Photoinduced Interfacial Electron Transfer and Lateral Charge Transport in Molecular Donor–Acceptor Photovoltaic Systems

Angela Punzi, Jan C. Brauer, Arianna Marchioro, Elham Ghadiri, Jelissa de Jonghe, and Jacques-E. Moser*

Abstract: Nanostructured liquid|solid and solid|solid bulk heterojunctions designed for the conversion of solar energy offer ideal models for the investigation of light-induced ET dynamics at surfaces. Despite significant study of processes leading to charge generation in third-generation solar cells, a conclusive picture of the photophysics of these photovoltaic converters is still missing. More specifically searched is the link between the molecular structure of the interface and the kinetics of surface photoredox reactions. Fundamental scientific issues in this field are addressed by the research project undertaken in the frame of the NCCR MUST endeavor, an outline of which is given here.

Keywords: Dye-sensitized solar cells · Organic photovoltaics · Photoinduced electron transfer · Terahertz spectroscopy · Ultrafast laser spectroscopy

Introduction

Current research activities of the Photochemical Dynamics Group of EPFL follow essentially three different directions. These fields of investigation have in common the use of high-resolution time-resolved spectroscopic techniques to study the dynamics of photoinduced electron transfer fast processes and the photochemical reactivity of supra-molecular and interfacial systems.

The first research direction deals with charge recombination and redox mediation in dye-sensitized nanocrystalline, hybrid inorganic–organic, and organic solar cells. These investigations are central to the understanding of the various electron transfer processes, the competition between which controls the energy conversion yield of functioning devices.[1,2] Experimentally, a very broad time window needs to be moni-

tored, covering ultrafast phenomena such as electron injection and exciton ionization up to the comparably slow dynamics of charge recombination.[3] This research is obviously related to the overall effort towards the development of cheap, efficient, and stable third-generation photovoltaic converters. These investigations also provide important spin-offs of basic scientific interest.

The second line of research is related to the dynamics of charge injection from a molecular vibronically excited state into the conduction band of a semiconductor. Such systems are characterized by a special energetic situation with a charge transfer reaction from discrete donor levels to a continuum of acceptor states. If a strong electronic coupling is ensured, electron transfer in these systems is amongst the fastest known chemical processes with transfer times of less than 10 fs. This situation is beyond the scope of current electron transfer dynamics theories and is still poorly understood. Research efforts in this field use femtosecond transient spectroscopy and aim towards a fundamental understanding of electron transfer processes and vibrational coherence associated with the superfast reaction.

A third field of investigation regards organic electronics. THz time-domain spectroscopy (THz-TDS) has emerged as a powerful probe of charge carriers and their transport processes in condensed matter. This method provides direct access to important parameters such as the charge density and scattering times.[4] Similarly, THz-TDS can probe long-range crystalline lattice vibrations in solids, low energy

torsion and hydrogen bonding vibrations. Solid-state lattice vibrations associated with the self trapping of photo-generated or injected carriers (small polarons) is detected and analyzed in real time, allowing in particular for a detailed study of vibrational coherence associated with electron transfer processes at solid|liquid and solid|solid heterojunctions. Recently, studies of the interplay between inter-ionic librations and complex conductivity in redox active ionic liquids allowed evidencing an efficient bond exchange mechanism for positive charge transport in redox-active ionic liquids containing the iodine/iodide couple.[5]

Non-equilibrium Vibration-mediated Electron Transfer

Because of both applied and fundamental interests, electron transfer dynamics between molecular adsorbate and semiconductor nanoparticles have attracted much attention. Following our pioneering work, ultrafast electron injection from dye-sensitizer molecules to nanocrystalline oxide semiconductor colloids and thin films has been intensely studied.[1,2] The experimental rate of an ET process is normally given as a single number for a complex system, at some specific temperature and environment. Theoretical models predict, however, significant rate changes for some molecules when excited vibrational modes are populated.[6] Evidence was obtained for photoinduced electron transfer in competition with vibrational relaxation of excited states[7] and of ET promoted by mo-

