Chloride affinities of these earlier cryptands (*3*, *6*–*9*) are not, however, as high as for the triazole cryptand of Liu *et al.*, even taking into account the large solvent effect on binding variabilities. Only a few reported receptors have affinities exceeding the 10^9 M^{-1} necessary to overcome the strong hydration energy of Cl^- in water. However, ligand design has reached a point where high binding affinities, in addition to other desirable qualities such as on-off switches and sensors, are possible with supramolecular chemistry. A key attribute of Liu *et al.*'s host, in addition to its bicyclic nature (structure **6**), is that the bridging CH donors (triazoles) impart a more rigid cavity than many other cryptands reported previously. This design builds on work reported by Flood and co-workers that used the triazolo CH donor group in chelating foldamers (*11*) that could bind and release Cl^-, and a triazolo macrocycle (*12*) that could bind Cl^- effectively, if not as strongly, as the cryptand.

The new class of cryptands possesses incredibly high attomolar affinities for Cl^- extraction into dichloromethane and potentially could inhibit Cl^--induced corrosion of iron. Indeed, the many cryptand design possibilities now allow for fine-tuning the complementarity of the cryptand cavities to targeted guests, ensuring expansion of the use of these supramolecular cages in future applications. Targeted recognition of molecular and ionic species impacts the vast arena of chemical fields, such as biology, medicine, agriculture, engineering, and materials technology, and in general the global environment. The results of Liu *et al.* are an excellent example of how design concepts in the field of supramolecular chemistry have been refined in the past 50 years. Many more exciting advances in anion coordination and the entire area of supramolecular chemistry are yet to come. ■

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ARTIFICIAL MUSCLES

Stronger artificial muscles, with a twist

Tailored fiber-shaped actuators with twisted and coiled designs have high energy densities

By **Sameh Tawfick**[1,2] *and* **Yichao Tang**[1]

Heat engines have long been used for transportation, but electric motors, which deliver clean mechanical actuation and come in a wide range of sizes, have enabled the spread of automated motion used, for example, in pumps, compressors, fans, and escalators. Nonetheless, natural muscles, their biological counterparts, are far more ubiquitous. Human bodies have more than 600 muscles that drive functions such as heartbeat, facial expressions, and locomotion. There are many opportunities for expanding the use of actuators that mimic muscles by directly using electric, thermal, or chemical energy to generate motion and enable more pervasive automation. In this issue, on pages 150, 155, and 145, Mu *et al.* (*1*), Yuan *et al.* (*2*), and Kanik *et al.* (*3*), respectively, describe new types of fiber-shaped artificial muscles that exploit advantages derived from the mechanics of twisted and coiled geometries.

These fiber-shaped actuators exploit tailored materials composition and architecture within the fiber diameter (see the first figure) to achieve record performance. External stimuli in the form of electricity, heat, or chemistry transform the material's microstructure and generate large motion (strain) and forces (stress) (see the second figure). These actuators are made from lightweight polymers, so they deliver energy densities more than 50 times that of skeletal muscles and can lift more than 1000-fold their own weight. All have similar twisted or coiled shapes and can be actuated by heating. Mu *et al.* and Kanik *et al.* also used spontaneously coiled fibers that contract in the axial direction when stimulated. Contraction is also used by skeletal muscles because it eliminates the risk of buckling encountered if the muscles were to do work by pushing against a weight.

