

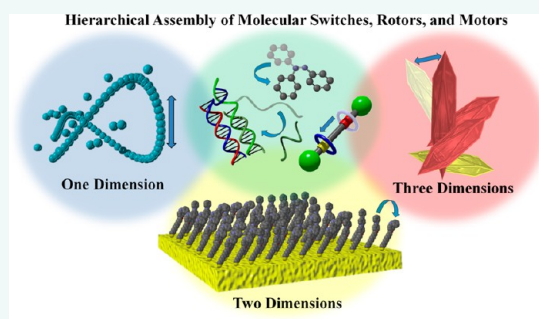
Controlling Motion at the Nanoscale: Rise of the Molecular Machines

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ABSTRACT As our understanding and control of intra- and intermolecular interactions evolve, ever more complex molecular systems are synthesized and assembled that are capable of performing work or completing sophisticated tasks at the molecular scale. Commonly referred to as molecular machines, these dynamic systems comprise an astonishingly diverse class of motifs and are designed to respond to a plethora of actuation stimuli. In this Review, we outline the conditions that distinguish simple switches and rotors from machines and draw from a variety of fields to highlight some of the most exciting recent examples of opportunities for driven molecular mechanics. Emphasis is placed on the need for controllable and hierarchical assembly of these molecular components to display measurable effects at the micro-, meso-, and macroscales. As in Nature, this strategy will lead to dramatic amplification of the work performed *via* the collective action of many machines organized in linear chains, on functionalized surfaces, or in three-dimensional assemblies.



KEYWORDS: molecular machines · molecular switches · rotors and motors · hierarchical assembly · azobenzene · mechanically interlocked molecules · DNA nanotechnology · amphidynamic crystals · thermo/photosensitive crystals · photomechanical crystals

Inspired by the complexity and hierarchical organization of biological machines, the design of artificial molecular machines that exhibit controlled mechanical motion and perform sophisticated tasks is an ultimate pursuit of molecular-scale engineering.^{1–7} The design and synthesis of molecules that can undergo reversible structural changes with various stimuli have received considerable attention, but there remain far fewer reports of dynamic molecular systems such as cleverly designed motors and pumps where the mechanistic action of their molecular components has been exploited to do controlled work on their environment. The very definition of a machine has been a fascinating debate since Isaac Asimov began to lay out the early laws of robotics over 70 years ago.⁸ In an effort to advance the field, a stringent language has been sought to differentiate simple molecular switches from motors that are capable of driving a system away from equilibrium.^{9,10} While the working principles of these molecular devices cannot be compared

to macroscopic analogues, a practical acceptance has emerged that a molecular machine can be a multicomponent system with defined energy input that is capable of performing a measurable and useful secondary function either at the nanoscale or, if amplified through collective action, at the macroscale. The system should ideally act in a reversible manner, with the capacity to complete repeated mechanical operations. Spatial control and temporal control over this motion, and work performed, are further hallmarks of successful machines, helping to differentiate deliberate actuated mechanics that leverage Brownian motion from undirected thermal effects, and machines from simple molecules that wiggle or diffuse randomly.^{11,12}

In this Review, we draw from this rapidly expanding and diverse field to highlight some of the most exciting recent reports of molecules and assemblies that (a) exemplify practical and advantageous attributes that can be applied to other systems and (b) show the most promise in successfully

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advancing the development of artificial molecular machines. We first summarize some of the key advances in the development of molecular switches and rotors ranging from simple hydrazone switches to complex deoxyribonucleic acid (DNA)-based nanomechanical walkers. Although these systems in isolation are distinct from scaled-up artificial machines, recent progress in the diversity and complexity of their design has facilitated greater control over mechanical motion at the molecular level. This control has enabled the conversion of simple molecular components into functional tools that can interact with one another or couple to their environment to operate as machines at the nanoscale. We highlight some of the most promising examples of the organization of switches and rotors into linear assemblies, then two-dimensional arrays on surfaces, and finally polymeric networks and dynamic three-dimensional crystals. Ultimately, the precise and robust integration into higher dimensional architectures that take advantage of mechanical action by many components is essential to bridge the gap between actuating molecular motion and performing microscopic, mesoscopic, and macroscopic work. Throughout, we address fundamental obstacles yet to be overcome to advance the field and to convert these molecular systems into functioning machines and offer a glimpse into the untapped potential of these versatile systems in an effort to identify some of the most viable directions toward future molecular machine design and implementation.

