarities between the theoretical and experimental results of 6SG and 6TG. Gas phase multistate complete-active-space second-order perturbation (MS-CASPT2) calculations of 6SeG suggested that triplet population originates from the S1 → T1 or T2 intersystem crossing following the S2 → S1 internal conversion.[51] Later MS-CASPT2 calculations of 6SeG in water and DNA duplex indicated the lack of a barrier for decay from the S2 state to the dark S1 state.[52] Using the second-order algebraic diagrammatic construction scheme (ADC(2)) as the quantum chemical method combined with molecular mechanics, a more recent dynamic simulation of 6SG in aqueous water solution found that 86% of the S2 state will decay to the S1 state, and, analogous to its thio-analogs, triplet generation follows the S2 → S1 → T2 → T1 path.[53] In a density functional theory (DFT) and linear-response time-dependent density functional theory (LR-TDDFT) study of sulfur, selenium, and tellurium-substituted deoxyguanosine, the S2 → S1 →
The T
t path was considered the favored one according to the calculated singlet-triplet
energy gap and spin-orbit coupling.[39] Theoretical simulations of
selenium-substituted uracils[54, 55] and thymines[56] also proposed Paths I and II as the
favorable relaxation paths. MS-CASPT2 calculation of 2-selenothymines considered
that Path I, II, and III are the three feasible paths to reach the triplet state.[57] Quantum
chemical studies of tellurium-substituted guanine[58] proposed that the twisted path of
S2 → S2/S1 → S1 → T1 prefers to the planar paths of S2 → S2/S1/T2 → S1 (or T2) → T1,
since the former has a lower energy barrier (3.0 vs 8.9 kcal/mol) from the S2
minimum to the corresponding S2/S1 intersection point. In that paper,[58] the twisted
(planar) paths were defined as those involving twisted (planar) excited-state structures
in term of Te-C6-C5-N1 dihedral angle of the tellurium-substituted guanine. Similar
twisted and planar paths were also theoretically proposed to be the possible electronic
deactivation pathways in the tellurium-substituted uracils.[59] In the indirect path
(Paths I and II), such efficient triplet generation benefits from ultrafast formation of
the S1 state and, subsequently, inhibition of the non-radiative S1 → S0 channel and
acceleration of the crossing from S1 to triplet states originating from larger spin-orbit
coupling and energetic closeness between S1 and triplet manifolds in the vicinity of
the S1 minimum.[14] However, intersystem crossing directly from higher singlet
excited state usually needs to compete with the internal conversion and other
processes. The quantum efficiency of intersystem crossing is closely relevant to
spin-orbit coupling strength, accessing the singlet-triplet crossing region, and other
factors. The sulfur-to-selenium substitution has been found to significantly accelerate
the S1 → T crossing, so does the heavier substitution also strength the direct S2 → T
crossing efficiency for the S2 decay of isolated chalcogen-substituted nucleobases?
Apart from substitution element, does the initial spectroscopic state also affect triplet
formation mechanism? With the aim to gain more insights into the intrinsic
photophysical properties of nucleobases-based photosensitizers, in this study we will
investigate the influences of both chalcogen element substitution and spectroscopic state on intersystem crossing mechanism. The present study combines both static and dynamic simulations to explore excited state relaxation of sulfur/selenium-substituted guanines in vacuum. Static quantum chemical studies use MS-CASPT2 to characterize the potential energy surfaces, and LR-TDDFT-based dynamic simulations are used to predict the timescale of and branching ratio among different competing pathways. We find that the main relaxation pathway for the lowest-energy spectroscopic S\textsubscript{2} state of sulfur-substitution is internal conversion to S\textsubscript{1}, whereas, direct intersystem crossing from S\textsubscript{2} to T\textsubscript{2,3} become comparably competitive with internal conversion from S\textsubscript{2} to S\textsubscript{1} upon selenium-substitution. Interestingly, relaxation of the spectroscopic S\textsubscript{3} state of both molecules is independent of substitution element and proceeds through S\textsubscript{3} \rightarrow S\textsubscript{2} \rightarrow S\textsubscript{1} to populate the ‘doorway’ S\textsubscript{1} state.

2. Computational details

Critical points in the ground (S\textsubscript{0}) and excited states of interest of both molecules were optimized using the MS-CASPT2 approach, based on the wave functions obtained from the six-state-averaged complete active space self-consistent field calculation. An active space including 12 electrons in 10 orbitals (12,10) was adopted, and the molecular orbitals in active space were displayed in Figure S1 of ESI. The numbers in the subscript of these orbitals refer to the atoms where the largest part of the orbital is localized. Both an imaginary level shift of 0.2 a.u. to avoid the intruder-state issue\cite{60} and an ionization potential-electron affinity (IPEA) shift of 0.0 a.u.\cite{61} in the zeroth-order Hamiltonian were applied. The cholesky decomposition technique was used for two-electron integral evaluation.\cite{62} Relativistically contracted atomic natural orbital basis sets of polarized double-ζ quality (ANO-RCC-VDZP) were used for all atoms.\cite{63, 64} The calculations of spin-orbit coupling matrix elements, \[ \langle \psi_S \left| \hat{H}_{SOC} \right| \psi_{T+1,0,-1} \rangle, \] adopted the atomic mean-field approximation\cite{65}, and the
spin-orbit coupling magnitudes were calculated as \[ |\langle \psi_S | \hat{H}_{\text{SOC}} | \psi_T \rangle| = \sqrt{\frac{\langle \psi_S | \hat{H}_{\text{SOC}} | \psi_{T+} \rangle^2 + \langle \psi_S | \hat{H}_{\text{SOC}} | \psi_{T0} \rangle^2 + \langle \psi_S | \hat{H}_{\text{SOC}} | \psi_{T-} \rangle^2}{3}} \]. The linear interpolation in internal coordinate (LIIC) paths connecting the relevant critical structures was used to determine the potential energy profiles. All the MS-CASPT2 calculations were performed using the OpenMolcas 21.2 suite programs.\[66\]