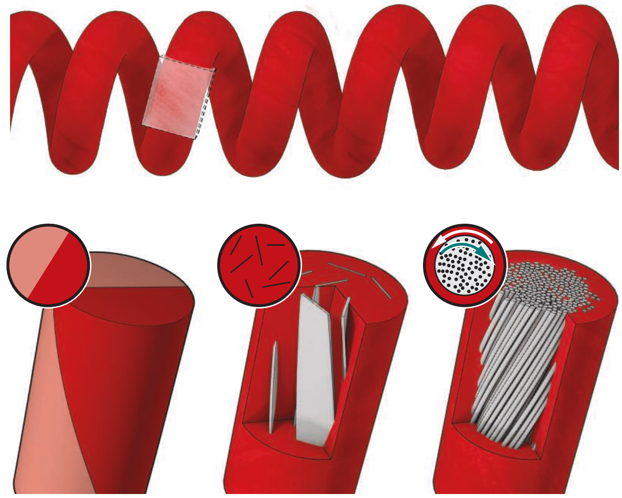
Mu *et al.* tailored the cross section of polymer yarns by selectively forming an active sheath that encloses a passive core to boost the performance of the muscles. The outer sheath expands in response to external stimuli. They used several different polymers as sheath materials to respond to various stimuli. For example PEO-SO_3 [a blend of poly(ethylene oxide) and a copolymer of tetrafluoroethylene and sulfonyl fluoride vinyl ether] responds to ethanol vapor. Polyurethane responds to heat, and carbon

Composition and architecture of artificial muscle fibers

Three designs for coiled and/or twisted actuators are illustrated schematically. The dashed box shows the region presented as exploded views below, where the circles are cross-sectional views.

Stimuli-responsive actuation
In all three designs, the fiber undergoes twist to store energy that enables motion.

Design differences
The design of Kanik *et al.* (left) uses a Janus fiber that has thermoplastic polymer on one side and an elastomer on the other side. The design of Yuan *et al.* (middle) uses a shape-memory polymer reinforced with graphene oxide platelets. The design of Mu *et al.* (right) uses a stimuli-responsive sheath surrounding a twisted yarn core.



GRAPHIC: V. ALTOUNIAN/SCIENCE

nanotube (CNT) sheaths swell in response to electrochemical charges.

The inner core provides restoring stiffness and directs the twisting motion of the fiber. Mu *et al.* demonstrated the use of several yarns as a passive core, including twisted CNTs, polyacrylonitrile, silk, and bamboo. The fiber composition is carefully tailored to boost the performance compared with existing uniform fishing-line muscles (*4*) by placing the stimuli-responsive material only on the outside sheath, which leads to faster responses because the diffusion path is shorter. The swelling forces are more effective when they act on the outermost surface of the yarn, where the local fiber bias is maximum. This material distribution simultaneously reduces the mass density of the muscle by keeping the core yarn unfilled to increase the energy density. As a result, these new muscles achieve 2.12 kJ/kg for sorption swelling–powered PEO-SO_3 sheath muscles and 1.33 kJ/kg for polyurethane sheath muscles actuated electrothermally.

The tailored fiber designs by Mu *et al.* explore untapped opportunities to boost the performance of artificial muscles while also reducing their cost. The fiber core can be essentially any commercial yarn that has reasonable high torsional stiffness and strength-to-weight ratio, such as bamboo or nylon 6 fibers, and the stimuli-responsive material is only a thin sheath-like coating on the outside. Only a thin layer of relatively expensive CNTs wrapped around a nylon yarn was needed to enable electrochemical actuation. This actuation is potentially more energy efficient than thermal actuation, which is limited by the Carnot cycle.

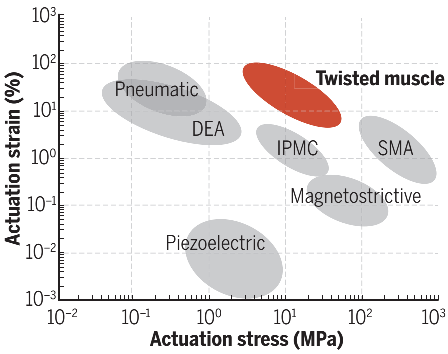
Yuan *et al.* also rationally designed high-performance microengines from twisted nanocomposite fibers. They synthesized the fibers from polyvinyl alcohol (PVA) as a matrix filled with dispersed graphene oxide platelets. PVA is a shape-memory polymer (SMP) that can be programmed at high temperature to adopt a certain shape—here, a highly twisted configuration—and then thermally quenched while the twisted shape is fixed. Upon reheating to just above the programming temperature, the twisted fiber recovered its straight shape by rapidly untwisting while delivering mechanical work.