MOLECULAR SWITCHES, ROTORS, AND MOTORS

Increasing Sophistication of Molecular Design. Numerous classes of molecules that reversibly isomerize between multiple structural configurations in response to external stimuli fall within the realm of molecular switches. Common examples of photochromic molecular switches are displayed in Figure 1. Some of the most extensively studied small-molecule motifs include (but are far from limited to) azobenzenes, whose isomerization between *E* and *Z* conformations about a double bond mimics flapping motions;^{13,14} diarylethenes and spiro-pyrans, in which conformational changes are accompanied by ring-opening or ring-closing reactions;^{15–18} anthracene and coumarin derivatives that reversibly dimerize with one another;^{19–21} and overcrowded alkenes, hydrazones, and imines, which behave as rotors that can revolve about a rigid internal axis.^{22–25} Covalent modification of parent switch and rotor molecules provides near infinite opportunities to design alternate isomerization pathways and to tune actuation stimuli. Additionally, noncovalent interactions between molecules such as hydrogen bonding, hydrophobic effects, and π – π stacking enable the construction of dynamic host–guest systems, expanding the versatility of switches *via* supramolecular self-assembly of two or more components.²⁶ These dynamic

VOCABULARY: Molecular machine - a multicomponent molecular system with defined energy input that is capable of performing a measurable and useful secondary function *reversibly* either at the nanoscale or, if amplified through collective action, at larger scales; **Hierarchical assembly** - the bottom-up arrangement or ordering of individual components that results in increased overall size, dimensionality, complexity, and/or functionality; **Cooperativity** - the property of complex action within coupled molecular systems that yields different results from isolated or ensemble (collective) switching events; **Mechanostereochemistry** - the relative spatial arrangement of atoms within mechanically interlocked molecules; **Amphidynamic crystal** - an ordered solid that has both rigid, ordered lattice constraints and highly mobile components, simultaneously; **Thermo/photosalient crystal** - an ordered solid that exhibits rapid phase transitions upon heating or irradiation resulting in jumping of the crystal, which may be accompanied by fracturing; **Photomechanical crystal** - an ordered solid that changes shape (expands, bends, or twists) under ultraviolet (UV) or visible light irradiation in the process of crystal-to-crystal chemical transformation

molecules represent the smallest building blocks available for a bottom-up approach to synthesize functional mechanical devices that exhibit motion. Increasingly complex mechanically interlocked molecules (MIMs) such as catenanes, rotaxanes, and pseudorotaxanes represent another class of switches and rotors and have regularly been targeted as promising architectures in the design of molecular muscles that facilitate contractile and extensile motions due to their mechanostereochemistry.^{27–29} Catenanes are MIMs constructed from two or more interlocked macrocycles in a chain-like architecture that may be designed to adopt distinct and stable conformations with controllable rotary motions (Figure 2a). Alternatively, rotaxanes, pseudorotaxanes, and their derivatives are molecules composed of a linear rod-like component threaded through a cyclic host; the exact position and orientation (station) of the relative components in the mechanically interlocked compound can be controlled by external stimuli. The macrocycle host may be sterically constrained by bulky end groups on the linear species, as in rotaxanes, or designed to possess sufficient free energy to dethread from the rod-like component, as in pseudorotaxanes (Figure 2b,c). Finally, nanomechanical switches, rotors, and walkers composed of a few to hundreds of DNA biopolymer strands, whose design and synthesis have developed into a rapidly burgeoning field of its own, offer the capability to extend the dynamic boundaries of individual molecular components to the submicrometer scale.^{30–32}

While diverse, all of the aforementioned switch and rotor components operate on similar principles.³³

The actuation of switching events, such as the absorption of a photon, electrochemical reduction or oxidation reactions, binding or unbinding of a ligand, or changes in temperature, manipulates the relative energy barrier(s) between two or more possible states. However, intra- or intermolecular rotational, translational, or extensile and contractile movements are ultimately driven by the irrepressible effects of thermal noise. This competing driving force highlights the