LR-TD-\(\omega\)B97XD/6-31G* based non-adiabatic molecular dynamics has been performed to determine the electronic relaxation pathways and timescales. For each molecule, ninety initial conditions (geometries and velocities) were stochastically generated from a quantum harmonic Wigner distribution around the Franck–Condon (FC) region. The trajectories were propagated using the SHARC (Surface Hopping including Arbitrary Couplings) algorithm.\[67, 68\] In our implementation, the LR-TDDFT excited states are constructed as a linear combination of singly excited configurations based on Casida’s wave function ansatz,\[69\] and the non-adiabatic couplings between excited states are numerically computed using the Hammes-Schiffer method.\[70\] The non-adiabatic couplings between the excited and ground states are neglected because of the incorrect description of the \(S_1/S_0\) intersection seam by LR-TDDFT in many cases.\[71, 72\] In addition, the effective charge approximation was employed in evaluation of spin-orbit couplings between the singlet and triplet manifolds.

Velocity-Verlet algorithm\[73\] with a time step of 0.5 fs was adopted for nuclear trajectories, and electronic wave function in the diagonal representation is propagated using a three-step propagator\[74\] with a time step of 0.02 fs. An energy-based decoherence correction with a empirical parameter of 0.1 au was employed for the electronic coefficients.\[75\] When a surface hop happens, the velocity vectors of all atoms are rescaled uniformly to conserve the total energy of the molecular system. In a frustrated hop velocities of all atoms were inverted. More details about the
implementation of this dynamic simulation method and the system setup for
simulations could be found in our previous paper.\cite{76} The dynamics simulations
included the lowest four singlet (S₀, S₁, S₂, S₃) states and lowest three triplet (T₁, T₂,
T₃) states. The simulation time was initially set to be 500 fs, and the trajectory was
stopped if some chemical bond(s) is (are) broken or the trajectory traps in the T₁ state
for about 100 fs. All (LR-TD)DFT electronic structure calculations have been done
using the Gaussian 09 package.\cite{77}

3. Results and discussion

A. Critical points and their relative energies

The MS-CASPT2/ANO-RCC-DZVP optimized critical points in/between different
potential energy surface(s) of both molecules and their relative energies are collected
in Figure S2 and Table S1 of ESI, respectively. The bond-lengths of C₆-X (X=S or
Se), C₂-N₃, C₄-C₅ bonds are defined as \( r_{610} \), \( r_{23} \), and \( r_{45} \) hereafter, respectively, and
the pyramidalization angles of C₆, C₂, and C₄ atoms are defined as \( p_{10615} \), \( p_{11213} \), and
\( p_{5439} \) hereafter, respectively. The pyramidalization angle \( p_{ABCD} \) is defined as the angle
between the A−B bond and the plane spanned by the B, C and D atoms,\cite{42} and the
positive or negative values of the angle \( p_{ABCD} \) imply the atom A be localized above or
below the plane spanned by the B, C and D atoms. Thus, in the calculation of the
algebraic mean of the angles \( p_{ABCD} \), the absolute value of the angle \( p_{ABCD} \) is used.

For excited-state minima of each molecules, the main geometrical difference with
respect to the S₀ minimum is an elongation of the C=X bond (by \( \sim 0.15 \) Å) in the
S₂(\( \pi_{45}\pi_{610}^* \)) minimum and a significant out-of-plane distortion of the stretched C-X
bond (by 0.1 Å) in the S₁(\( \pi_{10}\pi_{610}^* \)) (\( p_{10615} \sim 30^\circ \)) and T₁(\( \pi_{45}\pi_{610}^* \)) (\( p_{10615} \sim 40^\circ \))
minima. The main changes of bond-length in these excited state minima of both
molecules are also observed in the gas phase multi-reference calculations.\cite{45, 51} The
S₂/S₁ conical intersection has elongated C=X and C₄-C₅ bond-lengths by 0.08 and
0.14 Å for 6TG and 0.26 and 0.08 Å for 6SG. The C₅-C₆-Se angle in the S₂/S₁
conical intersection of 6SG is expanded by 7° compared with that in the ground state (136.8° vs 129.9°). In addition, the purine skeletons in the S2 minimum and S2/S1 conical intersection of both molecules are approximately planar with some pyramidalization of the C6 atom (\( \rho_{10615} \sim 7° \)). Instead, the S1/S0 conical intersection and T1/S0 singlet-triplet crossing structures present a strong out-of-plane distortion of the stretched C-X bond (\( \rho_{10615} \sim 60° \)). No change in orientation of the NH2 group with respect to the purine ring plane is observed when comparing the excited-state geometries with the ground state minimum. We also note that, except for C=X moiety, the minima and crossing points of 6TG are geometrically similar to those of 6SG.