Correspondence: Prof. Dr. J.-E. Moser
Photochemical Dynamics Group
Institute of Chemical Sciences & Engineering
Ecole Polytechnique Fédérale de Lausanne
EPFL SB ISIC GR-MO, Station 6
CH-1015 Lausanne
E-mail: je.moser@epfl.ch

lecular vibrations.[8] Wavepacket dynamics was studied and revealed the frequencies of the vibrational modes participating in an ultrafast heterogeneous electron transfer.[9,10] Unusually low distance dependence of femtosecond injection dynamics in donor–bridge–acceptor interface systems recently suggested non-equilibrium vibrations in the bridge induce a decrease of the tunneling energy gap.[11] The ET and the vibrational energy flow thus appeared to occur in a synchronized cooperative way. No detailed study was however reported on vibrational quantum state effects in this context.

The idea that multiple electron transfer rates, rather than a single kinetics, can be observed in the condensed phase has not been previously recognized as possible because it is usually thought that complex molecules redistribute vibrational energy much faster than they transfer electrons. The processes of intramolecular vibrational redistribution and vibrational relaxation are indeed generally quite fast. However, in certain molecules, some vibrational modes can have lifetimes in tens of picoseconds due to their high frequencies and wide separation from other mode frequencies. Photoinduced electron transfer in the sub-ps regime should thus be able to take place directly from higher electronic and vibronic levels long before internal conversion and thermalization of the electronic excited state (Fig. 1). To take place in such conditions, the reaction would however require the excess vibrational energy of the dye sensitizer's excited state to be converted to electronic energy in the products and thus the excited vibrational modes are coupled to the charge transfer process.

Charge injection dynamics from organic dyes, such as alizarin, coumarin derivatives,[12] squaraines,[13] and diphenyl-diketo-pyrrolopyrrole (DPP)[14] are scrutinized. These molecules are characterized by broad absorption spectra in the visible and possess a limited amount of vibrational modes of high energy. Series of donor–π conjugated unit–acceptor (D–π–A) organic dye equipped with a cyanoacrylate acceptor and anchoring group, an alkoxy-substituted triphenylamine donor moiety and a fused thienothiophene as the π-conjugated unit[15] are used as models for investigating vibrational energy flow along the bridge. Hot electronic excited states of these sensitizers are prepared with various excess vibrational energies by tuning the excitation photon energy in the vis-NIR spectral domain.

Phonon-driven Ultrafast Exciton Dissociation at Donor–Acceptor Organic Heterojunctions

Organic small molecules semiconductors and π-conjugated semiconducting polymers are promising low-cost and flexible materials for electronic devices such as organic light-emitting diodes (OLEDs) and organic photovoltaic solar cells (OPV). Excitonic states, *i.e.* electron-hole quasi particle states that diffuse in the solid, play a central role for the optoelectronic properties. Exciton formation can result from polaron recombination (*e.g.* in OLEDs), or else from the primary photoexcitation step (*e.g.* in photovoltaic systems). A key feature of organic semiconductors is the strong coupling between the elementary electronic processes and the material's phonon modes. We focus on the role of electron–phonon coupling in the charge-transfer processes at bulk heterojunctions,[16] as these provide conditions for an extremely efficient charge separation at the interface between different phase-segregated organic solids. The primary excitation is a photogenerated exciton stabilized by the electron-hole Coulombic interaction. Because of the highly folded interfacial area in bulk heterojunctions, the exciton has a high probability of reaching the interface within the diffusion length (typically ~20 nm). The exciton decay towards a charge-separated state is largely determined by molecular-level electronic interactions at the interface (Fig. 2).

