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Large-Area Molecular Junctions

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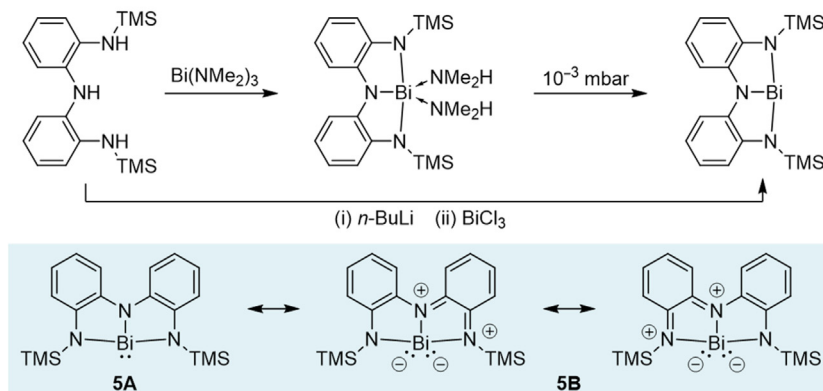
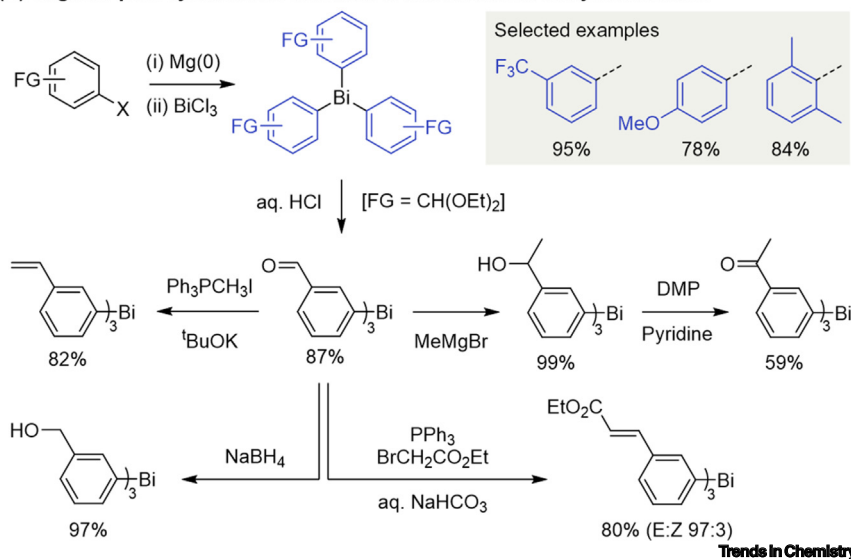
(A) Chitnis: redox-confused bismuth(I/III) triamide**(B) Gagnon: post-synthetic modification of functionalised triarylbiomethines**

Figure 2. Increased Diversity and Understanding of Organobismuth Architectures Will Underpin Future Synthetic Applications. (A) A redox-confused bismuth(I/III) triamide illustrates the key role of ligand design in redox behaviour [9]; (B) improved access to functionalised arylbismuth reagents will increase the widespread adoption of organobismuth chemistry [10].

rich and varied toolbox for synthesis. These new methodologies illustrate the dual ability of bismuth to mimic and to complement reactivity commonly associated with transition-metal-based systems. Detailed mechanistic studies performed by Hyvl [7], Cornella [5,8], and Ball [6] provide important fundamental insight into bismuth redox chemistry and will be likely to underpin the next generation of rationally designed systems. Recent advances in the synthesis of bismuth

reagents allow more convenient access to, use, and modulation of the metal's properties. It is anticipated that, by building on these foundations, organobismuth redox chemistry will continue to be the source of exciting new reactivity manifolds and synthesis tools for future applications.

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Spotlight

Large-Area Molecular Junctions: Synthesizing Integrated Circuits for Next-Generation Nonvolatile Memory

Xinkai Qiu^{1,2,*} and Ryan C. Chiechi^{1,2,*}



The development of high-speed, nonvolatile memory devices with low power consumption remains a significant challenge for next-generation computing. A recent study reported molecular switches operating at low voltages in large-area junctions by coupling supramolecular structural changes and counterion migration to bias-dependent redox, culminating in

proof-of-concept memory comprising self-assembled monolayers.