Energetically, vertical excitation energies of the \( S_2(\pi_{45}\pi_{610}^*) \) and \( S_3(\pi_{45}\pi_{23}^*) \) states at the \( S_0 \) minimum of 6TG are respectively 4.0 eV (Oscillator strength: 0.50) and 4.85 eV (Oscillator strength: 0.11), and their corresponding experimental absorption peaks are respectively at 341 nm (3.64 eV) and 254 nm (4.88 eV)\(^{[21, 50]}\) in aqueous solution. The adiabatic excitation energies of the \( S_1(n_{10}\pi_{610}^*) \) and \( S_2(\pi_{45}\pi_{610}^*) \) state minima are respectively 3.13 and 3.71 eV. The \( T_1(\pi_{45}\pi_{610}^*) \) state is 2.76 eV above the \( S_0 \) minimum, agreeing with an experimentally measured phosphorescence emission maximum 468 nm (2.65 eV) of 6TG.\(^{[21]}\) For 6SG, vertical excitation energies of the \( S_2(\pi_{45}\pi_{610}^*) \) and \( S_3(\pi_{45}\pi_{23}^*) \) states at its \( S_0 \) minimum are respectively 3.59 eV (Oscillator strength: 0.52) and 4.53 eV (Oscillator strength: 0.05), which are close to the experimental lowest absorption maximum 357 nm (3.47 eV) and a small UVC absorption peak 254 nm (4.88 eV).\(^{[50]}\) The calculated adiabatic excitation energies are 2.69, 3.26, and 2.44 eV for the \( S_1(n_{10}\pi_{610}^*) \), \( S_2(\pi_{45}\pi_{610}^*) \), and \( T_1(\pi_{45}\pi_{610}^*) \) state minima of 6SG, respectively. The presently reported excitation energies of 6SG are consistent with previous MS-CASPT2 and TD-B3LYP results.\(^{[39, 51, 53]}\)

The \( S_2/S_1 \) conical intersection is predicted 4.04/4.04 eV for 6TG and 3.68/3.66 eV for 6SG above their corresponding \( S_0 \) minimum. A singlet/triplet funnel between
S₂ and T₂ is optimized and found to be structurally and energetically similar to the S₂/S₁ crossing (S₂/T₂: 4.07/4.05 eV for 6TG and 3.66/3.66 eV for 6SG). An energy barrier from the S₂ minimum to the S₂/S₁ conical intersection is predicted to be 0.33 eV for 6TG and 0.42 eV for 6SG, and it has been reported about 0.2 eV for 6TG,[45] and 0.44 eV for 6SG[51] in vacuum. In both molecules the barriers from the S₁(n₁₀π₆₁₀*) minimum to the S₁/S₀ conical intersection and from the T₁(π₄₅π₂₃*) minimum to the T₁/S₀ crossing was predicted 1.0 and 0.33 eV, respectively, which are close to the previously calculated values of 0.9 eV[44] and 0.11 eV.[51, 52] Previous simulation of 6TG found that some trajectories evolve toward the S₀ state through C2-puckering,[45] thus we also consider this path here. Along the C=N twisting coordinate, we locate a C2-pyramidalized S₁(π₄₅π₂₃*)/S₀ conical intersection (p₁₁₂₁₃ ~60°) and its relative energy to the corresponding S₀ minimum is 4.73/4.71 eV for 6TG and 4.28/4.27 eV for 6SG.

B. LIICs

Figure 1 shows the evolution of electronic states along predefined LIIC paths connecting from FC to the T₁/S₀ crossing (C6-stretching path) and from FC to the S₁(π₄₅π₂₃*)/S₀ conical intersection (C2-puckering path) for both studied molecules. As seen in Figure 1(a), potential energy curve of the initially photo-populated S₂ state of 6TG descends from FC to its minimum and then rises to reach the S₂/S₁ conical intersection. When the S₁ state is populated after passing through this S₂/S₁ conical intersection, both the potential energy curve of the S₁ state from the S₂/S₁ conical intersection to the S₁ minimum and the potential energy curve of the T₁ state from the S₁ minimum to the T₁ minimum are descent. The relaxed T₁ state crosses to the ground state via a T₁/S₀ singlet-triplet crossing after overcoming a barrier. The potential energy curve of the T₂ state is overlap with that of the S₁ state along this pre-defined path. As shown in Figure 1(b), potential energy curves of the S₁, S₂, S₃, T₂, and T₃ states are close to each other in the midway along the C2-puckering
coordinate of 6TG, and the region of quasi-degeneracy among these electronic states is about 0.2 eV above the S_2 FC region. However, potential energy curve of the S_3 state from FC to the quasi-degeneracy region is descent, meaning that the lower states can be ultrafastly populated from the S_3 state. Evolution of these states along the pre-defined LIIC paths of 6SG was depicted in Figures 1 (c, d). As seen, the evolution of these considered electronic states of 6SG is very similar to that of 6TG, and a down shift of about 0.3–0.5 eV for these potential energy curves was observed due to selenium-substitution. A down-shift of about 0.4–0.6 eV of the vertical excitation energies and potential energy surfaces of 2-selenouracil, compared to 2-thiouracil, has been reported along the C6-stretching coordinate.\cite{55} In the C2-puckering path of 6SG, the energy difference between a region of quasi-degeneracy among the S_3, S_2, S_1, T_3, T_2, T_1 states and the S_2 FC is 0.16 eV.

