



## Molecular wires

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The drive to miniaturize the transistor, the primary building block of an integrated circuit, has come a long way since

its invention in the mid 1940s. The transistor is currently being manufactured with a characteristic dimension of around 20 nanometers, a factor of over a million smaller than the original one. This dramatic scaling over the past few decades is dictated by Moore's law, which was communicated in 1965. It has triggered an extreme need for the integration of a progressively larger number of transistors per square centimeter. This challenge has been accomplishable using top-down approaches by applying photolithography techniques that have become

more and more refined at, however, the expense of fabrication ease, bulkiness of the machinery and production costs. Notably, the wavelength of the incident light, which is nowadays already in the extreme ultraviolet range, limits these top-down fabrication techniques intrinsically. Bottom-up approaches involving molecular scale building blocks and self-assembly will be required to scale the size of functional electronic circuit elements further. The ultimate miniaturization of devices will involve structures at the atomic scale, which will be based on

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single-molecule elements. In this context, a deep and fundamental understanding of the properties of the molecular building block, in particular, when interfaced to electrodes is required.

A molecular wire is a structure which can serve as a conduit for electrons, and can function as an elementary building block for nanoscale devices. To determine structure–function relations for such wires requires probing electron transfer through these molecular components. Three different types of experiments are typically employed for this purpose. A molecule can be interfaced to two metal electrodes using a mechanically controllable break junction to measure conductance properties at the single-molecule level. Self-assembled monolayers can be created with a large number of molecules sandwiched between two electrodes to provide a wealth of information. Alternatively, photoinduced electron-transfer reactions can be studied with metal electrodes being replaced by appropriate molecular electron donor and acceptor components. The electron transfer rate between the electron donors and acceptors is mediated by a bridge unit, and determined by pump–probe experiments.

This themed issue brings together the contributions from some among the world leaders in the field, by combining the viewpoint of experiments and theory. In particular, the design and characterization of single-molecule and organic molecular wires are described and analyzed. This is rounded off with their applications as transistors, molecular machines, or light-harvesting devices.

Edmund Leary, Andrea La Rosa, M. Teresa González, Gabino Rubio-Bollinger, Nicolás Agrait and Nazario Martín (DOI: 10.1039/C4CS00264D) present a review on the impact of the chemical anchoring groups that are used to connect molecular wires to metal electrodes on the electronic properties of the molecular junctions.

Jianhui Liao, Sander Blok, Sense Jan van der Molen, Sandra Diefenbach, Alexander W. Holleitner, Christian Schönenberger, Anton Vladyka and Michel Calame (DOI: 10.1039/C4CS00225C) report recent developments in the research of two-dimensional close-packed arrays of metallic nanoparticles inter-linked by molecular compounds, which show diverse and controllable electronic and optoelectronic properties applicable to photo- and redox-switching devices, and chemical and mechanical sensors.

C. Schubert, J. T. Margraf, T. Clark and D. M. Guldi (DOI: 10.1039/C4CS00262H) highlight recent progress in the field of photochemically and thermally induced electron transport through molecular bridges as integrative parts of electron donor–bridge–acceptor conjugates. The major emphasis is hereby on the design and the modular composition of the bridges.

Mickael L. Perrin, Enrique Burzurí and Herre S. J. van der Zant (DOI: 10.1039/C4CS00231H) review the state-of-the-art in the field of single-molecule transistors which are created by gating a molecular junction with a third electrode. They discuss the experimental challenges and describe the advances

made in creating transistors using different methods.

Shinya Kano, Tsukasa Tada and Yutaka Majima (DOI: 10.1039/C4CS00204K) describe recent progress made in the study of nanoparticles characterized by scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS). In particular, the results of electrical and photonic properties on NPs studied by STM and STS are highlighted with emphasis on single-electron transport on individual nanoparticles including Coulomb blockades and resonant tunneling through discrete energy levels.

Takayuki Tanaka and Atsuhiko Osuka (DOI: 10.1039/C3CS60443H) describe conjugated porphyrin arrays that possess delocalised electronic networks. For the most part, they have been interconnected indirectly using alkene or alkyne type bridging units or directly by individual porphyrin chromophores with multiple bonds to form fused porphyrin arrays. They review the multitude of synthetic methodologies that have been developed for the construction of conjugated porphyrin arrays as well as their structure–property relationships.

Afzal Shah, Bimalendu Adhikari, Sanela Martić, Azeema Munir, Suniya Shahzad, Khurshid Ahmad and Heinz-Bernhard Kraatz (DOI: 10.1039/C4CS00297K) present a comprehensive review on the mechanism and kinetics of electron transfer in peptides, which is affected by various factors such as the chain length, the extent of the secondary structure, backbone conformation, dipole orientation, the presence of special amino acids, hydrogen bonding, and the dynamic properties of a peptide.

Cancan Huang, Alexander V. Rudnev, Wenjing Hong and Thomas Wandlowski (DOI: 10.1039/C4CS00242C) present a tutorial review in which they discuss methods to electrochemically gate a single-molecule junction which allows one to manipulate the energy alignment in a junction and also enable molecular redox processes which can be used to tune the electronic properties of the junction.

C. J. Lambert (DOI: 10.1039/C4CS00203B) presents a tutorial review where he outlines the basic theoretical concepts and tools which underpin the fundamentals of phase-coherent electron transport



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through single molecules, including quantum interference effects.

The tutorial review of Jesse J. Bergkamp, Silvio Decurtins and Shi-Xia Liu (DOI: 10.1039/C4CS00255E) focuses on fused thiafulvalene donor–acceptor systems, which exhibit unique electronic, electrochemical

and photophysical properties. The review also overviews their applications in areas such as solar cells and OFETs.

In their tutorial review Méline Gilbert and Bo Albinsson (DOI: 10.1039/C4CS00221K) focus on photo-induced charge/energy transfer in covalently linked

donor–bridge–acceptor systems. It is of utmost importance in such systems to understand how to control signal transmission, namely how fast electrons or excitation energy can be transferred between the donor and acceptor and the role played by the molecular wire as a bridge.