

## RESEARCH ARTICLE

# AIMD-Based Protocols for Modeling Exciplex Fluorescence Spectra and Inter-System Crossing in Photocatalytic Chromophores

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## ABSTRACT

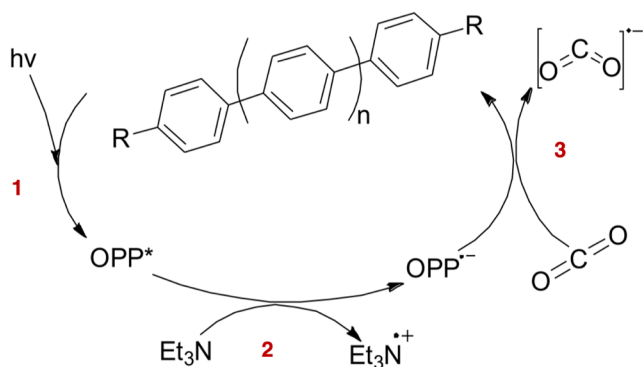
This study introduces a computational protocol for modeling the emission spectra of exciplexes using excited-state ab initio molecular dynamics (AIMD) simulations. The protocol is applied to a model exciplex formed by oligo-p-phenylenes (OPPs) and triethylamine (TEA), which is of interest in the context of photocatalytic reduction of CO<sub>2</sub>. AIMD facilitates efficient sampling of the conformational space of OPP3 and OPP4 exciplexes with TEA, offering a dynamic alternative to previously employed static methods. The AIMD-based protocol successfully reproduces experimental emission spectra for OPP-TEA exciplexes, agreeing with previous computational and experimental findings. The results show that AIMD simulations provide an efficient means of sampling the conformational space of these exciplexes, requiring less user input and, in some instances, fewer computational resources than multiple excited-state optimizations initiated from user-specified initial structures. The study also evaluates the yield of intersystem crossing (ISC) using AIMD and Landau-Zener probability. The results suggest that ISC is a minor decay channel for OPP3 and OPP4. This work provides new insights into the structural flexibility and emission characteristics of OPP-TEA photoredox catalyst systems, potentially contributing to improved design strategies for organic chromophores in CO<sub>2</sub> reduction applications.

## 1 | Introduction

Photoredox catalysis using organic chromophores is a promising sustainable alternative to energy-intensive thermally activated reaction pathways. Oligo-p-phenylenes (OPPs) have demonstrated successful reduction of CO<sub>2</sub> to synthesize formate, amino acids, and hydrocarboxylated styrene when paired with sacrificial electron donors like triethylamine (TEA) [1, 2]. Figure 1 shows a three-step catalytic cycle for the reduction of CO<sub>2</sub> proposed by Wada and coworkers [3]: (1) OPP is promoted to its excited singlet state, OPP\*, by absorbing light; (2) OPP\* is quenched by TEA, producing the radical anion of the arene, OPP<sup>•−</sup>; (3) the highly reactive OPP<sup>•−</sup>, which has sufficient reducing power, transfers an electron to CO<sub>2</sub>, regenerating OPP.

The last step in the cycle—electron transfer—has already been investigated in a computational study [4]. More recent computational work provided insights on the interactions between TEA and OPP\* during the 2nd step of the cycle as the formation of stable excited complexes (exciplexes) can impede the production of OPP<sup>•−</sup> [5, 6]. These studies employed quantum chemistry methods, particularly time-dependent density functional theory (TD-DFT), to optimize geometries and characterize exciplexes formed between electronically excited OPPs and TEA.

To model the emission spectra of the [OPP<sub>n</sub>-TEA]<sup>\*</sup> exciplex, one needs to sample over configurations of the exciplex. The main difference among the structures is in the relative position of TEA with respect to the aromatic rings of OPP<sub>n</sub>. Figure 2 shows



**FIGURE 1** | Catalytic cycle for the reduction of CO<sub>2</sub> proposed by Wada and coworkers in [3]. ‘R’ denotes potential substituents which may be used to tune up the electronic properties of OPPs.

several structures of the [OPP4-TEA]<sup>\*</sup> exciplex. In addition, each structure can undergo thermal motions, also contributing to inhomogeneous broadening of the emission. Patra, Krylov, and Sharada [6] developed a protocol for identifying unique exciplex structures with a series of excited-state optimizations starting from different guess structures. Specifically, a number of initial structures were generated and optimized with respect to the lowest singlet excited state, i.e., the state corresponding to the exciplex. The optimized structures were then screened based on structural parameters in order to identify unique configurations. A vibrational analysis was performed to identify local minima while natural transition orbitals (NTOs), exciton descriptors, and excited-state energy decomposition analysis (EDA) were used to identify the structures corresponding to exciplex configurations.