**C. Validation of LR-TD-ωB97XD/6-31G* for dynamic simulations**

A benchmark for the usage of LR-TDDFT in dynamic simulation is given below. Based on MS-CASPT2 optimized geometries, a benchmark of LR-TD-ωB97XD/6-31G*, against MS-CASPT2/ANO-RCC-VDZP, has been performed in terms of relative energies, spin-orbit couplings, and LIIC potential energy profiles for both molecules. As seen in Table S1 of ESI, compared with MS-CASPT2, LR-TDDFT predicts similar excitation energies for the S_1 and S_3 states but overestimates the S_2 state by 0.4–0.6 eV. LR-TDDFT also underestimates the excitation energies of triplet states by 0.3–0.5 eV. However, LR-TDDFT reasonably predicts the energy barrier (0.2 vs 0.33 eV for 6TG, and 0.4 vs 0.42 eV for 6SG) from the S_2 minimum to the S_2/S_1 point, compared with MS-CASPT2. Moreover, for LIICs (Figure S3 of ESI), LR-TDDFT predicts consistent results with MS-CASPT2 in terms of the shape and closeness of the potential energy curves along these predefined coordinates, although a down-shift of 0.2–0.5 eV for the LR-TDDFT LIICs of triplet states and an earlier crossing between T_1 and S_0. The LR-TDDFT calculated
spin-orbit coupling values (Table S2 of ESI) between S₂ and T₂ at the S₂/S₁ point and
between S₁ and T₂ at the S₁ minimum of 6TG (6SG) are 63 (412) and 85 (401) cm⁻¹,
respectively, agreeing well with the MS-CASPT2 ones, 78 (387) and 89 (427) cm⁻¹.
Overall, despite the applied DFT functional and basis set, LR-TD-ωB97XD/6-31G*
gives reasonable results compared with MS-CASPT2, which validates its usage in
dynamic simulations of the excited-state deactivation of chalcogen-substituted
nucleobase derivatives.

D. Dynamics starting from the S₂ state of 6TG

Figure 2(a) displays the time-dependent electronic population for dynamics
simulations initiated from the S₂ state of 6TG, and it is seen that the S₂ state
depopulation is accompanied with population of the S₁ state. The S₂, S₁ and the total
triplet-state (T₁+T₂+T₃) populations are 13%, 70%, and <10%, respectively, on the
500 fs time scale simulation. Figure 2(b) shows the net number of hops between each
pair of adiabatic states, and we observe that 81% (73/90) of the calculated trajectories
undergoes internal conversion from S₂ to S₁, and only 7% (6/90) of the calculated
trajectories deactivates directly from S₂ to T₂. This implies that intersystem crossing
will start mainly from S₁ but to a lesser extent from S₂ to T₂. Analysis of the nature
of electronic states shows that the S₂/S₁ hopping involves a transition from π₄₅π₆₁₀* to
n₁₀π₆₁₀*, although some trajectories have a hop from π₄₅π₂₃* to n₁₀π₆₁₀*. The
predominant pathway of the S₂ decay is in line to previous dynamics simulation
results of Martínez-Fernández et al.[45] and a recent spectroscopic experiment of 6TG
which supported an ultrafast internal conversion from the S₂(ππ*) state to the S₁(n₃π*)
state be the primary path for the S₂ state deactivation.[48] The state evolution is also
reflected in the time evolution of molecular geometries. For instance, as seen in
Figure S4 of ESI, the C6-S bond-length (r₆₁₀) quickly increases following
photo-excitation and oscillates around 1.72 Å after the time about 25 fs, and
pyramidalization of the C6 atom (p₁₀₆₁₅) shows a larger variance after the time 200 fs.
We also analyze the \( S_2 \rightarrow S_1 \) hopping events in terms of the hopping time and geometrical parameters to give further mechanistic insights into this internal conversion process. Figure 2(c) shows that, the \( S_2\)-\( S_1 \) energy gaps mostly are smaller than 0.2 (0.3) eV at the LR-TDDFT (MS-CASPT2) level, and about 75% of the \( S_2 \rightarrow S_1 \) hopping happens within 200 fs. The larger hopping time of \( S_2\)-\( S_1 \) internal conversion than the experimental value of about 80 fs in PBS\[48\] may be partly explained by the absence of solvent effect that decreases the \( S_2\)-\( S_1 \) gap along the relaxation pathway. Figure 2(d) collects some key geometrical parameters of these hopping points, and these hopping structures are characterized by \( r_{610} \), \( r_{23} \), and \( r_{45} \) ranging from 1.67–1.77, 1.35–1.45, and 1.42–1.52 Å, respectively, and \( p_{10615} \), \( p_{11213} \), and \( p_{5439} \) being mostly distributed in a range of -10°–10°, -30°–30° and -10°–20°, respectively. The averaged structure over all of these hopping structures (\( r_{23} = 1.38 \) Å, \( r_{45} = 1.47 \) Å, \( r_{610} = 1.73 \) Å, \( p_{10615} = 6.4° \), \( p_{11213} = 14.6° \), \( p_{5439} = 7.3° \)) geometrically close to the MS-CASPT2 optimized \( S_2\)/\( S_1 \) conical intersection (\( r_{23} = 1.35 \) Å, \( r_{45} = 1.54 \) Å, \( r_{610} = 1.74 \) Å, \( p_{10615} = 6.2° \). Please see 6TG\_S2S1 in Figure S2 of ESI). Some hops occur at structures having the \( r_{23} \) 1.35 Å and \( p_{11213} \) 30–50°, which is still far away from the optimized \( S_1(\pi_4\pi_2^*)/S_0 \) point that is about 0.7 eV above the \( S_2 \) FC and has a stretched C2-N3 bond-length 1.7 Å and \( p_{11213} \) 56°.

