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Conclusions and Outlook

6.1. CONCLUSIONS

To understand how to engineer molecular complexes able to achieve fast photoinduced unidirectional charge separation, static density functional theory calculations are performed on a series of molecular rectifiers employing the same PTZ donor, NDI1 antenna, and NDI2 acceptor subunits. The Marcus theory of electron transfer is used to predict the quality of the rectifiers, based on the calculated charge transfer rate constants.

All the molecular triads analyzed show absorption in the visible light spectrum leading to the formation of an excitonic state localized on the antenna. The Marcus parabolic terms $\Delta G$ and $\lambda$ between the exciton reactant state and product excited states with charge separated character are found to be dependent on the donor-antenna distance. At the same time, it is predicted that the electronic coupling between the donor and the acceptor is strongly influenced by the nature of the bridge units and by the strategy adopted to bind the bridges and the rectifier subunits. Molecular triads for fast charge separation can be then engineered by modifying the length and the nature of the bridge. Based on these findings, the complex PTZ-Ph-NDI1-C≡C-NDI2 is proposed as a promising molecular rectifier for photoinduced direct ultrafast charge separation.

Quantum coherence effects due to the coupling of the electron-nuclear motion are observed to play a fundamental role during the process of heterogeneous electron transfer from a molecular chromophore, designed for unidirectional electron transfer, to a semiconductor surface. Nonadiabatic electron quantum dynamics simulations are performed within a quantum-classical framework, allowing the description of the electron transfer process on the ps time scale. It is observed that the electron transfer is not instantaneous, but rather proceeds gradually through strongly nonadiabatically coupled electronic states forming a coherent superposition. The energies of these states periodically cross each other due to resonant coupling with
specific nuclear vibrations. The photo-induced exciton reactant state localized on the chromophore is able to evolve into a product state localized on the semiconductor by selecting and coupling to specific nuclear vibrational modes that facilitate the electron transfer. Particularly, a rotational mode localized at the interface between the chromophore and the anchoring bridge is shown to open a preferential channel for the heterogeneous electron injection. When the channel is open, the evolution of the electronic wavepacket can proceed by coupling to the fast stretching modes that modulate the energy levels and the nonadiabatic coupling between the reactant and product states involved in the electron transfer.

Quantum-classical tight-binding nonadiabatic dynamics and density functional theory based \textit{ab initio} MD simulations are used to investigate the first catalytic step in a fully solvated photoanode designed for solar water splitting. The photoexcitation leads to fast sub-picosecond electron injection from the sensitizing chromophore to the semiconductor electrode. The oxidized chromophore is then reduced to its neutral form by the water oxidation catalyst to which it is covalently bound. This process, leading to the first catalytic water splitting intermediate, occurs adiabatically via a proton-coupled electron transfer mechanism and has been estimated to take place on a sub-nanosecond time scale.

The presence of explicit solvent molecules surrounding the solute is found to be crucial for the catalysis. The water reorganization induces a stabilization of the catalytic intermediate, and provides the hydrogen bonding network necessary to accept and solvate a proton from the catalytically oxidized water molecule.

\textbf{6.2. Outlook}

Photoinduced electron transfer has a pivotal role in converting sunlight into power or solar fuel. Understanding the mechanisms that govern this process is thus essential to properly engineer devices for solar energy conversion.

Up until now, the Marcus theory of electron transfer\footnote{1} has been one of the most important theoretical tools for studying electron transfer processes and predict their rate constants. The quality of the materials for solar energy conversion is evaluated on the basis of the electron transfer rates obtained from Marcus theory. The design strategies for this type of materials are focused on optimizing the parameters entering the Marcus equation to increase the rate of electron transfer. The theory proposed by Marcus is fundamentally an equilibrium theory that considers reactant and product states at their equilibrium configurations. Thus, it can provide an accurate value for the electron transfer rate constant, but no information on the
microscopic mechanisms controlling the process. The major consequence of this methodological limitation is that material design and optimization are led by chemical intuition and trial and error approaches. This procedure could also be automatized by including a library of potentially useful building blocks and use genetic algorithms in combination with DFT to derive chromophores with specific optimized properties.

Recently, compelling evidences of quantum coherence effects driving electron transfer in artificial and natural systems have been reported. The analysis of such processes requires to move from a static Marcus representation of reactant and product equilibrium states to the realm of nonadiabatic dynamics. By following the evolution of the electronic wavefunction in real time, it is possible to identify the vibrational modes driving the electron transfer process and use this information to improve the original design of a certain system. In this scenario, it would be interesting to perform such an investigation of the molecular charge separator proposed in chapter 3 to verify its predicted performances and further improve its design by accounting for the effects of coherent exciton-vibrational coupling.

The results reported in chapter 4 are obtained using a trajectory which is evaluated on the ground state potential energy surface. Using this result as a reference, it would be interesting to repeat the analysis by applying the Ehrenfest nonadiabatic dynamics method. This comparison should provide information on the entity of the effect that the excited electronic wavefunction has on the nuclear motion, and thus on the necessity, or not, of using a trajectory evaluated on an excited state potential energy surface.

Finally, the results reported in chapter 5 for the photoanode for catalytic water splitting represent a very interesting starting point for the analysis of the entire catalytic cycle. The investigation of this complex should also be expanded to include structural modifications of the catalyst, the antenna and the anchoring unit aiming for rapid kinetics and optimal driving force for the catalytic and electron injection processes.

A risk associated with the current design of photoanode 1 is related to the possibility of exciton quenching by the electrons trapped at the TiO₂ surface along the catalytic cycle. This may be prevented by incorporating a molecular rectifier as separator between the antenna and the semiconductor. An obvious continuation of this work would be to integrate into the photoanode design the AM molecular rectifier, or one of its derivatives engineered to avoid charge recombination. The insertion of a molecular rectifier should elongate the lifetime of the charge separated state on a time scale sufficient to allow the different catalytic steps to take place.

Nonadiabatic simulations of the proton coupled electron transfer process will be
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crucial to suggest structural modifications able to control the electron injection through the molecular rectifier and enhance the photodriven catalytic mechanism. Due to the required time scale of the simulation, the tight-binding semi-empirical method based on the Extended Hückel Hamiltonian used in chapter 4 and 5 would be extremely useful for such calculations.

6.3. REFERENCES