This static approach requires multiple excited-state optimizations and frequency calculations, and depends on the initial guess structures. Although it was shown to yield accurate spectra, such a protocol may not fully capture the dynamic nature of the exciplex and its effects on the inhomogeneous broadening of the emission. Here we introduce an alternative protocol using excited-state *ab initio* molecular dynamics (AIMD) to sample various conformations of OPP3 and OPP4 exciplexes with TEA. By dynamically exploring the conformational space, our approach successfully reproduces the experimental emission

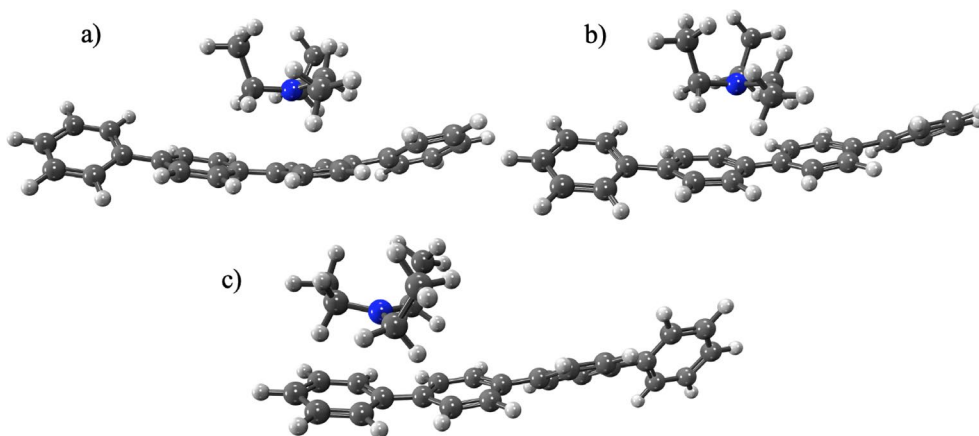
spectra for [OPP<sub>n</sub>-TEA]<sup>\*</sup> exciplexes. This dynamic sampling method is simpler to deploy. It also provides new insights into the structural flexibility and emission characteristics of these photoredox catalyst systems, potentially leading to improved design strategies for organic chromophores in CO<sub>2</sub> reduction applications. Here we compare the static protocol with the new approach of sampling the configurational space of the exciplex by means of excited-state AIMD simulations using the Q-Chem software package [7].

AIMD simulations of electronically excited states also allow one to address an important question of nonradiative decay channels, specifically intersystem crossing (ISC). ISC is undesirable for our purpose as it provides a nonreactive channel for OPP<sup>\*</sup> decay. As the catalyst needs to remain in the excited state in order to partake in the quenching step of the cycle (step 2), it is clear that ISC—as well as internal conversion—would negatively impact the efficiency of the reduction process of CO<sub>2</sub>. As we show below, we found many crossing points between the reactive excited singlet and low-lying triplet states along excited-state AIMD trajectories of OPP3. However, the crossing alone is not sufficient for ISC, which is facilitated by the spin-orbit coupling (SOC). To evaluate the yield of ISC, we combined AIMD trajectories with SOC calculations and Landau-Zener model to estimate the probability of transitions.

The structure of the paper is as follows. In the next section, we provide computational details for AIMD simulations and calculations of ISC efficiency according to the Landau-Zener model. This is followed by presentation of the results and discussion. We conclude with a summary of the main findings and an outlook for future work.