E. Dynamics starting from the \( S_2 \) state of 6SG

Figure 3(a) shows that the \( S_2 \) state depopulation induces a quick population of the \( T_2 \) state before the time 150 fs after which the \( T_2 \) population shows a steady value. Both \( S_1 \) and \( T_1 \) state populations show a gradual increase from the time 50 fs, and after the time 200 fs the \( S_1 \) population decreases. The \( S_1 \), \( T_1 \), and \( T_2 \) state populations are respectively about 10%, 36% and 40% at the final simulation time. Other state populations are negligible during our simulation time. Accordingly, at our simulation time of 500 fs, the mainly populated states are the \( T_1 + T_2 \) states whose population amounts to 76%, whereas the total triplet population is less than 10% in 6TG. For
relaxation paths of the S\textsubscript{2} state, as Figure 3(b) shows, the S\textsubscript{2} state of 6SG deactivates
to the S\textsubscript{1}, T\textsubscript{2} and T\textsubscript{3} states in 42% (38/90), 24% (22/90), and 23% (21/90),
respectively, of the calculated trajectories, and the lowest triplet state formation is
identified as S\textsubscript{2} → S\textsubscript{1} → T\textsubscript{2,3} → T\textsubscript{1} and S\textsubscript{2} → T\textsubscript{2,3} → T\textsubscript{1}. These state crossings from
the S\textsubscript{2} state to lower states mostly happen before the time about 150 fs (Figure 3(c)),
which is in line with an experimentally value of 130 fs that was assigned to
intersystem crossing of 6SG in aqueous solution.\textsuperscript{50} Previous ADC(2)-based dynamic
simulation of 6SG in water showed that the experimental time scale should be an
effective time constant that includes multiple processes, such as initial relaxation from
the FC region, internal conversion, intersystem crossing, or solvent relaxation.\textsuperscript{53} The
time evolution of molecular geometries is given in Figure S5 of ESI, and the main
changes occur at the C=Se moiety. The C-Se bond-length (r\textsubscript{610}) oscillates around 1.90
Å after the time 20 fs, and pyramidalization of the C6 atom (p\textsubscript{10615}) shows a larger
variance after the time 150 fs. At the molecular structures that induce both internal
conversion and intersystem crossing, the C6-Se (r\textsubscript{610}), C2-N3 (r\textsubscript{23}), and C4-C5 (r\textsubscript{45})

bond-lengths vary in the range of 1.8~2, 1.3~1.42, and 1.37~1.52 Å, respectively, and
the C6-, C2-, and C4-pyramidalization angles vary in a range of -20~20° (Figure
3(d-f)). The averaged structure over all of these crossing points has a geometry of r\textsubscript{23}
1.35 Å, r\textsubscript{45} 1.46 Å, r\textsubscript{610} 1.95 Å, p\textsubscript{10615} 16°, p\textsubscript{11213} 9.4°, and p\textsubscript{5439} 7.2°, which is
geoemtrically close to the MS-CASPT2 optimized S\textsubscript{2}/S\textsubscript{1} conical intersection (see
6SG_S2S1 Figure 2 of ESI). A few trajectories are observed to undergo state
crossing at molecular structures having a C-Se bond-length >2 Å and a significant
out-of-plane displacement of selenium atom (p\textsubscript{10615} ca. 80°). The S\textsubscript{2}/S\textsubscript{1} energy gap is
<0.3 eV at the S\textsubscript{2}/S\textsubscript{1} crossing points at both level of theory (Figure 3(g)), and these
S\textsubscript{2}/S\textsubscript{1} crossings involve a transition from π\textsubscript{45}π\textsubscript{610}* to n\textsubscript{10}π\textsubscript{610}*. The S\textsubscript{2}/T\textsubscript{2} energy gaps at
the S\textsubscript{2}/T\textsubscript{2} crossing points and the S\textsubscript{2}/T\textsubscript{3} energy gaps at the S\textsubscript{2}/T\textsubscript{3} crossing points have
an averaged value of 0.8 and 0.1 eV, respectively, at the LR-TDDFT level, but they
become 0.4 and 0.6 eV at the MS-CASPT2 level (Figure 3(h)). At these singlet-triplet crossing points, the spin-orbit coupling magnitudes vary but are on average about 30 cm\(^{-1}\) between \(S_2\) and \(T_3\) and about 380 cm\(^{-1}\) between \(S_2\) and \(T_2\) as estimated by both computational methods. The large spin-orbit couplings occur between \(^1\pi_{45}\pi_{610}^*\) and \(^3n_{10}\pi_{610}^*\), and the small spin-orbit couplings occur between \(^1\pi_{45}\pi_{610}^*\) and \(^3\pi_{45}\pi_{23}^*\).

Additional calculations of both energy gaps and spin-orbit couplings at these singlet-singlet and singlet-triplet points (Figure S6 of ESI) at different level of theory demonstrate that these crossing points represent a region of multi-state quasi-degeneracy involving the \(S_2\), \(S_1\), \(T_2\), and \(T_3\) states (referred as \(S_2/S_1/T_{2,3}\) hereafter). In comparison, the energy gaps and spin-orbit couplings between \(S_2\) and \(T_3\) and between \(S_2\) and \(T_2\) at the \(S_2/S_1\) hopping structures of 6TG are also calculated (Figure S6 of ESI). It is found that these hopping structures in 6TG also represent a region of multi-state quasi-degeneracy among the \(S_2\), \(S_1\), \(T_2\), and \(T_3\) states (\(S_2/S_1/T_{2,3}\)), and at this region the spin-orbit couplings between \(S_2\) and triplet states vary from 5 to 80 cm\(^{-1}\) but are on average about 30 cm\(^{-1}\) as predicted by both computational methods.

