Supplementary Material

Supplementary Material: First-principles quantum simulations of exciton diffusion on a minimal oligothiophene chain at finite temperature†

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S1. Hartree approximation for torsional modes

Besides the use of the mean-field description for the harmonic oscillator baths, we also employ the Hartree approximation for the torsional modes, as mentioned in the main manuscript text. Here, we show that this approximation is valid, by explicitly comparing our previous zero-temperature reference calculations [Binder et al., *Phys. Rev. Lett.* 120, 227401 (2018)] – which were carried out at a multiconfigurational, correlated level for all modes, including a single active torsion ($\theta_{10,11}$) – with calculations at the present level of treatment (see main text) where the Hartree approximation is employed for both the active torsion and the harmonic-oscillator baths. As can be inferred from Figure S1, this approximation gives very accurate results.

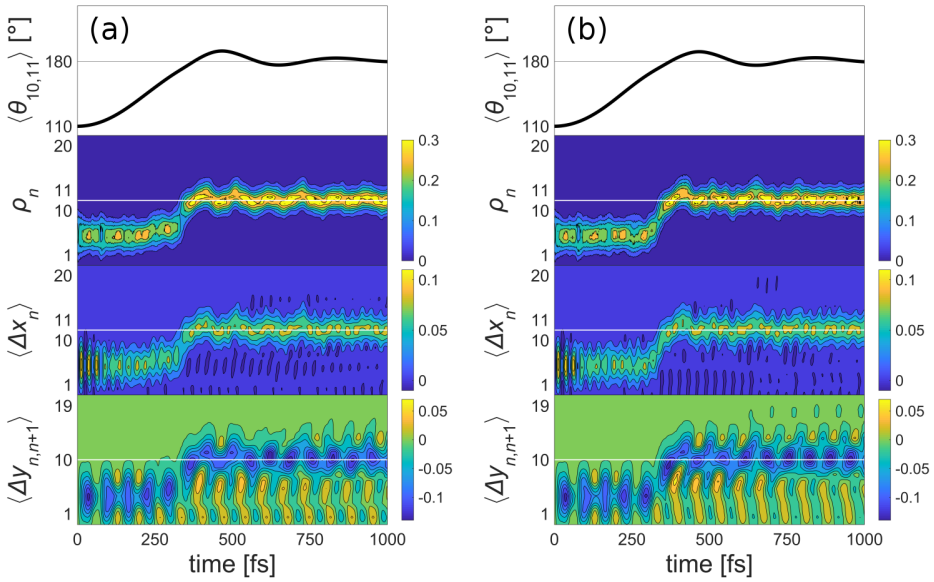

Fig. S1 Results of quantum dynamical simulations for exciton migration at $T = 0$K, for an oligothiophene OT-20 system with a propagation time up to 1 ps. From *top* to *bottom*: Time-dependent expectation value of the active torsion $\langle\theta_{10,11}\rangle$, excitonic site populations, expectation values of the ring-breathing modes (x_n) and bond stretch modes ($y_{n,n+1}$) relative to their ground-state equilibrium positions. (a) Propagation results obtained with a correlated, multiconfigurational treatment of the active torsional mode, within the ML-MCTDH set-up employed in [Binder et al., *Phys. Rev. Lett.* 120, 227401 (2018)]; (b) propagation results obtained with the ML-MCTDH set-up of the present work, where a Hartree approximation is used for the torsional modes and bath modes, while a multiconfigurational treatment is retained for the high-frequency modes.

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S2. Subset of bifurcating trajectories

Within the ensemble of 200 wavefunction realizations propagated at each temperature, we found that in about 10 instances, the exciton splits up, and possibly recombines at a later point in time. This is demonstrated in Figure S2, for a specific realization of this type. For these trajectories, a pronounced mixing of the adiabatic states is observed, as shown in Fig. S3. These realizations are more frequent in the case of a symmetric initial condition, and we cannot exclude that these represent numerical artifacts.

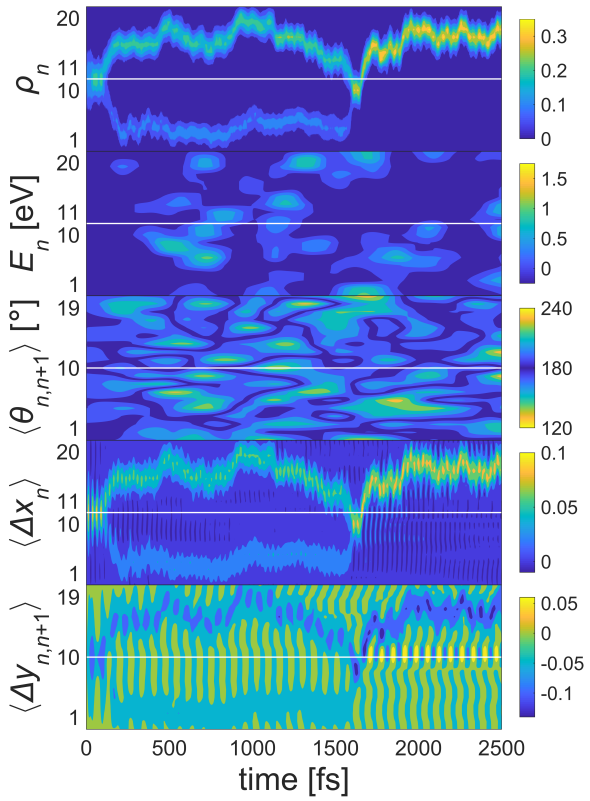

Fig. S2. Results of quantum dynamical simulations of exciton migration at $T = 300$ K, for a particular realization that exhibits a bifurcation effect, i.e., the excitonic density splits up, here at an early point in time.