## 2 | Computational Protocol

In the first series of calculations, we used the 27 optimized exciplex structures obtained with the previous protocol as starting points for the dynamics [6]. All trajectories were calculated on the lowest excited singlet state of the [OPP<sub>n</sub>-TEA]<sup>\*</sup> exciplex at the ωB97X-D/6-311G<sup>\*</sup> level of theory and using a time step of 40 a.u. (≈ 1 fs). We note that using range-separated



**FIGURE 2** | Representative structures for the [OPP4-TEA]<sup>\*</sup> exciplex taken from the 27 structures identified in [6].

functionals, such as  $\omega$ B97X-D [8, 9] is important for correct description of systems with charge-transfer character [10]. We used the velocity Verlet integrator to compute 100 simulation steps (about 100 fs) for each structure within an NVE ensemble at 200 K.

In both our and Patra's protocols [6], calculations include cyclohexane as an implicit solvent using the polarizable continuum model (PCM) with dielectric and optical dielectric constants of 2.020 and 2.036, respectively. Using the PCM solvent model captures bulk solvation; however, within the NVE ensemble, the thermal relaxation of hot molecules is not captured. We observed that within the timescale of the simulations, the kinetic energy of the complex fluctuates around 100 K.

In the second set of calculations (for [OPP4-TEA]\*), we use only one trajectory (also about 100 fs long) initiated from one exciplex structure (*rotate\_-3\_opp4.xyz*). The relevant Cartesian geometries are available in the Supporting Information of [6]. In the third calculation (also, for [OPP4-TEA]\*), we propagated a longer trajectory (2 ps) starting from the ground-state optimized geometry of the [OPP4-TEA] complex. This trajectory was initiated from a 500 K velocity distribution and resulted in a 300 K average kinetic energy.

We use the excitation energies calculated at each point of the AIMD trajectory to compute the emission spectra of the exciplex using a convolution of Gaussian functions with a width of 0.4 eV (the same broadening factor as in [6]). The exciplex snapshots were identified by their energy and oscillator strength. To evaluate ISC, we rely on the Landau-Zener treatment, similar to other theoretical studies [11, 12]. We considered a  $\sim 2$  ps long excited-state trajectory of OPP3 initiated at the ground-state geometry and Maxwell-Boltzmann distribution of velocities corresponding to  $T = 200$  K. This simulation corresponds to the initial excited-state dynamics following vertical excitation of an isolated molecule. To estimate possible effects of TEA on SOCs, we also computed SOCs for a [OPP3-TEA] structure. In the course of AIMD simulations, OPP3 goes through multiple crossing points between the lowest excited singlet and low-lying triplet states. To estimate the probability of ISC, we evaluated the Landau-Zener probability ( $P^{LZ}$ ) at each crossing point.  $P^{LZ}$  is computed according to the following formula (in a.u.):

$$P^{LZ} = e^{-\left(\frac{SOC^2}{v \cdot |\Delta G|}\right)} \quad (1)$$

where  $SOC$  is the spin-orbit coupling between the crossing singlet and triplet states,  $v \cdot |\Delta G|$  is the dot product between the vectors of the atomic velocities at the crossing point and the difference in gradients of the two crossing PESs (the dimension of  $v$  and  $\Delta G$  vectors is  $3N$ , where  $N$  is the number of atoms).  $P^{LZ}$  represents the probability of a molecule to remain in the same diabatic (spin) state during a crossing event between PESs of different spin multiplicity. At each crossing point, we calculate the SOC with single-point calculations at the  $\omega$ B97X-D/cc-pVDZ level of theory using the recent density-based implementation [13, 14] with the two-body part evaluated by the mean-field approximation [15, 16]. We then compute  $P^{LZ}$  using gradients and

velocities from the AIMD trajectory. To evaluate the total yield of ISC, we compute the survival probability (probability to remain in the  $S_1$  state) as

$$P_{tot}(t) = \prod_i P_i^{LZ} \quad (2)$$

where time  $t$  corresponds to the length of the simulation, index  $i$  marks the crossing events, and  $P_i^{LZ}$  are the Landau-Zener probabilities at each crossing point  $i$ .