We also analyze intersystem crossing from the \(S_1\) state of 6SG (Figure S7 of ESI) and find that, the \(S_1\)-\(T\) crossings happen in an extended time and at molecular structures characterized by a stretched C-Se bond-length of about 1.9 Å and also a stretched C4-C5 bond-length (1.48 Å) in the crossing from \(S_1\) to \(T_3\). At these \(S_1\)-triplet crossing points of 6SG, although LR-TDDFT overestimates the \(S_1\)-\(T_1\) gap, the \(T_1\), \(T_2\), and \(T_3\) states become energetically close to \(S_1\) at the MS-CASPT2 level, implying that these crossing points represent a region of quasi-degeneracy among \(S_1\), \(T_1\), \(T_2\), and \(T_3\) (referred as \(S_1/T_{2,3}/T_1\) hereafter). At this \(S_1\)-triplet crossing region, the spin-orbit coupling magnitudes are on average about 80 or 400 cm\(^{-1}\) depending on the involved states.

**F. Relaxation dynamics starting from the \(S_3\) state**
Figure 4(a) shows time-dependent state population for dynamics simulations initialized from the S$_3$ state of 6TG. It is seen that the S$_3$ state of 6TG quickly decays to the S$_2$ and S$_1$ states, and the S$_2$ population has a maximum at about 50 fs and then gradually transfers its population to the S$_1$ state. The S$_1$, S$_2$, and T$_1$ + T$_2$ state population are respectively 68%, 12%, and 20% at the end of simulation time. The predominant pathway for the S$_3$ state deactivation of 6TG is identified as S$_3 \rightarrow$ S$_2 \rightarrow$ S$_1$ (Figure 4(b)). Electronic wave function analysis shows that the S$_2$ state has a π$_{45}\pi_{610}^*$ or π$_{45}\pi_{23}^*$ character after the S$_3 \rightarrow$ S$_2$ hopping, and the S$_2 \rightarrow$ S$_1$ hops produces the S$_1$ state of π$_{610}^*$ character. As Figure S8 of ESI shown, photo-excitation induces essential elongation of the C6-S (r$_{610}$), C4-C5 (r$_{45}$), and C2-N3 (r$_{23}$) bond-lengths and pyramidalization of the C2 atom (p$_{11213}$). After the time 20 fs, the r$_{610}$ oscillates around 1.73 Å, while the r$_{23}$ and r$_{45}$ oscillate around 1.35 and 1.45 Å, respectively, and show a gradual decrease to their respective ground state values before the time 100 fs. In most trajectories the p$_{11213}$ varies in a range of -20 ~ 20° while p$_{10615}$ starts to show a larger variance after the time 100 fs. The structural changes implies an electronic state evolution from those localized on the C=N moiety to those located on the C=S moiety. As Figure 4(c) shows, the S$_3 \rightarrow$ S$_2$ and S$_2 \rightarrow$ S$_1$ hopping times are <50 and <150 fs, respectively, and the energy gap is mostly <0.2 eV in both transitions as predicted by both computational methods. The state crossings in this S$_3 \rightarrow$ S$_2 \rightarrow$ S$_1$ process mostly occur at a region of molecular structures having r$_{23}$, r$_{45}$, and r$_{610}$ 1.32~1.46, 1.4~1.55, and 1.65~1.82 Å, respectively, and pyramidalization angles at the C2, C4, and C6 atoms <20° (Figure S9 of ESI). The averaged structure over all of these hopping points of 6TG has a geometry of r$_{23}$ 1.39 Å, r$_{45}$ 1.46 Å, r$_{610}$ 1.72 Å, and pyramidalization angles at the C2, C4, and C6 atoms being 10°, 6°, and 6°, respectively.

For relaxation dynamics starting from the S$_3$ state of 6SG, Figure 4(d) shows that the S$_3$ state population becomes negligible before the time 80 fs, at the same time, the
S₂ and S₁ state populations quickly increase and reach a maximum value of 45% and 38%, respectively. After that time, the S₂ state population shows a quicker decrease than the S₁ state and has a population of <10% after the time 200 fs, while the S₁ state population is ~30% before the end of simulation. The T₂ and T₁ states start to be populated already around 10 fs, and the total T₂+T₁ population is ~60% at the end of simulation. The predominant pathway of the S₃ state deactivation of 6SG, analogous to 6TG, is also S₃ → S₂ → S₁, and the selenium substitution results in a more efficient intersystem crossing from S₁ to triplet states (Figure 4(c)). The state crossing events in the S₃ → S₂ → S₁ process happen within 80 fs with an energy gap of <0.4 eV for the S₃ → S₂ hop and <0.1 eV for the S₂ → S₁ hop as predicted by both computational methods (Figure 4(f)). The change of electronic state character from π₄₅π₂₃* to π₄₅π₆₁₀* and to n₁₀π₆₁₀* during the successive S₃ → S₂ → S₁ hopping is also observed in time evolution of geometrical parameters. As seen in Figure S10 of ESI, photo-excitation into the S₃ state of 6SG induces quick increase of the C6-Se (r₆₁₀), C2-N3 (r₂₃), and C4-C5 (r₄₅) bond-lengths and pyramidalization of the C2 atom (p₁₁₂₁₃). The r₆₁₀ oscillates around 1.88 Å after the time 20 fs, while the r₂₃ and r₄₅ oscillate around 1.31 and 1.42 Å, respectively, before the time 80 fs after which they gradually decrease to their respective ground state values. The p₁₁₂₁₃ varies in a range of -20–20° after the time 80 fs, and the p₁₀₆₁₅ starts to become active after 100 fs. The hopping points during the S₃ → S₂ → S₁ hopping show a geometry having r₂₃, r₄₅, and r₆₁₀ being in a range of 1.32–1.48, 1.4–1.6, and 1.8–2 Å, respectively, p₁₁₂₁₃ -30–30°, and the p₅₄₃₉ and p₁₀₆₁₅ angles -20–20° (Figure S11 of ESI). The averaged structure over all of hopping points of 6SG has a geometry of r₂₃ 1.4 Å, r₄₅ 1.47 Å, r₆₁₀ 1.86 Å, and pyramidalization angles at the C2, C4, and C6 atoms being 11°, 6°, and 6°, respectively.