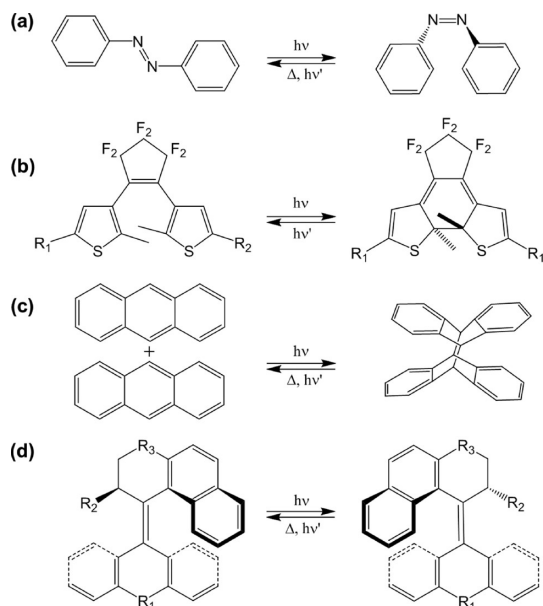


Figure 1. Examples of common small-molecule switch motifs that undergo various types of chemical bond rearrangements. (a) Isomerization of azobenzene between *trans* and *cis* conformations upon irradiation or heating. (b) Photoinduced ring-opening and ring-closing reactions of diarylethene derivatives. The closed-ring form is thermally stable and will generally not return to the open-ring configuration under ambient conditions when kept in the dark. (c) Formation and disassociation of cyclic dimers of anthracene molecules. (d) Rotation about a central double bond in a sterically overcrowded alkene. Numerous structural possibilities exist, but the general form consists of a tricyclic stator (bottom) connected to a heterocyclic rotor (top) by a double bond. The reverse reaction most often proceeds *via* helix inversion of the tricyclic stator upon heating.

importance of molecular switch designs to consider the potential energy landscape to facilitate thermodynamically uphill transformations with sufficiently deep new minima and spatiotemporal control over biased switching events. The most remarkable examples of mechanical control employed to overcome the randomizing effect of Brownian motion impart necessary directionality to molecular rotations or translations.^{34,35} Typically, this control is achieved in a variety of systems by maintaining a judicious balance between molecular flexibility and rigidity and utilizing sterically demanding or asymmetric molecular geometries. Examples include the unidirectional rotation about double bonds in chiral overcrowded alkenes and imines,^{36,37} circumrotation in catenanes,³⁸ preferential threading and dethreading of MIMs,^{39,40} and directed walkers and nanocars.^{41–43} Recently, Stoddart and co-workers successfully demonstrated the energetically uphill, unidirectional threading of a dumbbell-shaped molecular rod containing a noninteracting oligomethylene chain by tetracationic macrocycle hosts.⁴⁴ This redox-driven molecular pump performs work by first confining one macrocycle on the rod and subsequently threading a second ring against a local concentration gradient into an entropically unfavorable configuration on the oligomethylene chain, in close proximity to the first macrocycle. The proposed flashing energy ratchet mechanism for the energetically demanding action of the pump can be described by modulation of the potential energy landscape of the molecule upon redox-switching events.

A significant yet challenging goal in molecular design that has received less attention, however, is the development of switches whose actuation is engineered to trigger *cooperative* or coordinated action, thus amplifying motion where a switching event directly influences simultaneous or subsequent conformational change in another molecule. Here, the intermolecular coupling of switching events is distinct from *collective* ensemble motion. The paradigmatic example of cooperativity found in Nature is the uptake