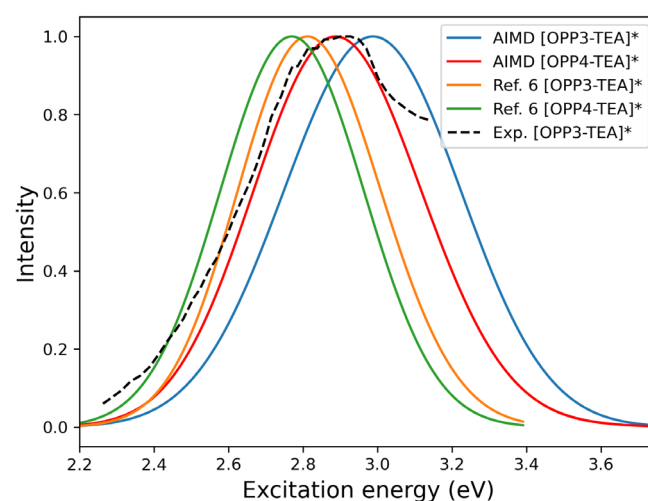
All calculations were carried out using the Q-Chem 6.2 software package [7, 17].

## 3 | Results and Discussion

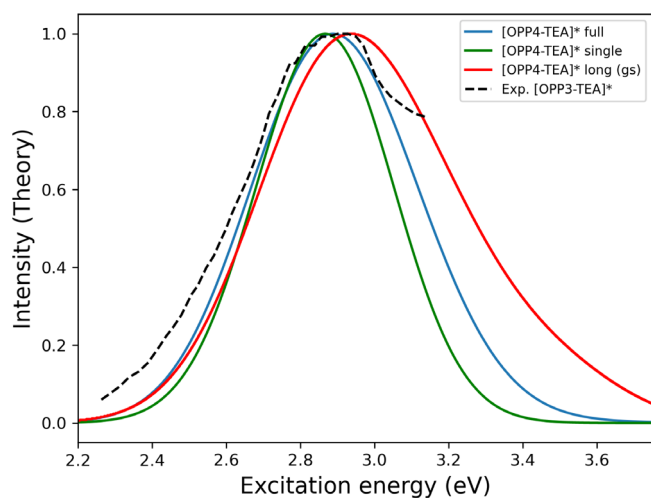
### 3.1 | Exciplex Spectra

Figure 3 shows the emission spectra of OPP3 and OPP4 exciplexes with TEA obtained with the static [6] and the AIMD-based protocol using 27 initial structures as well as the experimental emission spectrum of [OPP3-TEA]\*. Both computational protocols agree with the experiment in locating the emission peak of the exciplexes around 2.97 eV and capturing inhomogeneous broadening. Additionally, they both reproduce a red-shifted emission energy for OPP4 with respect to OPP3.

In order to test whether one AIMD trajectory can provide an adequate sampling, we also show the spectra computed starting from a single initial structure of [OPP4-TEA]. Figure 4 shows the results of these simulations. As one can see, the three AIMD-based spectra are very similar, suggesting that a single AIMD trajectory may be sufficient to reproduce the main spectral features of the [OPPn-TEA]\* exciplexes. The comparison of the trajectories initiated from the optimized ground-state structure and an excited-state structure shows



**FIGURE 3** | Emission spectra for OPP3 and OPP4 exciplexes with TEA. Plots are generated from AIMD (blue and red), static approach [6] (orange and green), and experiments (dashed black). The spectra are normalized to one at their maxima. Peaks maxima in eV: blue-2.99, red-2.89, orange-2.81, green-2.77, black-2.93.



**FIGURE 4** | Emission spectra of [OPP4-TEA]<sup>\*</sup> obtained from different AIMD simulations. Blue: 22 AIMD trajectories (each 100 fs long) initiated from optimized excited-state structures (peak max = 2.89 eV); Green: One 100 fs-long AIMD trajectory initiated from a representative excited-state structure (peak max = 2.86 eV); Red: One 2 ps long AIMD trajectory initiated from the ground-state structure (peak max = 2.93 eV). The experimental spectrum of [OPP3-TEA]<sup>\*</sup> is shown by a dashed black line (peak max = 2.93 eV).

that the exciplex emission spectrum can be described by an AIMD trajectory initiated from the ground-state geometry, without the need to obtain a representative exciplex structure. Figure 4 also shows that the effect of temperature on the computed spectrum is relatively minor—the higher-temperature simulation results in a broader spectrum (note the higher-energy shoulder), while the maximum of the peak is not affected. While these comparisons provide an estimate of the effects of the temperature on the spectrum, we note that a proper treatment of temperature in such simulations requires further investigation.