In both molecules, the molecular structures that induce hopping from S₃ to S₂ and to S₁ represent a region of multi-state quasi-degeneracy among the S₃, S₂ and S₁ states.
(referred as $S_3/S_2/S_1$ hereafter), and, stating from FC, this quasi-degeneracy region is reached through bond elongation by about 0.07 Å and little C-pyramidalization (<10°) at the C=N, C=C, and C=X moieties. We analyze the intersystem crossing from $S_2$ upon hopping from $S_3$ based on the calculated energy gaps and spin-orbit couplings at the $S_2/S_1$ and $S_2/T_{2,3}$ crossing points of both molecules. As seen in Figure S12 of ESI, at these crossing points of both molecules, the $S_2$-$T_3$ and $S_2$-$T_2$ energy gaps are about 0.3 and 0.7 eV, respectively, at the LR-TDDFT level, whereas, the $S_2$, $S_1$, $T_2$, and $T_3$ states are close-lying within about 0.3 eV at the MS-CASPT2 level. In these crossing points, the spin-orbit coupling values vary from 5 to 80 cm$^{-1}$ but are on average 25 cm$^{-1}$ for 6TG and vary from 10 to 400 cm$^{-1}$ but are on average 120 cm$^{-1}$ for 6SG in both computational methods (Figure S12 of ESI). The smaller spin-orbit coupling values in the $S_3/S_2/S_1$ region can give an explanation of a lower quantum efficiency for direct population transfer from $S_2$ to $T_{2,3}$ after the $S_3 \rightarrow S_2$ hopping in 6SG, compared with those after initial photo-excitation to the $S_2$ state. Passing through the $S_3/S_2/S_1$ region, the $S_1$ state is populated and will undergo intersystem crossing to the triplet manifolds. We thus analyze the intersystem crossing starting from the $S_1$ state (Figure S13 of ESI) and find that, in both molecules the $S_1 \rightarrow T$ intersystem crossings happen in an extended time and at molecular structures having a stretched C-X bond-length (about 1.78 Å for 6TG or 1.9 Å for 6SG) and also a stretched C4-C5 bond-length (1.48 Å) in the $S_1$ $\rightarrow T_{2,3}$ crossing, as well as some C-pyramidalization (-20°-20°). MS-CASPT2 calculations of the $S_1$-$T$ energy gap indicate that these crossing structures in each molecule represent a region of quasi-degeneracy among the $S_1$, $T_{2,3}$ and $T_1$ states (referred as $S_1/T_{2,3}/T_1$ hereafter). At this $S_1$-triplet crossing region, the spin-orbit couplings vary from 5 to 80 cm$^{-1}$ of 6TG and from 10 to 300 cm$^{-1}$ for 6SG. The larger singlet-triplet spin-orbit coupling magnitude due to
selenium-substitution in this crossing region leads to a more efficient intersystem
crossing from $S_1$, compared with sulfur-substitution.

G. Relaxation mechanism

The relaxation mechanisms for both molecules are presented here. After initial
photo-excitation, the first bright state $S_2(\pi\pi^*)$ of 6TG relaxes toward a multi-state
quasi-degeneracy region $S_2/S_1/T_{2,3}$ through bond-stretching and some
C-pyramidalization in the C=S, C=C, and C=N moieties. From this degeneracy
region, the $S_2$ state predominantly deactivates to the $S_1$ state from which intersystem
crossing happens through accessing the quasi-degeneracy region $S_1/T_{2,3}/T_1$. This
relaxation pathway are in line with previous theoretical simulation and experimental
evidence about the ‘doorway’ role of the $S_1(n_S\pi^*)$ state for intersystem crossing in
6TG and other thionated nucleobases.

The $S_2$ state deactivation of 6SG leads to simultaneous population of the $S_1$ and
$T_{2,3}$ states happening in the same time scale of 100 fs and region of molecular
structures characterized with stretched bond-lengths and some C-pyramidalization at
the C=Se, C=C, and C=N moieties. Our proposed pathways for the $S_2$ state relaxation
of 6SG in the gas phase are more complex than the previous one where only paths
involving the dark $S_1(n\pi^*)$ state were discussed.$^{[39, 51]}$ The direct $S_2 \rightarrow T_2$ path
accounts for only 13% of the calculated trajectories in dynamic simulation of 6SG in
water,$^{[53]}$ whereas, 53% of the trajectories undergo the direct $S_2 \rightarrow T_2$ crossing in our
simulations. This may be explained by the solvent effect that can accelerate the $S_2$-$S_1$
internal conversion$^{[52]}$ and by different crossing region sampled during relaxation. The
trajectories of 6SG in water,$^{[53]}$ after photo-excitation to the $S_2$ state, evolve toward an
$S_2$/$S_1$ crossing region where molecular structures have a strong out-of-plane
displacement of the selenium atom within 100 fs, however, in our simulations the
trajectories visit the $S_2$/$S_1$/$T_{2,3}$ region having approximately planar molecular
structures. Since the studied molecules sample similar region of potential energy
surface \((S_2/S_1/T_{2,3})\), the larger quantum efficiency of \(S_2 \rightarrow T_{2,3}\) in 6SG, compared with 6TG, may be ascribed to a large spin–orbit coupling magnitude (about 400 cm\(^{-1}\)) in this region.

