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Managing Complex Photophysical Pathways for Solar Energy Conversion

Light-induced processes in molecular-based systems, such as energy and electron transfer, represent the elementary photophysical phenomena that drive life on earth. Use of the stored form of this energy, that is, fossil fuels, our energy “inheritance”, has contributed to a substantially improved quality of living in contemporary societies. The current trends in energy production and consumption and associated anthropogenic generation of greenhouse gases threaten to complicate matters for future generations, however. Utilizing the energy incident on the earth from the sun is one strategy to circumvent the issues associated with burning fossil fuels as solar energy is abundant, clean, and renewable. For example, nearly 3×10^{24} J of solar energy reaches the earth’s surface each year.¹ We need only to harvest a small fraction of this incident solar energy to satisfy the annual global demand for energy. In nature, photosynthetic organisms like plants have developed sophisticated, regulated solar cells that are assembled with molecular-scale complexity.^{2,3} The photochemical energy transduction of photosynthesis starts with photoinitiated electron-transfer reactions and proton transfers in photosystems embedded in the thylakoid membrane. These fast energy- and charge-transfer processes set up a stored transmembrane electrochemical potential that later drives chemical transformations called the “dark” reactions. Ultimately, stored energy in the form of energy-rich molecules like sugars as well as biochemical fuels that power the organism are produced, all from sun, water, and carbon dioxide.

Solution-processable organic materials are attractive owing to their potential to greatly drive down the cost typically associated with solar energy conversion. Understanding the nature of the electronic excited states present in excitonic solar cells and their interconversion is critical considering the complexity of events comprising the essential physics of these materials, that is, light absorption (exciton formation), charge separation, carrier diffusion, and subsequent carrier extraction. There are many misunderstandings prevalent in the literature that arise from the highly interdisciplinary nature of this research community. For example, it is not often appreciated that the promotion of a single electron from the highest occupied molecular orbital to lowest occupied molecular orbital is not suitable to describe the electronic transitions in these materials. One reason why this is a concern is that most electronic transitions are necessarily linear combinations of occupied to unoccupied orbital one-electron transitions.⁴ More crucially, a configuration obtained by a one-electron promotion does not produce a singlet spin eigenstate. It is one of the configurations that are combined to form a correct spin eigenstate and, hence, the singlet or the $M_s = 0$ triplet electronic state.^{5–7} Molecular spectroscopy makes no sense unless we think in terms of states and not orbital configurations! Another conceptual misunderstanding highlighted by Zhu in his Perspective (Zhu, X.-Y. How to Draw Energy Level Diagrams in Excitonic Solar Cells. *J. Phys. Chem. Lett.* **2014**, *5*, 2283–2288) is that the energy level diagrams often invoked to

describe the interconversion of excitons and charge carriers in excitonic solar cells need to be reconsidered. Zhu provides us with a refreshing discussion of the advantages and limitations of models presently employed to depict the interconversion of excitons and charge carriers and proposes a new energy level diagram for this purpose based exclusively on single-particle energies of ground and optically excited states. The interconversions of excitons and carriers are treated on equal footing in this way, unifying both the initial photophysics of light absorption and exciton formation with the transport levels of carriers that are critical to the overall device physics. Zhu proceeds to discuss his group’s work using time-resolved two-photon photoemission spectroscopy to develop a more detailed understanding of the electronic structure of organic semiconductors along with the dynamics of electronic excited states in these materials and concludes with a perspective on the key components of the electronic energy landscape of organic semiconductors necessary for efficient solar energy conversion.

Singlet fission in molecular systems, a subset of the more general multiexciton generation phenomenon, has emerged as an exciting contemporary topic of physical chemistry research. The complex and multistep nature of singlet fission is highlighted in the Perspective by Piland, Bardeen, and co-workers (Piland, G. B.; Burdett, J. J.; Dillon, R. J.; Bardeen, C. J. Singlet Fission: From Coherences to Kinetics. *J. Phys. Chem. Lett.* **2014**, *5*, 2312–2319). These authors provide us with an enlightening perspective, including an overview of singlet fission in organic semiconductors, and highlight their recent work investigating the mechanism of singlet fission. First, the electronic structure of organic semiconductors is reviewed and compared with that of their inorganic counterparts, and the authors point out the key advantages that organic materials have in effectively exploiting multiexciton generation. This is followed by a discussion of their work investigating the nature of an elusive intermediate in singlet fission, the triplet pair superposition state, as well as their studies on the dynamical evolution of singlet and triplet populations, including the effect that an external magnetic field has on their interconversion. This group has done a remarkable job gaining critical insights into the mechanism of singlet fission by connecting experimental observables to theoretical models. Leveraging upon years of pioneering work on the subject, Bardeen and co-workers leave us with a stimulating and thought-provoking perspective on open opportunities and potential new directions for the field.

In artificial light-harvesting systems, it is possible to begin to isolate and understand elemental photophysical processes such as energy and electron transfer. Their design can be guided by natural systems occurring in photosynthesis that have had billions of years to evolve sophisticated molecular assemblies optimized for solar energy conversion. The Perspective by

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Zhang, Li, and co-workers (Zhang, X.; Zeng, Y.; Yu, T.; Chen, J.; Yang, G.; Li, Y. *Advances in Photofunctional Dendrimers for Energy Conversion*. *J. Phys. Chem. Lett.* **2014**, *5*, 2340–2350) provides us with an overview of light-harvesting dendrimers, studies on the elementary photophysical processes occurring in these systems, and their applications ranging from dye-sensitized solar cells to photochemical production of hydrogen. These authors demonstrate the power of chemistry to isolate fundamental photophysical processes such as energy and electron transfer for systematic investigation through a perspective highlighting historic work as well as work by their own group. Not only can dendritic systems serve as a scaffold upon which fundamental photophysical processes such as electronic energy transfer and electron transfer can be tailored and controlled, they also provide the opportunity to exploit perhaps a more important role played by nature—to protect and regulate these processes. This nature-driven inspiration is particularly eloquently demonstrated through examples of dendrimer-encapsulated photocatalysts for hydrogen production. Dendritic, artificial light-harvesting systems, highlighted in the Perspective by Li and co-workers, appear to represent ideal systems where the tools of chemistry can be applied to isolate and more clearly understand elementary photophysical processes as well as draw inspiration from the complex photosynthetic machinery in nature that have evolved to efficiently exploit these elementary photophysical processes for solar energy conversion.

In sum, understanding the elementary photophysical processes of solar energy conversion and managing complex photophysical pathways comprised of such elementary photophysical processes continues to remain a challenging and exciting area of research motivated by the quest for clean and renewable energy.

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Notes

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