The main advantage of the AIMD protocol is its black-box nature. AIMD simulations naturally sample the conformational space of the exciplexes, without the need for different initial conditions from the user, and do not require tightly converged structures. Additionally, our results indicate that computational costs are also modest—and maybe even less compared to the static protocol [6], which involves series of excited-state optimizations. One 100 fs trajectory with a 1 fs timestep involves 100 energy and force calculations, which means 2,700 for a set of 27 initial structures or 2,000 for one 2 ps long trajectory. For comparison, an average optimization with tight convergence thresholds (such as 0.02 a.u. optimization step size and a maximum gradient tolerance of  $2 \times 10^{-5}$  a.u.) takes about 40 steps. In [6], 130 initial structures were screened, which amounted to 5,200 energy and gradient calculations, plus frequency calculations for the optimized structures.

### 3.2 | Inter-System Crossing in OPP3

The top panel of Figure 5 shows PESs along a 2 ps-long excited-state AIMD trajectory of excited OPP3 (in the  $S_1$  state),

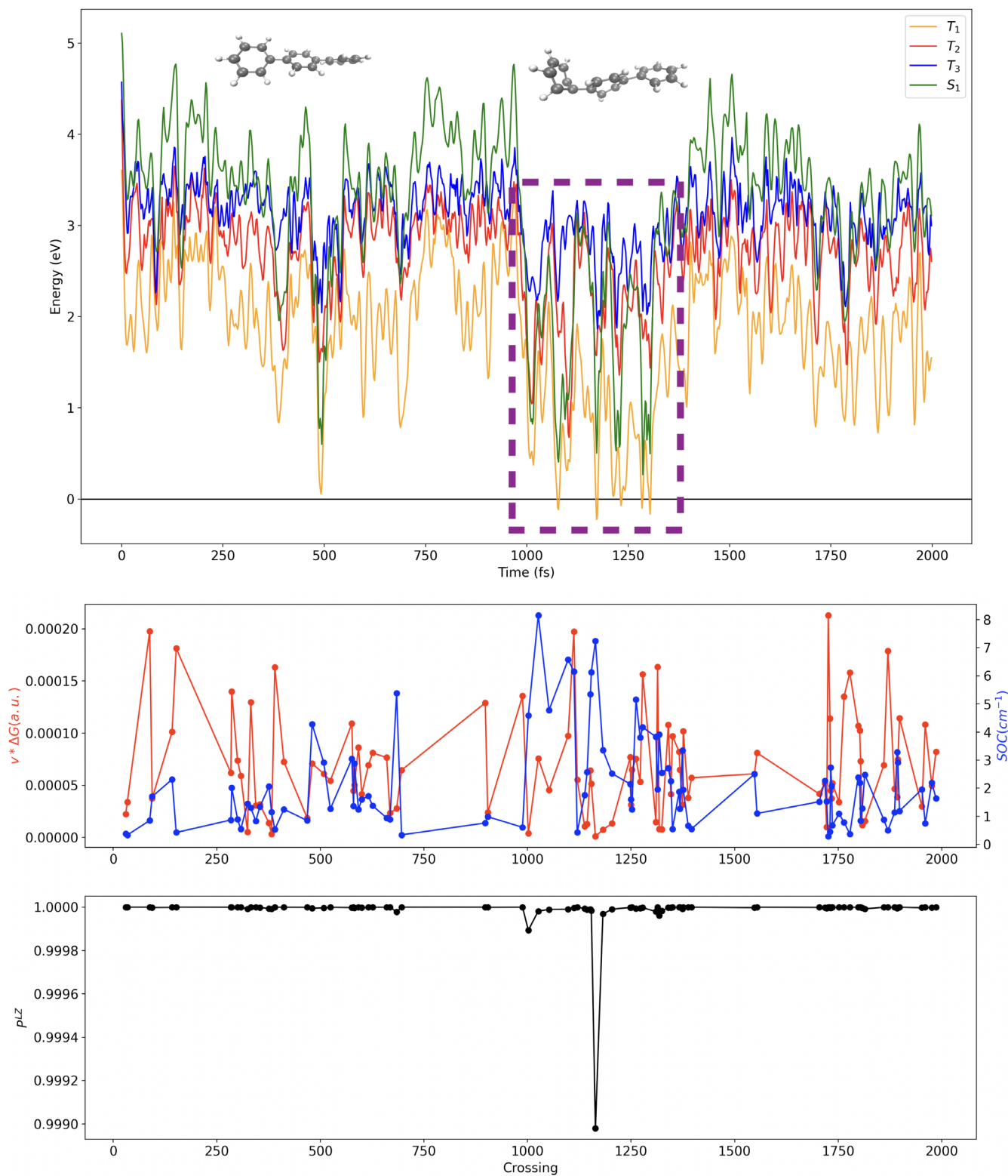
showing multiple crossings between the singlet and triplet PESs. To compute Landau–Zener probabilities, we first analyze the AIMD trajectory to locate crossing points at which the state ordering between states of different spin multiplicity changes for consecutive steps. We then compute SOCs and  $P^{LZ}$  at the snapshots before the state ordering changes. Note that  $S_1$  crosses with different triplet states at different points of the trajectory.

