NANOSCIENCE

Designing a robust single-molecule switch

A single-molecule switch works at room temperature

By C. Daniel Frisbie

n molecular electronics, researchers combine atomic control of molecular structure with high-precision nanofabrication techniques to connect individual molecules to tiny electrodes (1). The aim is to understand electrical transport, such as conductivity in individual molecules, and to uncover phenomena with practical utility in nanoelectronic devices. On page 1443 of this issue, Jia et al. (2) report robust, room-temperature optoelectronic switching of a single molecule connected to conducting carbon (graphene) contacts. In terms of the magnitude of the switching effect, its reversibility, and stability at room temperature, the results represent the state of the art for single-molecule electronics.

The electronic properties of all materials, molecules included, reflect their atomic-scale architecture. Molecules thus offer potentially limitless opportunities for tailoring electronic function. In addition, their conduction mechanisms (such as quantum tunneling) can minimize heat dissipation. Combined with the compact size of most molecules, this offers the potential for higher numbers of devices per area, meaning faster computation in smaller computer chips.

However, unlike in silicon microelectronics, there are no firmly established design rules for electronic functions in molecular electronics. Rational design means knowing how structure predicts function. To make headway, molecular electronics researchers must uncover rules for how to assemble functional molecules and how to connect them to electrodes to form junctions with predictable electrical behavior, such as current rectification or switching. Structural design parameters include the choice and location of all atoms in the molecule, the pattern of chemical bonding, the total molecular length, and the type of functional groups used to link the molecule to the electrical contacts (see the figure). Symmetry considerations are also crucial, as is the strategy for making nanoscale contacts.

Jia *et al.* report a convincing step toward rational design in molecular elec-



Design features for a single-molecule switch. Jia *et al.* create a room-temperature switch by linking a diarylethene chromophore to graphene nanocontacts with strong covalent bonds and positioning it precisely within the junction with molecular spacers. The switch can be turned on through irradiation with ultraviolet light; visible light switches it off again.

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tronics by describing the creation of a high-performance molecular switch. The main switching component of their junction is the well-known chromophore diarylethene. The open (less conjugated) form of this molecule is insulating. Exposure to ultraviolet light drives a reversible isomerization to a more conjugated-and more conductive-closed structure; irradiation of the conductive closed state with visible light brings the molecule back to the insulating open state. Thus, incorporation of diarylethene into a solid-state molecular junction produces a light-activated toggle switch. Repeatedly exposing the junction to ultraviolet and visible light turns the current on and off.

Previous studies have shown this switching behavior (3-5); however, the junctions were not stable, and the on-to-off current ratio degraded over time. In the present study, Jia et al. achieve both high on-tooff current ratios and remarkable device stability at room temperature. They do so by using strong covalent bonds to link the molecule to the graphene nanocontacts and molecular spacers to precisely position the chromophore within the junction (see the figure). Many prior molecular junction studies have reported switching by mechanisms other than light exposure, but these were performed at cryogenic temperatures (6), which limits application possibilities.

The study complements a string of recent

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advances toward rational design in molecular electronics. These include demonstration of quantum interference effects (7), strong current rectification (8), and commercial application (9). In these and other reports, researchers were successful in intentionally creating molecules to produce desired electrical behaviors-a crucial step toward rational design. Theoretical models of molecular junction behavior have also converged, and the current-voltage characteristics of many simple, nonswitching junctions are well understood (10).

The work of Jia et al. also raises questions. As the authors note, the precise mechanism by which electrons are transported through the light-switchable junction is not entirely clear. The mechanisms may even be different for closed and open forms of the molecule. Understanding the mechanistic details of the transport is crucial for further improvements not just in this particular study but more broadly in molecular electronics.

As scientists become more adept at creating molecular junctions with prescribed electrical functions, are there new behaviors that can be envisioned that differ fundamentally from those seen in silicon? Recent efforts to understand spin transport (11), thermoelectric transport (12), and biomolecular electron tunneling (13) in molecular junctions provide possible inspiration. In the broadest sense, however, molecular electronics need not be simply about creating the next tiny switch.