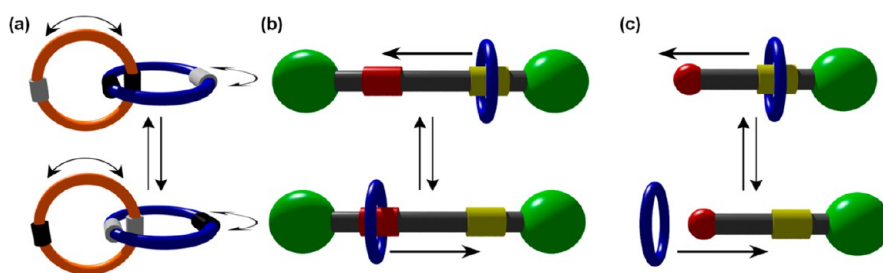


Figure 2. Example schematics of switchable mechanically interlocked molecules (MIMs). Functional groups incorporated within the molecular architecture that are influenced by various stimuli including light, pH, redox activity, and ions program the switching of stable recognition stations. The actuation stimuli thus facilitate movement of the interlocked components with respect to one another. (a) Catenane composed of interlocked macrocycles that are free to rotate and contain multiple thermodynamically stable configurations. (b) Shuttling motion of a threaded macrocycle (blue) between two stable states within a rotaxane motif in which sterically bulky end groups (green) on the rod-like component prevent dethreading of the macrocycle. (c) Unidirectional dethreading and rethreading of a macrocycle host from the rod in a pseudorotaxane.

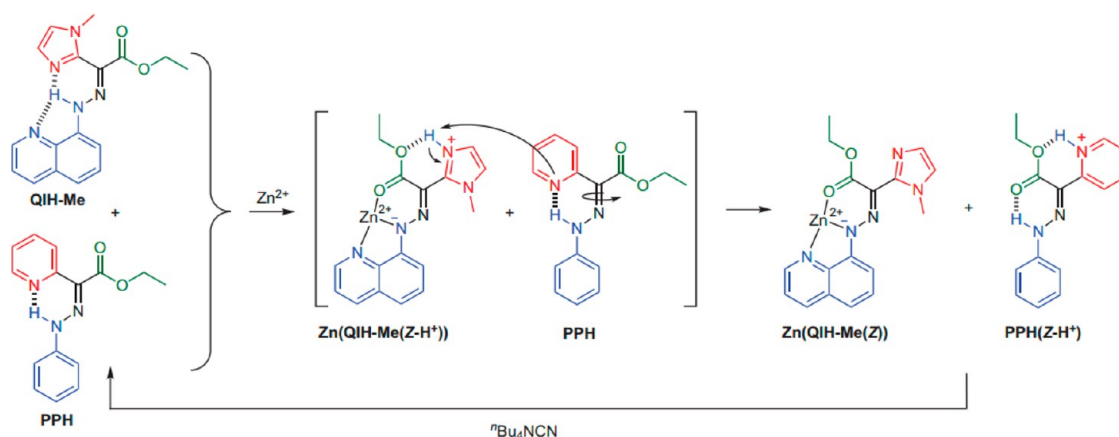


Figure 3. Cooperative switching events between two distinct molecular switches: an imidazole-containing hydrazone switch (QIH-Me) and pyridine-containing hydrazone switch (PPH). Upon addition of Zn²⁺, QIH-Me isomerizes to a structure that contains an acidic imidazolium ring (Zn(QIH-Me(Z-H⁺))). The PPH switch subsequently isomerizes to PPH(Z-H⁺) upon proton transfer from Zn(QIH-Me(Z-H⁺))). The addition of tetrabutylammonium cyanide (tBu₄NCN) to the reaction mixture regenerates the original switch configurations. The scheme illustrates coupled switching events between two molecules through proton relay. Reproduced with permission from ref 47. Copyright 2012 Nature Publishing Group.

of molecular oxygen (O₂) by the metalloprotein, hemoglobin.^{45,46} The binding of O₂ by one of four heme groups induces intramolecular conformational changes in the protein that triggers the favorable uptake of three additional O₂ molecules. While examples of cooperativity are abundant in Nature, there has been little success in the field of molecular machine design in synthesizing and operating switchable moieties whose states are influenced directly by other molecules. An early example of an artificial multistep switching cascade was recently reported by Aprahamian and co-workers, in which structurally simple hydrazone-based switches were shown to facilitate cross-talk between molecules, reminiscent of biological proton-relay processes (Figure 3).⁴⁷ The input of Zn²⁺ initiates *E/Z* isomerization and deprotonation of a hydrazone molecule that contains hydrogen-bond-accepting methylimidazole and quinoline groups to stabilize a metal-ion binding pocket. The subsequent proton transfer to a structurally related hydrazone switch that does not interact strongly with Zn²⁺ results in the isomerization of a second molecule. Capitalizing on the leveraging of intermolecular interactions to influence switching events represents a paradigm shift in the design of next generation molecular switches, as it exemplifies active and dynamic communication between separate components to work in tandem.^{48–50} If analogous approaches toward amplifying molecular motion can be applied to other switching motifs with greater specificity and without the use of sacrificial reagents, substantial increases in the operational yield of isolated or hierarchically assembled systems can be envisioned and may thereby increase their practicality in real-world applications.