Cyanines are polymethine cationic dyes that benefit from high extinction coefficients and a tunable absorption spectrum by varying the number of double bonds. Different from most small molecules, cyanines are easily processed from solution, which makes them attractive for technological applications. Low-bandgap cyanine dyes have been studied for photovoltaic applications up to 800 nm. Their photophysical properties have been extensively investigated in solution or when anchored to silver halide or TiO_2 surfaces, however, solid organic films and blends have received little attention. We then specifically consider heterojunctions composed of cyanine dyes–fullerene C_{60} bilayers and cyanine dyes in solid-state blends with poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene] (MEH-PPV) conjugated polymer.[17] Preliminary transient absorption measurements applied to double layer photovoltaic devices using cyanines as electron acceptors and MEH-PPV as donor indicated unit hole-charge separation quantum yields.[18] This exceptionally high charge separation efficiency implies primary exciton dissociation takes place in the fs time scale and definitely calls for a more detailed investigation. While the elementary processes at the solid–solid interface are crucial for
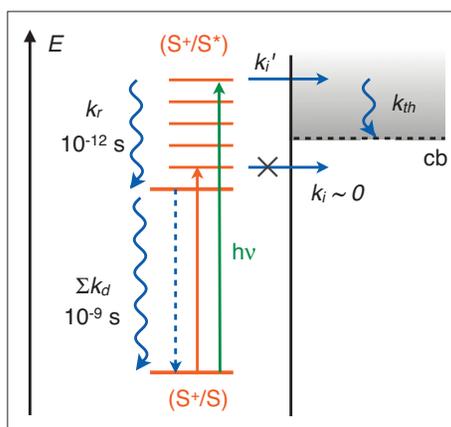

Fig. 1. Energy scheme for photoinduced electron injection from the electronic excited state (S*) of a redox dye sensitizer (S) into the conduction band (cb) of a wide-bandgap semiconductor. ET from a higher vibronic state (rate constant k_i') competes kinetically with vibrational relaxation of the excited state (k_r).
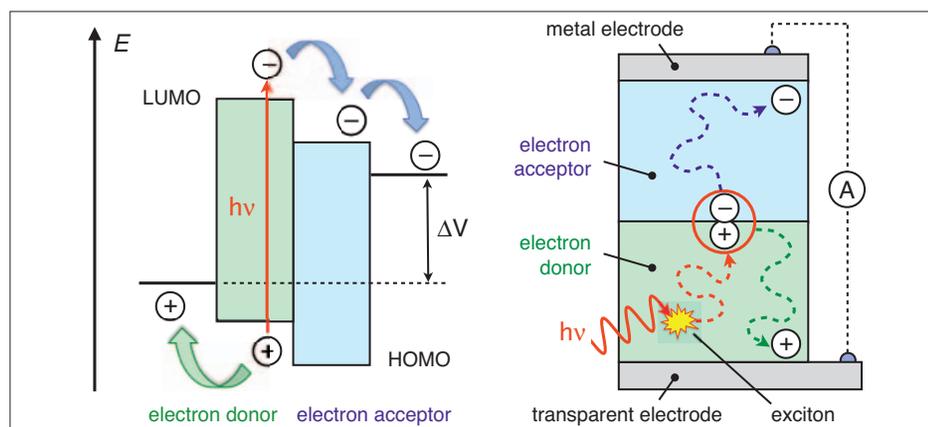

Fig. 2. Principle of a donor-acceptor bilayer organic solar cell. Here, the electron-donor material gathers the functions of light absorber, and exciton- and hole-transporter. Note that the conventional picture, in which the exciton has to diffuse to the interface prior to carrier separation, is not always compatible with the observed ultrafast photoinduced charge generation.[18]

the device function and optimization, these processes are not well characterized as yet on the microscopic scale.