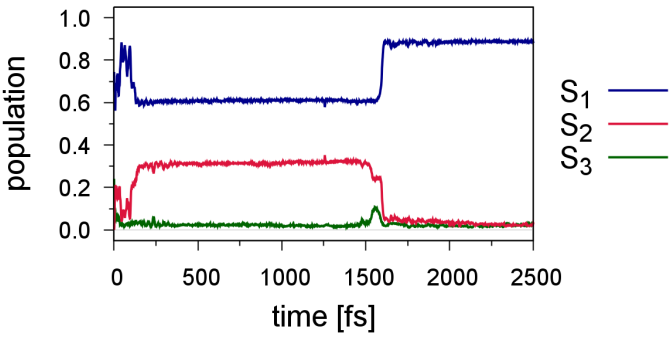

Fig. S3. Time-evolving adiabatic state populations for the simulation that is shown in Fig. S2. The wavepackets pertaining to the torsional and high-frequency modes remain compact, such that our approximate diabatic-to-adiabatic transformation scheme as a function of the time-evolving mode expectation values remains valid.

S3. Initial transients in the MSD calculations

As explained in the main text, the mean squared displacements (MSD) shown in Fig. 9 exhibit an initial deviation from linearity that we attribute to an induction period which is also observed in the individual realizations and in the average quantities of Fig. 8. This initial period of 200-500 fs is due to the fact that the initially "cold" torsional subsystem is gradually thermalized by the interaction with the reservoir. Here, we report on MSDs for the initial 500 fs interval (using an ensemble average, but no time average), to illustrate that this period is characterized by ballistic diffusion, along with reflections from the lattice boundary, see Figure S4 (panels (c) and (d)). For reference, we also reproduce the MSD results given in the main text (panels (a) and (b)).

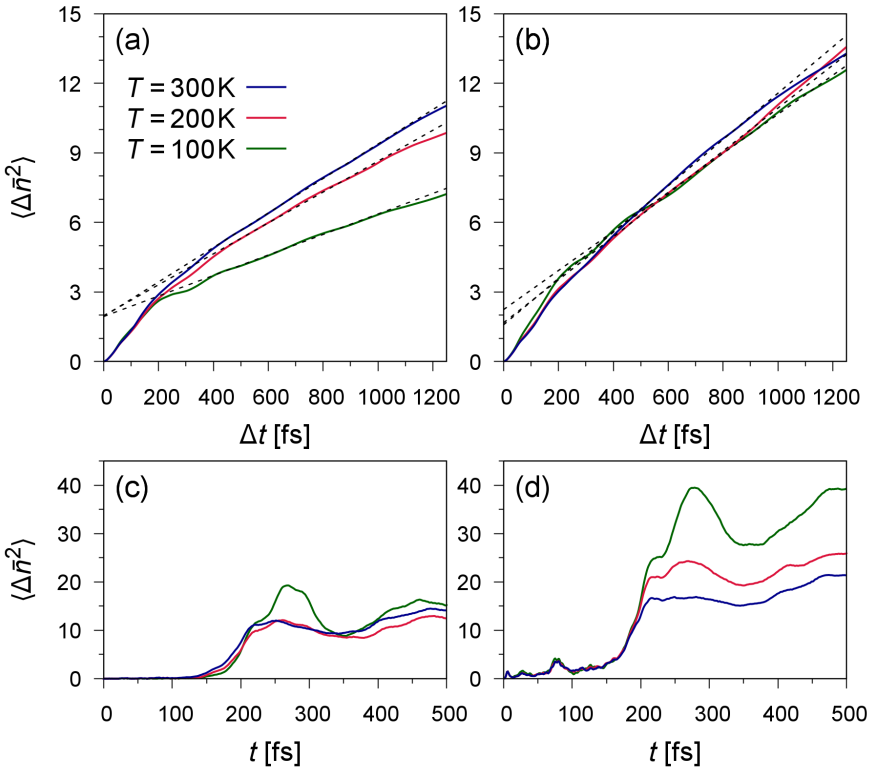

Fig. S4. As in Fig. 9 of the main text, time-dependent MSD values are shown for a symmetric initial condition (l.h.s.) and an asymmetric initial condition (r.h.s.). For convenience, the results of Fig. 9 of the main text are reproduced in panels (a) and (b). Panels (c) and (d) show the MSD for the initial time interval of 500 fs (calculated as an ensemble average, in the absence of time averaging), illustrating that the exciton mobility is negligible during the first ∼150 fs, followed by a rapidly increasing MSD that is due to an onset of exciton motion triggered by the thermalization of the torsions. On a slightly longer time scale (∼300 fs), the MSD drops due to reflections from the lattice boundary. Overall, the initial transient period leads to an overestimation of the time-averaged MSD during the $\Delta t \sim 400$ fs interval, as shown in panels (a) and (b). In the case of the asymmetric initial condition, a drift term persists during the full observation interval of 1.25 ps.