"... Jia et al. achieve both high on-to-off current ratios and *remarkable device stability* at room temperature."

The science as exemplified by Jia et al.'s study represents exquisite control over matter at nanometer length scales and is a worthy intellectual pursuit in its own right with broad, long-term benefits.

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10.1126/science.aag0827

APPLIED PHYSICS

Tuning organic band structures with Coulomb interactions

The smooth change of band gaps in blends of organic semiconductors arises from long-range electronic interactions

By Nobuo Ueno

he working principles of semiconductor devices are crucially determined by their band gap-the amount of energy needed to excite immobile charge carriers into ones that conduct current. In many inorganic semiconductors, band gaps can be tuned in a systematic way by alloying or inducing strain in the material. Although devices based on organic semiconductors are already in commercial use, there are few rational approaches for similar "band structure engineering" of these materials. On page 1446 of this issue, Schwarze et al. (1) now demonstrate, using long-range Coulomb interactions, a tuning effect of the band structure for organic semiconductors that are weakly bound by van der Waals forces. This effect, which has been totally neglected in discussions of the electronic states, is rather closely related to universal features of organic molecular crystals (2).

Organic semiconductors have gained increasing attention for their application in flexible large-area devices, including organic solar cells (OSCs), light-emitting diodes (OLEDs), and field-effect transistors (OFETs). An accurate energy-level tuning of electron- or hole-transporting states, which are represented by the frontier orbitals-the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO)-is necessary for optimal device efficiency (3, 4). The relative energy position of the HOMO of the donor and the LUMO of the acceptor material controls the open-circuit voltage V_{oc} in OSCs. Also, the tuning of the energy level alignment at the electrode-organic semiconductor interface is crucial for efficient charge injection in OLEDs and OFETs and extraction in OSCs (5).

As depicted in the figure, Schwarze et al. discovered a simple method of energy-level tuning of organic semiconductors over a wide energy by long-range Coulomb interactions. Charge-quadrupole intermolecular interactions provide the key for tuning the ionization energy (IE) and electron affinity (EA); the figure shows how these properties are related to the energies of the HOMO and LUMO levels. When they blended zinc phthalocyanine (ZnPc) with different fluorinated derivatives (F_x ZnPc, where x can be 4, 8, or 16), they observed by ultraviolet photoemission spectroscopy that the IE shifted from 5.55 eV for ZnPc continuously with blending (up to 7.17 eV for x = 16, an energy width is as large as 1.62 eV).

In the absence of intermolecular interactions, the density of states (DOS) of the binary mixture should consist only of two peaks corresponding to the gas-phase ionization energies of ZnPc and the particular F_zZnPc used. Instead, as seen in the figure, the HOMO levels of two different molecules, ZnPc and F₁₆ZnPc, are observed at very close position on the ionization energy scale and give approximately a "single HOMO band" with greater width in the mixed film. This single HOMO moves from the ZnPc HOMO position to the F₁₆ZnPc HOMO position linearly as its fraction in the film increases. Schwarze *et al.* theoretically show that the LUMO represents a behavior similar to that of the HOMO.

Because the IE tuning originates from a superposition of long-range Coulomb interaction from two compounds, the ideal molecular alloy would be the most beneficial for the tuning. The photogenerated hole interacts with molecular quadrupoles, so all of the molecules surrounding the photohole contribute the polarization energy and shift the IE. Contributions of the molecular quadrupole to the polarization have been discussed in the study of polarization energy P_{+} for the hole (IE) and P_{-} for the electron (EA) (6-8).

From theoretical simulations, Schwarze et al. found that the long-range Coulomb interactions tend to smooth out electrostatic potentials contributed from even larger domains of neat phases where the molecules have not mixed completely. Moreover, the simulations revealed that the microscopic mechanism responsible for the linear IEtuning behavior is the superposition of quadrupolar molecular fields of two mixed compounds that are acting on the excess hole. They obtained similar simulation results for the EA, and further confirmed



Designing a robust single-molecule switch C. Daniel Frisbie (June 16, 2016) *Science* **352** (6292), 1394-1395. [doi: 10.1126/science.aag0827]

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