Modern general-purpose computers are predominantly based on the von Neumann architecture, in which information is moved between fast, volatile (i.e., information is lost if the power supply is interrupted) random-access memory (caches) and a processing unit and is later moved to slow, nonvolatile memory for storage; it is optimized for fast calculations on small sets of data. Unlike volatile memory, nonvolatile memory does not require a constant power supply to retain the data; the limitations of modern electronic materials are such that volatile memory is limited in capacity and nonvolatile memory is limited in speed. Modern computing paradigms, however, demand specialized calculations on very large sets of data, creating a demand for new materials. Molecular-electronic junctions effect charge transport predominantly in the tunneling regime (meaning charge transport occurs by the quantum mechanical tunneling of electrons between electrodes rather than the formation of charges on the molecules in a junction) either through a single molecule or a molecular ensemble spanning two electrodes. They have been extensively studied over the past several decades as a potential successor to standard, inorganic semiconductor materials because they intrinsically operate in the fast, quantum regime; changes at the Ångström scale translate into exponential changes in the electrical output of a molecular junction. These changes can arise from chemical phenomena such as photoisomerization, ion/molecule binding, reduction/oxidation in electric field; any phenomenon that alters their chemical properties.

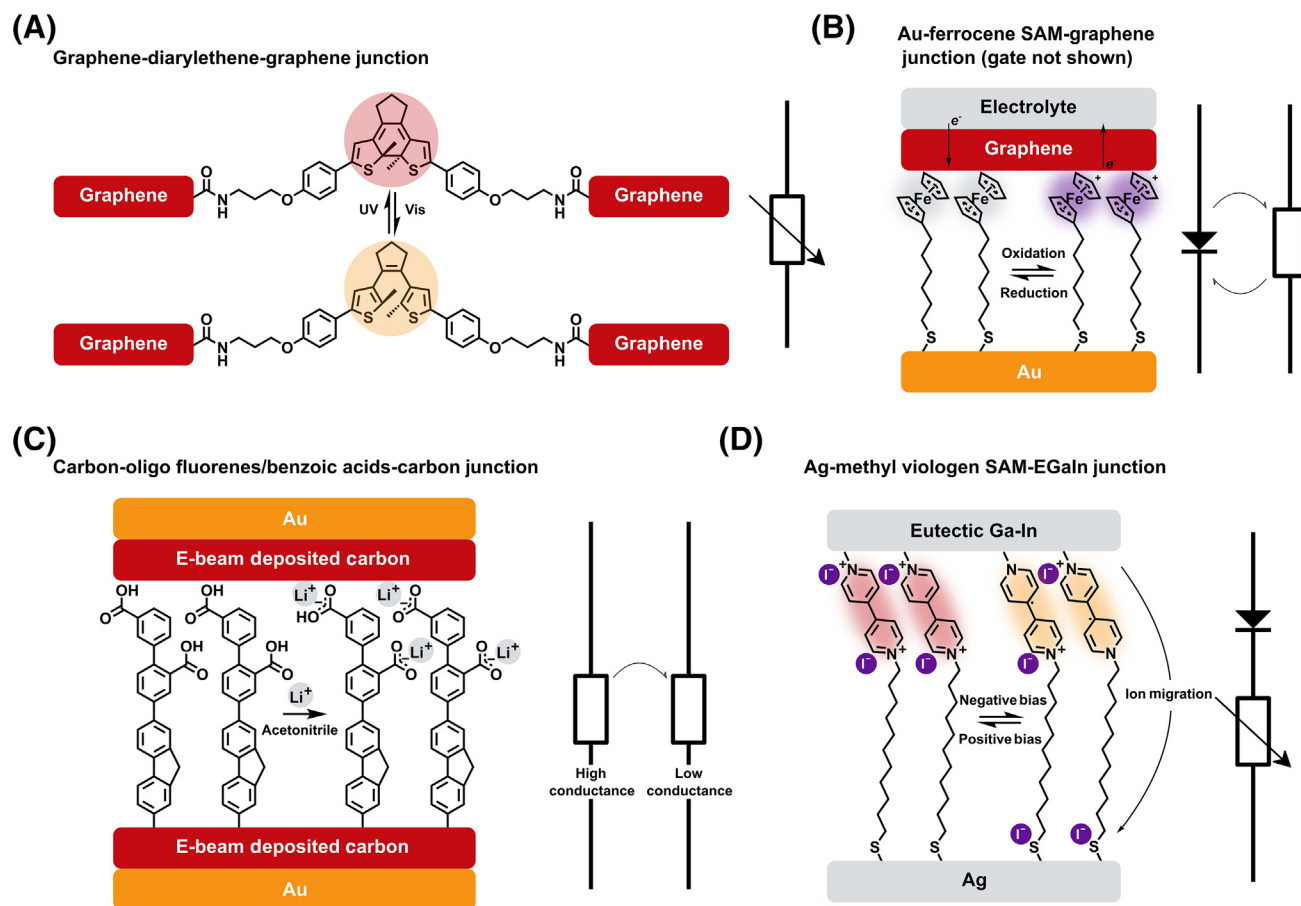
There are two, broad approaches to molecular electronics: single-molecule and large-area (ensemble) junctions. Single-molecule techniques like break-junctions, in which the electric leads repeatedly