Independent of the substitution element, the \(S_3\) relaxation of both molecules non-adiabatically decays to the \(S_1\) state through a successive \(S_3 \rightarrow S_2 \rightarrow S_1\) path, and these state crossings are mediated by a multi-state quasi-degeneracy \(S_3/S_2/S_1\). The populated \(S_1\) and \(T_2\) states will act as doorway states to mediate the lowest triplet state formation, and the large spin-orbit coupling interaction due to selenium substitution significantly accelerates triplet formation in the \(S_1/T_{2,3}/T_1\) region, compared with sulfur substitution.

Totally, this study proposed the path of \(S_2\) FC \(\rightarrow S_2/S_1/T_{2,3} \rightarrow S_1 \rightarrow S_1/T_{2,3}/T_1 \rightarrow T_1\) for triplet state formation of thionated nucleobases and both paths of \(S_2\) FC \(\rightarrow S_2/S_1/T_{2,3} \rightarrow S_1 \rightarrow S_1/T_{2,3}/T_1 \rightarrow T_1\) and \(S_2\) FC \(\rightarrow S_2/S_1/T_{2,3} \rightarrow T_{2,3} \rightarrow S_1/T_{2,3}/T_1 \rightarrow T_1\) for triplet generation in selenium even tellurium substitution. The triplet generation mechanism starting from the \(S_3\) state of chalcogen-substituted nucleobases is \(S_3\) FC \(\rightarrow S_3/S_2/S_1 \rightarrow S_1 \rightarrow S_1/T_{2,3}/T_1 \rightarrow T_1\).

4. Conclusion

We have applied the combined static electronic structure calculations and non-adiabatic molecular dynamic simulation to investigate the excited state deactivation of sulfur- and selenium-substituted guanine. We find that sulfur-substitution leads to the \(S_2\) state relaxation being dominated by internal conversion to the intermediate \(S_1(n\pi^*)\) state, whereas, in the heavier selenium-substitution the direct \(S_2 \rightarrow T_{2,3}\) intersystem crossing becomes comparably competitive with the \(S_2 \rightarrow S_1\) internal conversion due to enhanced spin-orbit coupling. Independent of the substitution element, the \(S_3\) state of both molecules non-adiabatically decays to the \(S_1\) state via \(S_3 \rightarrow S_2 \rightarrow S_1\). During the excited-state relaxation, multi-state quasi-degeneracy regions play important roles in mediating
these efficient state-crossings. In summary, our simulation results reveal the influences of both substitution element and initial spectroscopic state on excited-state relaxation and highlight the important role of multi-state quasi-degeneracy in driving the complex photo-induced process of chalcogen-substituted nucleobases.

These results provide additional insights to the intrinsic excited-state dynamics of nucleobase-based photosensitizers and are helpful for molecular design to screen potential photosensitizers targeting in various applications. Moreover, we suggest that, apart from characterizing the potential energy surfaces through static quantum chemical calculations, excited-state non-adiabatic molecular dynamics should become an indispensable tool used in our theoretical investigations of the photo-induced process in molecules and materials.

Conflicts of interest

The authors declare no competing financial interest.

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Supporting Information

Active orbitals included in the active space, the MS-CASPT2 optimized geometries and their relative energies, data used to benchmark LR-TDDFT, and the time evolution of geometrical parameters and geometrical parameters of crossing points for both studied molecules, as well as hopping times and energy gaps for different crossings.

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Figure 1. LIICs along the C6-stretching and C2-puckering coordinates.
Figure 2. (a) Time-dependent state population for dynamics simulations initialized from the S$_2$ state, in which the three sub-levels of each triplet state are summed together, (b) net number of hops between each pair of adiabatic states, (c) energy gap vs hopping time for the S$_2$ → S$_1$ internal conversion, and (d) geometrical parameters of the hopping points of 6TG.

Figure 3. (a) Time-dependent state population for dynamics simulations starting from the S$_2$ state, in which the three sub-levels of each triplet state are summed together, (b) the net number of hops between each pair of adiabatic states, (c) distribution of the crossing time from the S$_2$ state to other states, (d-f) geometrical parameters for different state-crossing points, (g) energy gap vs hopping time for the S$_2$ → S$_1$ internal conversion calculated in the different level of theory, and (h) energy gap vs spin-orbit coupling (SOC) for the S$_2$ → T$_2$ and S$_2$ → T$_3$ intersystem crossings calculated in different level of theory, for 6SG.
Figure 4. Time-dependent state population for dynamic simulations initialized from the $S_3$ state, net number of hops between each pair of adiabatic states, and energy gap vs hopping time for the $S_3 \rightarrow S_2 \rightarrow S_1$ internal conversions are respectively given in (a-c) for 6TG and in (d-f) for 6SG.