Polaronic Transport in Liquid and Solid Hole-conducting Media as Probed by Terahertz Time-domain Spectroscopy

Some redox-active ionic liquids, organic amorphous solids containing electron-donating moieties, and conductive polymers can efficiently transport positive electrical charges. These hole-conducting media find increasing applications in unconventional solar cells and organic light emitting diodes. Appropriate methods are required to unravel the detailed conduction and trapping mechanisms in these materials and fully understand the interplay of molecular vibrations and charge transport processes. Terahertz time-domain spectroscopy (THz-TDS) is a powerful technique, allowing for the direct determination of the complex conductivity of hole transporting materials in a contactless, purely optical manner.[4] By combining THz-TDS with synchronous optical excitation, one has optical-pump THz-probe spectroscopy (OPTP) available with the ability to temporally resolve phenomena at the fundamental timescales of nuclear and electronic motion.

Application of the THz-TDS technique has been illustrated by examples provided by the study of the molecular liquid hole-conductor 10-methylphenoxazine[4] and that of the ionic liquid 3-methyl-1-propylimidazolium iodide (PMII).[5] Both systems are of particular interest, as both are successfully used as alternatives to solvent-based electrolytes in dye-sensitized solar cells.

THz-TDS and OPTP spectroscopies are used to study photogenerated charge carriers transport and dynamics in organic charge transport materials and nanocomposite systems. Electron injection and trapping dynamics in dye-sensitized nanocrystalline anatase films have been recently scrutinized by use of OPTP.[19] Amorphous solid organic hole-conducting materials, such as spiro-MeOTAD,[20] as well as cyanine, DPP and squaraine dye layers are also studied. The effect of the crystallinity of the materials upon the mobility and trapping of charge carriers, as well as the influence of nanostructuring is in the focus of this research. Low frequency vibrations that are associated with the self trapping of charges in small polarons are observed in the frequency range 0.2–4.5 THz. Application of OPTP spectroscopy is thus expected to provide invaluable information on the detailed mechanism of interfacial light-induced electron transfer and charge transport processes in dye-sensitized photoactive hybrid and organic photovoltaic devices.

[1] M. Grätzel, J.-E. Moser, in 'Electron Transfer in Chemistry', Vol. 5, Ed. V. Balzani, Wiley-VCH, Weinheim, **2001**, pp 589–644, and references therein.

[2] J.-E. Moser, in 'Dye-sensitized Solar Cells', Ed. K. Kalyanasundaram, EPFL Press, Lausanne, **2010**.

[3] V. K. Thorsmølle, B. Wenger, J. Teuscher, C. Bauer, J.-E. Moser, *Chimia* **2007**, *61*, 631.

[4] J. C. Brauer, V. K. Thorsmølle, J.-E. Moser, *Chimia* **2009**, *63*, 189, and references therein.

[5] V. K. Thorsmølle, G. Rothenberger, D. Topgaard, J. C. Brauer, D.-B. Kuang, S. M. Zakeeruddin, B. Lindman, M. Grätzel, J.-E. Moser, *ChemPhysChem* **2011**, *12*, 145.

[6] a) M. D. Newton, *Chem. Rev.* **1995**, *91*, 767; b) K. G. Spears, *J. Phys. Chem.* **1995**, *99*, 2469.

[7] a) R. S. Becker, A. P. Pellicioli, A. Romani, G. Favaro, *J. Am. Chem. Soc.* **1999**, *121*, 2104; b) E. M. Lindsay, C. H. Langford, A. D. Kirk, *Inorg. Chem.* **1999**, *38*, 4771.

[8] Y. Huang, C. T. Rettner, D. J. Auerbach, A. M. Wodtke, *Science* **2000**, *290*, 111.

[9] a) C. Zimmermann, F. Willig, S. Ramakrishna, B. Burfeindt, B. Pettinger, R. Eichberger, W. Storck, *J. Phys. Chem. B* **2001**, *105*, 9245; b) S. Ramakrishna, F. Willig, V. May, *J. Chem. Phys.* **2001**, *115*, 2743.

[10] R. Huber, J.-E. Moser, M. Grätzel, J. Wachtveitl, *Proc. SPIE* **2003**, *5223*, 121.