form and rupture by the trapping and releasing of individual molecules, are primarily spectroscopic tools for investigating the detailed mechanisms of charge transport, but are not (yet) useful as devices because they are transient. Jia and colleagues fabricated static single-molecule junctions comprising diarylethenes that are covalently bound to the edges of graphene electrodes (Figure 1A) [1]. The exposure to UV and visible light enabled reversible switching between two highly distinguishable conductance states in the junctions that corresponds to resonant tunneling through the molecules in their ring closed/open forms. This work is an important step towards single-molecule devices, however, the junctions exhibited stochastic switching between conductance states in the absence of illumination, highlighting the ongoing challenge of building memory devices based on single-molecule junctions.

Large-area junctions comprising molecular ensembles, however, are difficult to interrogate at the level of individual molecules, but are demonstrably useful and have engendered many approaches to nonvolatile molecular memory in a broad range of scenarios. And because large-area junctions can be fabricated as static, solid-state devices, they can be directly integrated for on-chip advanced functions that are commonly used on silicon, such as diode-based logic gates [2]. In their pioneering work, Collier and colleagues discovered that a Langmuir-Blodgett monolayer of redox-active rotaxanes sandwiched between electrodes can be switched from a high- to a low-conductance state upon applied anodic (oxidizing) potentials, with asymmetric charge transport that is related to diode properties observed at both states [3]. More recently, Carlotti and colleagues reported the reversible switching and hysteresis of conductance states in large-area junctions comprising self-assembled monolayers of redox-active tetracyanoquinone derivatives [4]. At

anodic potentials, the molecules in the monolayer are oxidized into their cross-conjugated form and the junction is switched to the low-conductance state due to quantum interference effects in which electron wave functions are canceled by the bond topology. At cathodic potentials, the molecules are reduced to their linearly conjugated form, restoring the high-conductance state. This proof-of-concept work yielded uselessly low conductance ratios, but demonstrated stable, two-terminal redox switching. Jia and colleagues demonstrated that the reversible switching between conductance states can also be operated in a three-terminal, large-area junction comprising redox-active self-assembled monolayers (Figure 1B) [5]. The junctions are constructed in a vertical geometry, in which the monolayers of ferrocenyl alkanethiols are sandwiched between an Au bottom electrode and a graphene top electrode, while a bias is applied through a third electrode (gate) and an electrolyte to enable oxidation/reduction of the molecules. The oxidation of the ferrocene moiety set the conductance state of the junction to low with symmetric charge transport that resembles the behavior of a resistor, while the reduction of the oxidized ferrocene moiety reset the high-conductance state of the junction and regenerated the rectification induced by a hybrid tunneling-hopping transport process, demonstrating external control over the mechanism of charge transport.

The conductance state of large-area junctions can also be gated by other stimuli. Viero and colleagues reported that the photoisomerization of azobenzene derivatives gives rise to conductance switching in large-area junctions comprising molecules/nanoparticles, in which the variability of the output signals can be further implemented for neuromorphic computing [6]. Chandra Mondal and colleagues observed the transition in the conductance states of large-area



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Figure 1. The Evolution of Molecular Junctions with Switchable Electrical Properties. (A) A single-molecule junction comprising diarylethene photoswitches covalently bound to the edge of graphene electrodes. (B) A large-area junction comprising self-assembled monolayers of ferrocenyl alkanethiols that switches electrical properties under chemical oxidation/reduction. (C) A large-area junction comprising electrochemically grafted oligofluorenes/benzoic acids on carbon electrodes switches conductance upon binding to lithium cations. (D) A large-area junction comprising self-assembled monolayers of methylviologens switches conductance and rectification over a two-step mechanism, the dimerization of reduced methylviologens and the migration of counterions.

junctions upon ion binding (Figure 1C) [7]. Junctions comprising electrochemically grafted oligofluorenes/benzoic acids produced a high-conductance state that could be switched to a low-conductance state by chelating lithium ions delivered in acetonitrile. This observation was explained by the reorientation of acetonitrile molecules and the motion of lithium cations in the junction under an external electric field, which gives rise to the screening of the electrodes and the modification of internal potential profile, demonstrating the influence of counterions in molecular junctions.

