

# Focus on Molecular Electronics - IOPscience

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The notion 'molecular electronics' has been used more frequently since the 1970s and summarizes a series of physical phenomena and ideas for their application in connection with organic molecules, oligomers, polymers, organic aggregates and solids. The properties studied in this field were connected to optical and electrical phenomena, such as optical absorption, fluorescence, nonlinear optics, energy transport, charge transfer, electrical conductance, and electron and nuclear spin-resonance. The final goal was and is to build devices which can compete or surpass some aspects of inorganic semiconductor devices. For example, on the basis of organic molecules there exist rectifiers, transistors, molecular wires, organic light emitting diodes, elements for photovoltaics, and displays. With respect to applications, one aspect of the organic materials is their broad variability and the lower effort and costs for their processability.

The step from microstructures to the investigation of nanostructures is a big challenge also in this field and has led to what nowadays is called molecular electronics in its narrow sense. In this field the subjects of the studies are often single molecules, e.g. single molecule optical spectroscopy, electrical conductance, i.e. charge transport through a single molecule, the influence of vibrational degrees of freedom, etc. A challenge here is to provide the techniques for addressing in a reproducible way the molecular scale. In another approach small molecular ensembles are studied in order to avoid artefacts from particular contact situations. The recent development of the field is presented in [1–8].

In this Focus Issue we present new results in the field of 'molecular electronics', both in its broad and specialized sense.

One of the basic questions is the distribution of the energy levels responsible for optical absorption on the one hand and for the transport of charge on the other. A still unanswered question is whether the Wannier exciton model applies in which the excitation is distributed over several molecules or whether a good description is given by the Frenkel exciton model with the electron and the whole being localized at the same molecular unit.

In organic semiconductors the charge transport usually occurs on the basis of holes because of the presence of many defects giving rise to a localization of the electrons. It is therefore a challenge to produce materials with both positive and negative mobile charge carriers. In the 1990s V M Agranovich introduced the idea of hybrid excitons, i.e. of nanostructured materials consisting of both organic and inorganic semiconductors. At the interface between the organic and inorganic parts new excitons can appear, being a superposition of both Frenkel and Wannier excitons and having both the high oscillator strength of the Frenkel and the large optical nonlinearity of the Wannier exciton. The problem is to find optimum combinations of the organic and inorganic parts to enable the hybrid structure concept to work.

Micro-cavities also play an important role in the investigation of organic materials resulting in a new state (polariton) as the superposition of a photon and an exciton because of the large exciton–photon interaction. A similar excitation arises because of the interaction between plasmons and photons. A special geometrical shape of a nano-cavity increases the interaction between the electromagnetic radiation and a dipole sitting in the cavity.

The interaction between vibronic degrees of freedom and electronic excitations plays an important role for various phenomena such as nonlinear processes, the question of

coherence, information on the shape of a potential hypersurface, etc. With the help of femtosecond laser pulses, detailed information on such vibrations can be obtained. Also of great importance is the investigation of the energy transfer in artificial light-harvesting systems, e.g. in dendrimers. Finally the combination of experimental and theoretical investigations allows for a comparison of the spectra of two molecules with the same backbone (tetracene and rubrene).

The transport of charge through a molecule occurs possibly in a stationary, but at any rate in a non-equilibrium situation. The study of dissipation in such situations requires special approaches, both in theory and in experiments. One key issue is the understanding of the role of the microscopic phenomena such as the excitation of vibrational modes and their macroscopic outcome, i.e. the dissipation. This topic is addressed in several contributions both theoretically and experimentally.

From the theoretical side, for the investigation of the heat production during the electron transfer, non-equilibrium Green's functions have been utilized. In another contribution a combination of the non-equilibrium Green's function technique together with the density functional method has been developed for the calculation of the elastic and inelastic electronic transport. To calculate the transport of indistinguishable particles a path integral Monte Carlo approach has been put forward. In single-molecule transistors the gate-voltage dependence on the Kondo temperature and an accompanying strong Coulomb blockade can be explained by taking into account a strong electron–vibron interaction including anharmonicities of the molecular potential surface.

The transport of charges is heavily influenced by disorder. The case of static disorder is investigated for linear chains, carbon nanotubes and graphene ribbons. Finally it is shown that the charge transport through a single energy level coupled to a localized vibrational mode and two leads shows hysteretic effects which could possibly be used in a memory device. For applications the control of the current through a molecular junction is considered theoretically. Two possible mechanisms are discussed: the control via coherent destruction using predefined ultrafast laser pulses and the formation of laser pulses using optimal control theory.

A group of contributions is dedicated to the study of electronic transport through molecules using various techniques ranging from scanning-tunnelling methods via controllable break-junctions to printing techniques and molecular networks. The molecules under study can be classified into two main groups. On the one hand the functionalization of aromatic or alkane molecules with thiols is used for establishing chemical binding to metal electrodes; in the other set of experiments fullerenes are used as model systems for studying the influence of orientation and heat dissipation. Molecular conducting networks are important under various aspects. Such networks are formed by an array of gold nanoparticles connected by conjugated molecular chains with one or two thiol ends and conduction investigations are performed under various conditions. A careful investigation of the experimental conditions is necessary when comparing conductance measurements using the break junction method. For example there are results demonstrating that several molecular junctions are formed in parallel between the electrodes. Other experiments use different materials for the junctions and measurements are performed at various temperatures. The transport of charge through an alkane-monolayer is investigated using micro-transfer printing to establish contacts without shorts. It is shown that both tunnelling between the electrodes and transport through the states of the molecules contribute to the conductance.  $C_{60}$  plays a role in various fields of molecular electronics. One aspect is the conductance through the molecule as a function of the orientation of the molecule on the surface. It is found that there is a strong orientation dependence of the transport on Au(111) surfaces and that it is almost independent on a Cu(100) surface.

A further important phenomenon is the heating and cooling of  $C_{60}$  during charge transport depending on the surface of  $C_{60}$  adsorption. The differences are ascribed to the amount of charge transfer into  $C_{60}$  upon adsorption on different surfaces.

In summary, in the field of molecular electronics new materials and structures are developed and investigated, both with respect to a basic understanding of the materials and their compositions and with respect to possible applications in electronics. While in the field of molecular electronics on the microscale the techniques are well established, they still need to be refined in the field of nano-molecular electronics. Nevertheless, both subfields share some of the most challenging questions: e.g. the problems of charge and energy transport, of excitations and the formation of new quasi-particles. Another question is the role of vibrational degrees of freedom, where on the one hand one has to cope with the unavoidable effect of heat dissipation. On the other hand, vibrational excitations are intimately connected to the individual molecule under study and thus offer the possibility to be used in functional devices based on intrinsic molecular properties. This Focus Issue represents a snapshot of the state of the art of this emerging field in the first half of 2008. We expect that the fast development which the research has undergone in recent years will even speed up in the near future.

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