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Review

Computational studies of charge transfer in organic solar photovoltaic cells: A review

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ABSTRACT

Photoinduced charge transfer (CT) is a fundamental process that determines the overall energy conversion efficiency of organic solar photovoltaic cells (OPVs). This review focuses on the advantages and pitfalls of theoretical/computational methods available to describe CT excitations in donor–acceptor (D–A) complexes. Studies of porphyrin–fullerene constructs as model D–A systems will be used to illustrate progress in this area.

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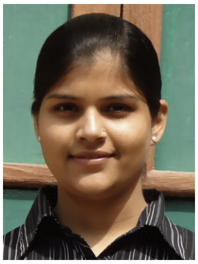

Neha Agnihotri received her Ph.D. degree in physics from Banaras Hindu University (India) in 2011 on the quantum theoretical study of electronic structures, properties and reactions of biologically important molecules. She started working on theoretical modelling of novel materials relevant to organic solar photovoltaic cells with Prof. Ronald P. Steer at the Department of Chemistry, University of Saskatchewan (Canada) in 2012. She is currently involved in designing novel donor–acceptor systems for light harvesting in organic photovoltaic devices.

1. Introduction

Ever-growing global demands for energy combined with the depletion of inexpensive petroleum resources and the risks of global warming illustrate the urgent need for a transition towards alternate sources of renewable energy. Solar photovoltaic cells are an excellent potential "green" alternative for the generation of electrical energy [1] and, consequently, thousands of articles have been published on their development and properties. To date, a maximum solar to electrical energy conversion efficiency of ca. 42% for silicon-based photovoltaics with multi-junction concentrators has been achieved [2]. However, these efficient devices are currently too expensive to replace inexpensive petroleum fuels as a widespread source for generating electrical energy. Organic solar photovoltaic cells (OPVs) are potentially attractive due to their low

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cost of manufacture (e.g., by roll-to-roll printing processes), their physical flexibility, and their relatively good performance in diffuse sunlight. However, their energy conversion efficiencies are relatively low and the current generation is not sufficiently robust to be deployed in large-scale solar energy farms requiring 30+ year life cycles. Research to improve the efficiency and longevity of OPVs is therefore intense.

The active layers in OPVs typically consist of two components, an absorbing electron donor (D) and an electron acceptor (A), assembled either into a bi-layer structure or in the form of a blend [3,4]. Initially these D–A systems were used to test the theories of energy [5–14] and electron transfer [15–27]. Later, the main focus of research shifted to the use of D–A systems in artificial light-harvesting, in OPV devices, and in the electrochemical storage of solar energy. Practical devices used for these purposes are complex, and involve many inter-related processes. Consequently, much research and development over the past decades in these areas has relied on empirical experimental approaches with the hope of obtaining improved efficiency by multi-dimensional parameter optimization. Theoretical and computational methods can help reduce the degree of empiricism in this research. In particular, photo-initiated charge transfer (CT) processes are fundamental to all of these applications, but are still not fully understood [28–30]. Theoretical and computational simulation methods can play a particularly important role in understanding CT processes in light-harvesting systems at the molecular level [31] and in the rational design of new ones.

The primary processes involved in OPVs mimic those of photosynthesis: (i) the absorption of light by donor molecules, (ii) the transfer of excitation energy to a light-harvesting reaction centre, and (iii) the separation of charges at the reaction centre prior to the initiation of further electron-transfer steps. In photosynthesis, these last steps precede the synthesis of energy-rich chemical compounds, but in OPVs they are eliminated so as to capture the transiently stored energy immediately following charge separation. Photo-initiated charge separation can be modelled theoretically using quantum mechanical methodologies applied to molecular (and supramolecular) systems.

Recently, considerable progress has been made to devise quantum chemical methods that accurately describe the excited electronic states of polyatomic organic molecules [32–35], and these methods are now being used to predict the excited-state properties of components of light-harvesting systems. Nevertheless, this is still a difficult task. Most light harvesting complexes typically consist of more than 100 atoms and systems of this size pose a great challenge for present-day quantum chemical methods for excited states.

Calculations and theoretical simulations are particularly valuable when used in conjunction with experiments that measure important CT parameters and rates. Thus, exciton binding energies can be determined from optical absorption studies [3]. Electrochemistry experiments can be used to measure the oxidation and reduction potentials of OPV components and their values related to their computationally determined HOMO–LUMO gaps [36]. Femtosecond transient absorption and time-resolved emission measurements can be employed to study the dynamics of charge transfer and charge recombination [36], and can be related to the transport of charge under the influence of an external electric field [37]. Such theoretical/computational and experimental studies also rest on the well-tested and fully developed theories of electron transfer [38], energy transfer [39–46] and their thermodynamic and kinetic implications [47].

The development of a low cost and efficient computational protocol that could be used to identify promising D–A combinations that increase the rates of charge separation and charge transfer, and that slow the rates of charge recombination (CR), could save substantial experimental time and resources [48]. In this review, an overview is provided of recent theoretical and computational studies relevant to understanding excited state and CT processes in OPVs. The discussion focuses on a unique density functional theory (DFT) protocol that allows for an accurate and balanced treatment of electronic and spectroscopic properties in different phases. This is followed by a review of the application of these methods to several porphyrin–fullerene constructs that serve as D–A model systems for OPVs. The final section summarizes the current status of quantum chemical methods for excitation and charge transfer in porphyrin–fullerene supramolecular complexes and by extension OPVs in general.

2. Background theory

It is not necessary to review here the properties of excitons and the theories of energy transfer, electron transfer, and charge separation by electron–hole transport that serve as background for understanding OPV processes. Nevertheless readers are provided with several useful references to OPV-related aspects of each of these important subjects for completeness and convenience.

In efficient OPVs, photogenerated excitons must have intrinsic lifetimes that are long in comparison with time required for them to diffuse to the D–A interface and undergo CT. The properties of excitons in relevant polymer-based materials are reviewed in references [49–61].

In light harvesting systems, the initial photon absorber and the excited donor in the D–A pair may be different entities, with electronic excitation energy transferred from the excited absorber to the donor by a number of possible mechanisms. Theories describing these processes are based on the Förster long-range dipole–dipole mechanism [39–41], the Dexter short-range electron exchange mechanism [42] and their extensions to large scale systems [43–46].

The key CT step in OPVs involves transfer of an electron or hole between the donor and acceptor. For efficient OPVs this process must be fast relative to the exciton lifetime and must be uni-directional so that charge recombination (CR) at the D–A interface is minimized. The fundamental basis for understanding CT and CR processes is found in the thermodynamic treatment of Rehm-Weller [62], and Marcus-Hush theory of electron transfer [38,63–65] and its quantum chemical extensions [66–70].

3. Computational methodologies

Computer simulations and computational chemistry can play important roles in the development of OPV science and technology, since these techniques permit deeper insight into the structural and electronic properties of the systems under study. The information gained from such calculations can serve as a low-cost guide for the development and improvement of photovoltaic materials.

3.1. Quantum mechanical theories for CT excitations

During the past decade time-dependent density functional theory (TDDFT) has become the workhorse of quantum chemistry for computations of excited state properties and charge transfer excitations in large systems [71,72]. This popularity may be ascribed to the attractive scaling of computational requirements with system size, and the large range of methodologies available for computations of linear and non-linear responses. Nevertheless, TDDFT calculations on photovoltaic systems pose a number of challenges, particularly with respect to long-range CT interactions. Approximations embedded in routine TDDFT programs can sometimes introduce severe systematic errors in the calculated results, and