Isolated Small-Molecule Machines. The rational design of switches and rotors, or even the impressive directional control over walkers and motorized nanocars, is

clearly not a final objective (unless, of course, the design is to be entered in a molecular nanocar race).^{51,52} It is instead necessary to harness and to amplify the mechanical motion of individual components to drive iterative chemical processes or to complete complex tasks in order to qualify these dynamic systems as functional machines. Some of the most innovative examples of mechanistic function of isolated molecules are switchable catalysts that are capable of raising or lowering the energetic barriers to chemical transformations.^{53–55} Molecular machines that control bidirectional enantioselectivity in asymmetric catalysis are particularly exciting, as the preparation of enantiopure catalysts and the separation of racemic mixtures of synthetic products are typically tedious and cumbersome processes. Wang and Feringa demonstrated *in situ* switching with enantiomeric preference of the chiral product of a conjugate addition reaction using a rotary-motor catalyst fueled by light.⁵⁶ More recently, Leigh and co-workers described a rotaxane-based asymmetric catalyst that can be switched on and off by revealing and concealing, respectively, a chiral organo-catalytically active amine built into a mechanically interlocked axle *via* simple protonation or deprotonation of the amine group.^{57,58} Temperature may also be used as a means to control product enantioselectivity with a single switchable catalyst, as reported by Storch and Trapp, to direct asymmetric hydrogenation reactions upon catalyst epimerization.⁵⁹ The precise spatial control afforded by these dynamic molecular designs facilitates the integration of enzymatic behavior with mechanical motion, thus exemplifying the potential of small-molecule machines to perform useful tasks at the molecular level for applications ranging from catalysis to photopharmacology.⁶⁰

Another ingenious example of leveraging fueled molecular motion for performing useful operations at