The bottom panel of Figure 5 shows the computed SOCs and the respective  $P^{LZ}$ . The SOC values are small—ranging between 1 and 8  $\text{cm}^{-1}$ . This is not surprising for an aromatic hydrocarbon in which the low-lying excited states are of  $\pi\pi^*$  type—hence, El-Sayed’s rules [18] predict small SOCs. We note that this might change upon substitution. To test the effect of the complexation with TEA, we also computed SOCs for one [OPP3-TEA] structure. The results showed the same-magnitude SOCs as in the bare OPP3, which is expected given the local nature of the SOC.

The small values of SOC result in small values of  $1 - P^{LZ}$  (i.e., small probability of changing the spin state). The largest value of  $1 - P^{LZ}$  (0.001) occurs about 1.2 ps, where a relatively large value of SOC coincides with a small value of  $v \cdot \Delta G$ . To estimate the total probability of ISC in the course of excited-state lifetime, we compute cumulative survival probability by multiplying individual probabilities, as per Equation (2), at each crossing point. This yields a 0.9985 probability for the chromophore to stay on the singlet PES in the first 2 ps of dynamics. Extrapolating this value to 1 ns yields  $P_{tot} = 0.93$ —hence, the ISC yield during the first nanosecond is about 7%, which is relatively minor but non-negligible. We note that such an estimate can only provide an upper bound of the survival probability, because for a more accurate estimate one needs to also compute the rates of other relaxation channels, such as electron transfer and internal conversion. As one can see from the top panel of Figure 5, the trajectory visits the area where  $S_1$  and  $S_0$  become nearly degenerate, facilitating internal conversion. We also note that functionalization of OPPs can result in larger SOCs—hence, computational design of better photocatalytic chromophores should involve estimates of ISC.

## 4 | Conclusions

We presented computational protocols based on AIMD simulations for the modeling of the emission spectra of exciplexes formed by OPPs and TEA. The results of the simulations agree well with previous computational and experimental findings. The AIMD simulations offer a straightforward way to sample the conformational space of [OPP-TEA]<sup>\*</sup> exciplexes. Further work will include elucidating the effect of initial structure, dealing with temperature in the excited-state simulations, and developing more general protocols. We also investigated the probability of ISC by computing Landau–Zener probabilities along the excited-state AIMD trajectory of OPP3. The results show that the cumulative probability of ISC is about 2% in the first 2 ps of the dynamics, meaning that this is a relatively minor relaxation channel. However, this might change upon substitutions, which may increase the SOCs. Since ISC is undesirable in the context of photocatalysis, the monitoring of



**FIGURE 5** | Top: Energies of the 4 lowest excited states (1 singlet and 3 triplets) of OPP3 along a 2 ps AIMD trajectory on the lowest singlet-state PES. The purple dashed box highlights a time interval in the simulation where all states decrease in energy due to the bending of a benzene ring in OPP3. Bottom: Evaluation of the Landau-Zener probability and its components for each crossing point (time step) extracted from the AIMD trajectory.

ISC should be a part of the computational design of new photocatalysts, and our computational protocol provides an inexpensive way to do such calculations. Future work will include calculations of the rates of other relaxation channels, such as

internal conversion and electron transfer, as well as calculations beyond the Landau-Zener model, by using, for example, a general surface-hopping method treating all electronic transitions on the same footing [19].

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## Conflicts of Interest

The authors declare the following competing financial interest(s): A.I.K. is the president and a part-owner of Q-Chem Inc.

## Data Availability Statement

The data that support the findings of this study are available within the article.

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