A recent article by Han and colleagues is the apotheosis of conductance-switching in large-area junctions, drawing on the aforementioned phenomena to produce truly useful molecular-electronic devices [8]. A widely investigated implementation of conductance-switching materials in random-access memory is the one-diode-one-resistor architecture. It facilitates miniaturization by reducing crosstalk between junctions, however, it introduces considerable complexity to the fabrication process and large potential drops along the cascaded circuits that require high operating voltages. The tunneling junctions reported

by Han and colleagues combine diode and resistor elements into individual molecules. The accessible frontier orbitals of the methylviologen head groups, in combination with alkanethiol tails, behave like a diode and resistor wired in series, rectifying current in self-assembled monolayers on Au with eutectic Ga-In top-contacts, as shown in Figure 1D. A full bias sweep on the junction shows hysteresis in electrical current, predominantly at negative bias (cathodic potentials), as the redox state of the methylviologens lowers, effecting conductance-switching of several orders of magnitude at only ± 1 V. The key to this

switching process is the commensurate migration of counterions to the Au electrode as the reduced viologens dimerize, which locks in the conductance state, making these junctions useful as memory.

During the past decade, large-area molecular junctions comprising ensembles of molecules directly wired to two electrodes emerged as a platform capable of extracting useful functionality from tunneling charge transport mediated by molecules [9]. Han and colleagues show that the next decade is likely to see the further evolution of molecular electronics as active components that can compete with conventional semiconductor materials by harnessing the unique properties of molecules through clever design to extract useful functionality that brings real advantages in performance (e.g., low operating voltages), while simplifying fabrication through the self-assembly of molecules that function as nanoscale integrated circuits.

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Spotlight

Dual-Core Fe Catalyst Brings Major Enhancements in ORR Kinetics

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The sluggish kinetics and side reactions of the oxygen reduction reaction have impeded deployment of proton-exchange-membrane fuel cells. A recent article (Xie *et al.*) introduces an efficient nonprecious metal catalyst (Fe_2N_6) that enhances the kinetics of 4-electron O_2 reduction by more than seven times compared with that of the well-documented single-site FeN_4 catalysts.



Proton-exchange-membrane fuel cells (PEMFCs) have been widely investigated in recent decades as one of the most promising alternatives to fossil fuel-based power sources [1]. However, PEMFC commercialization has been hindered in large part by the sluggish oxygen reduction reaction (ORR) at the cathode, resulting in inevitable losses in energy and power density [2]. Platinum group metal (PGM) catalysts possess the highest reported electrocatalytic activity and stability, representing the most widely used electrocatalysts for PEMFCs [3]. Unfortunately, due to the high cost and scarcity of PGMs, it is difficult to commercialize PGM catalysts on a large scale.

Atomically dispersed metal–nitrogen (M-N_x) species are an emerging class of electrocatalysts because of their high atom-utilization efficiency of active sites [4,5]. However, single-site M-N_x catalysts usually bond with only one oxygen atom of the reaction intermediates (i.e., end-on adsorption) during the ORR, rendering cleavage of the O–O bond energetically

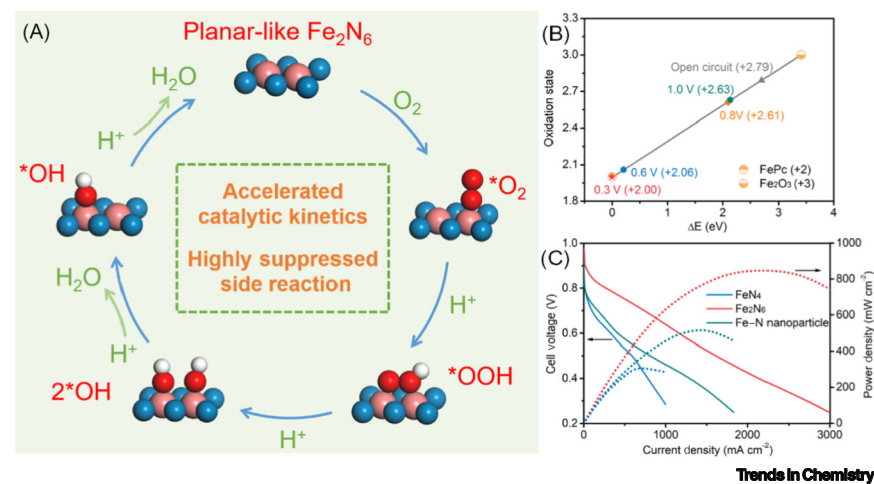


Figure 1. Demonstration of the Planar-like Fe_2N_6 Structure for Oxygen Reduction. (A) Proposed oxygen reduction reaction mechanism on planar-like Fe_2N_6 surface. (B) Fitted averaged oxidation state of Fe in the Fe_2N_6 structure, according to the operando X-ray absorption spectroscopy (XAS) spectra. (C) Polarization and power density curves of proton-exchange-membrane fuel cells using different cathode catalysts, including single-site FeN_4 , dual-site Fe_2N_6 , and Fe-N -containing nanoparticles. Reproduced, with permission, from [9].