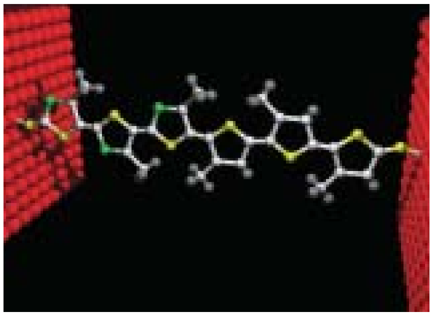
Single-molecule diode explained

MOLECULAR ELECTRONICS

Theorists from the University of South Florida, and the Russian Academy of Sciences, Moscow, have explained why and how the chemical asymmetry of diblock oligomer molecules translates into electrical asymmetry [Oleynik *et al.*, *Phys. Rev. Lett.* (2006) **96**, 096803]. The work builds on experimental results by coworkers at the University of Chicago showing rectification to be an intrinsic property of such molecules.

The molecular diode in this study consists of two parts, each containing an equal number of thiophene (C_4N) and thiazole (C_3NS) rings. Sequential assembly of this diblock oligomer molecule between Au electrodes produces a two-terminal molecular circuit. Current-voltage (*I-V*) characteristics of the individual molecules can then be measured using scanning tunneling spectroscopy. The *I-V* spectrum for a molecular diode typically shows a threshold voltage, below which current is absent. The threshold is observed for both polarities of applied bias.


Diblock oligomer molecules respond to voltage asymmetrically. Channels conduct electrons in one direction but limit flow in the opposite direction, even if the voltage polarity reverses. (Credit: Trent Schindler, National Science Foundation.)

To explain the observed phenomenon, Ivan Oleynik and colleagues reconsidered the standard approach to molecular electron transport based on the energy levels of neutral molecules. They instead show that the conductance in diode molecules occurs via resonant energy levels of an extra electron interacting with the neutral molecule. “Effectively, these are the energy levels of negative molecular ions,” says Oleynik. “Each event of electron conductance is [one] when an incoming electron from one of the electrodes tunnels through the molecule to disappear in the second electrode.” He notes that the bound wave functions of resonant states of negative molecular ions have unusual localization properties in external electric fields. Localization is sensitive not only to applied bias but to polarity as well. This can be used to explain very high conductance in one direction and small conductance in the other when voltage polarity is reversed. “The strong asymmetry of the conductance as a function of the polarity of applied voltage constitutes the rectification of the current by the molecular diode,” says Oleynik.

The researchers are confident that their account will provide experimentalists with a conceptually simple framework in which to interpret data. They also hope that their theoretical studies will be used to guide and challenge the experimental search for fundamentally new phenomena. “This work has opened up exciting opportunities to understand, interpret, and predict new phenomena of electrical conductance in molecular systems,” says Oleynik.

Paula Gould

Spider silk displays torsion shape memory

MECHANICAL PROPERTIES

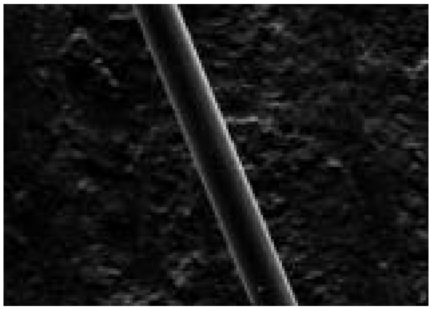
Materials scientists have long envied the strength and toughness of spider draglines. Now researchers from the Universities of Rennes in France and Oxford in the UK have shown that the naturally spun silk possesses unrivalled torsional qualities too [Emile *et al.*, *Nature* (2006) **440**, 621]. Their findings explain why spiders do not twist when hanging from a thread.

The researchers investigated spider silk’s twist properties using a torsional pendulum to keep the period of oscillation independent from its amplitude. A small Cu or plastic rod was used to mimic the spider. This was suspended from a 10 cm long thread of silk from either the *Araneus diadematus* spider or one of two comparison materials. The ‘spider’ was twisted through 90° and released. The resulting oscillations were recorded by a camera linked to a computer.

The dynamical responses of the three threads turned out to be quite different. When a ‘spider’ suspended from the synthetic organic polymer Kelvar is subjected to an initial 90° twist, it returns to its original position and oscillates gently, indicating an elastic response. If this was the case for natural dragline silk, suspended spiders would be more likely to be spotted by predators, suggest coauthors Olivier Emile and Albert Le Floch of the University of Rennes.

A Cu thread exhibits far greater torsional stability. The metal deforms after its initial twist producing a new equilibrium position about which the rod barely oscillates. But the thread becomes brittle after only a few twists. The twisted spider silk, however, produces highly damped oscillations around a new equilibrium point as well. Unlike the Cu, it retains its torsional properties through several experimental cycles. The dragline also recovers its original position over time in what appears to be an exponential manner.

The behavior of spider silk is similar to that of synthetic shape memory materials, such as the Ni-Ti alloy Nitinol, the authors note. An additional trial using Nitinol thread produced a comparable oscillation curve to that of the spider dragline. The key difference is that while spider silk recovers its original shape unaided, Nitinol must be heated to 90°C.


Scanning electron micrograph of a spider dragline, 3 μm in diameter. (Photo acquired using SEM equipment from the Department of Physics and Chemistry, University of Rennes.)

“The selection against twisting and swinging in the spider dragline has led to the evolution of a shape memory material that does not need any external stimulus to give total recovery,” say Emile and Le Floch. “The twist properties add another beneficial quality to the famously strong silk. This has evolved so that an abseiling spider does not swing in a way that might attract predators.”

The researchers hope to model the protein systems responsible for the unusual torsional response from dragline silk. Working predominantly with the amino acids alanine and glycine, they will assess whether the reconstruction of sacrificial hydrogen bonds and van der Waals interactions form the basis for explaining the observed mechanical behavior.

Paula Gould