The performance of these fiber-shaped engines is greatly enhanced by the use of 5% weight graphene oxide platelets, which provide several benefits. First, they increase the stiffness so that the fiber delivers higher torque and work upon untwisting. The geometry of the graphene oxide platelets is critical to this enhanced performance as they undergo substantial bending, folding, and twisting within the fiber to store a large amount of elastic energy during the twist-programming step. Moreover, the graphene oxide platelets offer critical strength and toughness benefits that allow more mechanical energy to be stored within the fiber before it fails by fracture. These enhancements can perhaps be tracked to prior work by Poulin and co-workers on the exceptional toughness of nanocomposite PVA fibers (*5*).

The fabrication process uses scalable nanoparticle dispersion and wet-spinning techniques. This thermally driven nanocomposite SMP fiber delivers a record work density of ~2.8 kJ/kg and can be manually reprogrammed and used at least 10 times before failure. This actuator can potentially be coupled to an elastic yarn-like core to provide a restoring torque that allows it to actuate repeatedly like an artificial muscle.

Artificial muscle metrics

Performance of actuators and artificial muscles shows the trade-off between actuation stress (force generated) and strain (amount of deformation that results). Twisted artificial muscles have at least twofold lower mass density than that of other metal and ceramic technologies.



DEA, dielectric elastomers; SMA, shape-memory alloys; IPMC, ionic polymer–metal composites.

Kanik *et al.* produced an artificial muscle fiber with a Janus-like architecture by mechanical drawing of large heterogeneous polymer ingots (*3*). One side of the fiber consists of a cyclic olefin copolymer elastomer (COCe), and another side is polyethylene (PE). This Janus cross section enables the self-coiling of these muscles driven by residual stresses developed during cold drawing. PE deforms during drawing, elongating at the same rate of the external drawing, whereas COCe elastomer only partially extends while storing some elastic energy during the drawing process. When released from the drawing process, the fiber coils spontaneously. The mismatch in thermomechanical behavior between the PE and COCe causes the fiber to contract when thermally stimulated and produces maximum work capacity of 7.42 kJ/kg by heating to merely ~40°C. The process to make these fibers could scale to industrial production.

The mechanism leading to the extremely energy-dense actuation in these three reports is still unclear. The key factor is the elastic energy stored during the twisting and coiling process that is reminiscent of mechanical spring batteries, in which the stimulated swelling releases some of the elastic energy stored during winding (*6*). The amount of energy that can be stored is related to the toughness of the fibers—the energy to failure. This heterogeneous composition of each of the three fibers enhances fracture toughness. The fraction of energy released upon stimulation is also a function of the amount of swelling of these fibers and the changes in their elastic modulus during swelling.

These three studies allow a glimpse of the future automation opportunities with these materials. Mu *et al.* demonstrated textiles made of these fibers that can expand and vary their porosity when stimulated. The textile can be designed to respond to various stimulations such as glucose sensing, which could enable biomedical applications. Yuan *et al.* demonstrated the use of their fiber to propel a small boat, and one can see these used in the future to propel microswimmers, especially given the similarity to the flagella of bacteria. Kanik *et al.* used a nanowire mesh sprayed on the fibers to measure their contraction by means of a piezoresistive effect, which enabled feedback control to precisely actuate these muscles.

Although all of these three fiber actuators are extremely energy dense, their energy efficiency is typically <6%, which is quite low. Even with such low efficiency, they could be used to propel small robots, in drug-delivery systems, or to morph textures that do not require large mechanical work. Like natural skeletal systems, they will use hinged and articulated mechanisms to facilitate complex kinematics. In the long term, these muscles could be very suitable for environmentally responsive morphing architectures and kinetic materials, where new high-energy efficiency designs are needed. ■

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