[11] a) B. Wenger, C. Bauer, M. K. Nazeeruddin, P. Comte, S. M. Zakeerudin, M. Grätzel, J.-E. Moser, *Proc. SPIE* **2006**, *6325*, 63250V; b) C. Bauer, J. Teuscher, S. Pelet, B. Wenger, P. Bonhôte, M. K. Nazeeruddin, S. M. Zakeeruddin, P. Comte, M. Grätzel, J.-E. Moser, *Curr. Sci.* **2010**, *99*, 343.

[12] Z. S. Wang, K. Hara, *J. Phys. Chem. B* **2005**, *109*, 3907.

[13] a) J.-H. Yum, P. Walter, S. Huber, R. Rentsch, T. Geiger, F. Nüesch, F. De Angelis, M. Grätzel, M. K. Nazeeruddin, *J. Am. Chem. Soc.* **2007**, *129*, 10320; b) D. Rocca, R. Gebauer, F. De Angelis, M. K. Nazeeruddin, S. Baroni, *Chem. Phys. Lett.* **2009**, *475*, 49.

[14] a) M. Eschle, 'Photochemical and Photophysical Properties of Diketopyrrolopyrrole Organic Pigments', PhD Thesis EPF Lausanne No 1616, **1997**; b) P. Sonar, G.-M. Ng, T. T. Lin, A. Dodabalapur, Z.-K. Chen, *J. Mater. Chem.* **2010**, *20*, 3626.

[15] a) D. Shi, Y. Cao, N. Pootrakulchote, Z. Yi, M. Xu, S. M. Zakeeruddin, M. Grätzel, P. Wang, *J. Phys. Chem. C* **2008**, *112*, 17478; b) G. Zhang, Y. Bai, R. Li, D. Shi, S. Wenger, S. M. Zakeeruddin, M. Grätzel, P. Wang, *Energy Environ. Sci.* **2009**, *2*, 92;) J. Teuscher, 'Dynamics of Electron Transfer Processes at the Surface of Dye-Sensitized Mesoporous Semiconductor Films', PhD Thesis EPF Lausanne No 4731, **2010**.

[16] a) G. Yu, J. Gao, J. C. Hummelen, F. Wudl, A. J. Heeger, *Science* **1995**, *270*, 1789; b) J. J. M. Halls, C. A. Walsh, N. C. Greenham, E. A. Marseglia, R. H. Friend, S. C. Moratti, A. B. Holmes, *Nature* **1995**, *376*, 498; c) H. Tamura, J. G. S. Ramon, E. R. Bittner, I. Burghardt, *Phys. Rev. Lett.* **2008**, *100*, 107402.

[17] a) B. Fan, R. Hany, J.-E. Moser, F. Nüesch, *Org. Electronics* **2008**, *9*, 85; b) B. Fan, R. Hany, J.-E. Moser, F. Nüesch, *Org. Electronics* **2009**, *10*, 1645; c) B. Fan, 'High Performance Cyanine Solar Cells', PhD Thesis EPF Lausanne No 4804, **2010**.

[18] F. A. Castro, H. Benmansour, J.-E. Moser, C. F. O. Graeff, F. Nüesch, R. Hany, *Phys. Chem. Chem. Phys.* **2009**, *11*, 8886.

[19] J. C. Brauer, J. Teuscher, A. Punzi, J.-E. Moser, in 'Ultrafast Phenomena XII', Oxford University Press, New York, **2011**; pp. 358-360.

[20] a) U. Bach, D. Lupo, P. Comte, J.-E. Moser, F. Weisörtel, J. Salbeck, H. Spreitzer, M. Grätzel, *Nature* **1998**, *395*, 583; b) S.-J. Moon, 'Solid-State Sensitized Heterojunction Solar Cells: Effect of Sensitizing Systems on Performance and Stability', PhD Thesis EPF Lausanne No 4977, **2011**; c) J.-E. Moser, *Nature Mater.* **2005**, *4*, 723.