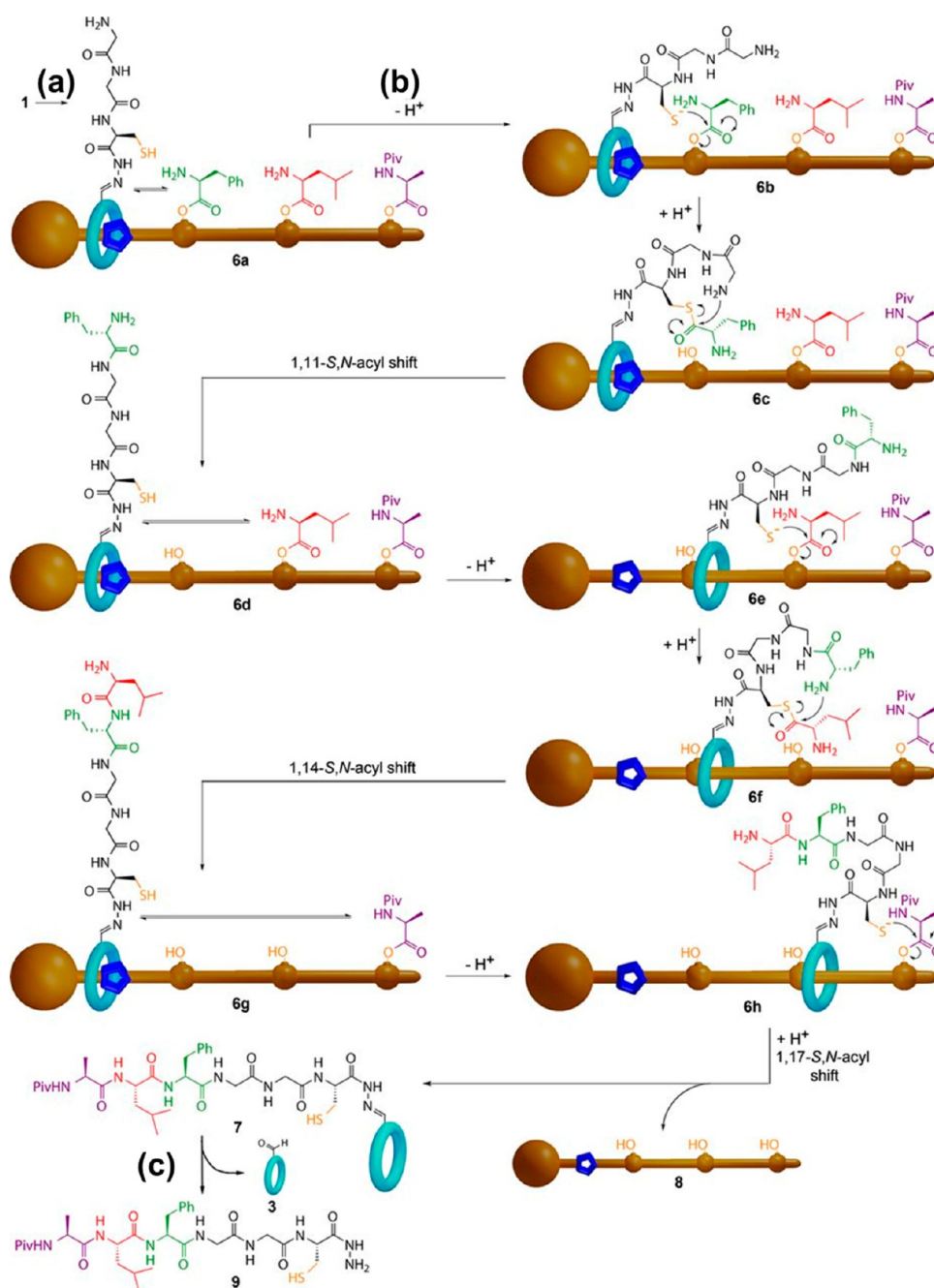


Figure 4. Scheme depicting the proposed mechanism for sequence-specific oligopeptide synthesis using a rotaxane-based molecular machine. (a) Machine is activated upon removal of protective groups from the macrocycle. (b) Under basic conditions, the amino acid moieties that are tethered to the rod-like component are sequentially transferred to the macrocycle as it unidirectionally dethreads from the rod. (c) Macrocycle can then be subsequently hydrolyzed to obtain the isolated oligopeptide-containing motif. The stimulated, directed motion facilitates small-molecule synthesis by a molecular machine through the intelligent functionalization of the cyclic host and threading strand. Reproduced with permission from ref 62. Copyright 2013 American Association for the Advancement of Science.

the molecular scale is the sequence-defined synthesis of oligomer chains. In Nature, the polyribosome has been shown to have roles in both biosynthesis and protein assembly.⁶¹ Utilizing the mechanically interlocked nature of rotaxanes, Leigh and co-workers designed a ribosomal mimic that travels along a molecular strand to assemble amino acids iteratively by native chemical ligation (Figure 4).⁶² Once assembled,

the rotaxane-based machine is activated by acidic cleavage of protecting groups on the macrocycle, allowing its movement along the strand bearing amino acid building blocks. A bulky terminal-blocking group on one end of the strand facilitates unidirectional dethreading once all amino acids have been sequentially added to the macrocycle. Although the reaction kinetics remain slow (the formation of each amide

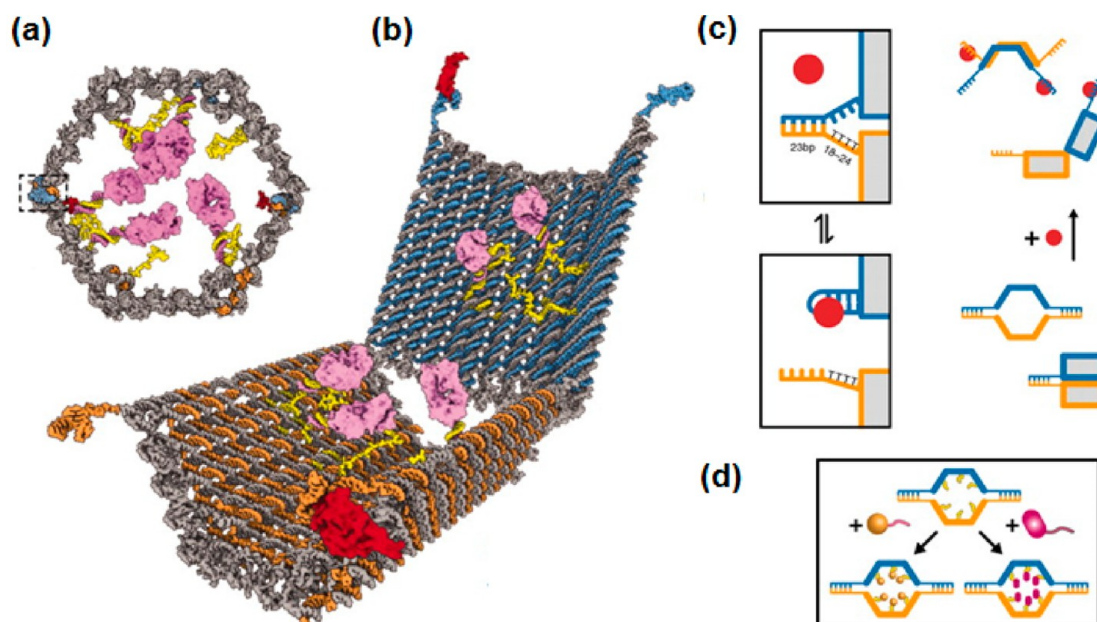


Figure 5. Design of a logic-gated DNA nanorobot. (a) Front and (b) perspective view of a DNA nanorobot loaded with a protein payload (pink). The boxed area denotes one of the two aptamer locks that clasp the front of the nanomechanical device. (c) Aptamer-based gate is composed of an aptamer (blue) and a partially complementary DNA strand (orange). The “open” configuration can be stabilized by an antigen key (red circle). (d) Payloads including gold nanoparticles (gold) or small proteins (magenta) may be tethered inside the nanorobot. The DNA-based nanomechanical device enables the loading and cell-specific delivery of various cargo that utilizes an AND gate: both aptamer-based lock sites must be unlocked with their antigen key for the nanorobot to open. Reproduced with permission from ref 77. Copyright 2012 American Association for the Advancement of Science.

bond takes approximately 12 h), the modular design and new threading protocol in machine preparation offer the possibility of analogous molecular synthesis from other monomer types and the employment of longer oligo- or polymer tracks.⁶³

DNA-Based Machines and Walkers. DNA-based nanomechanical devices such as tweezers and gears have also shown promise as artificial molecular machines, as demonstrated by the specificity and predictability with which these molecules can be modified.^{64,65} Boosted by the advent of DNA origami, the advances in programmability of these devices have enabled rapid strides toward the design and operation of DNA machines.⁶⁶ These devices are engineered for a variety of applications including catalysis and the capture and release of targets ranging from single metal ions to large proteins.^{67–69} Their motion may be actuated by the targets themselves, sacrificial staple strands or aptamers (synthetically designed DNA/RNA motifs), or light-utilizing oligonucleotide sequences chemically modified with photoswitching molecules such as azobenzene.^{70–73} The recognition of targets by DNA or RNA devices that induce sophisticated secondary functions based on Boolean logic-gated mechanisms is particularly impressive, utilizing conjunction (AND), disjunction (OR), or negation (NOT) operations.⁷⁴ Logic-gate operations performed by DNA were demonstrated by Adleman and Lipton two decades ago, but DNA-based computing remains underdeveloped due to

challenges associated with scale-up and slow reaction kinetics.^{75,76} Church and co-workers recently designed a DNA nanorobot composed of over 200 unique oligonucleotides and capable of delivering payloads such as antibody fragments or nanoparticles to cells by incorporating an AND gate based on two locking aptamer-complement duplexes (Figure 5).⁷⁷ Upon simultaneous recognition of their targets, the duplexes dissociate and the nanorobot undergoes a structural rearrangement to expose the sequestered payloads. While the implementation of such complex proof-of-principle nanorobots *in vivo* is not likely in the near future, analogous logic-gated target discrimination may be advantageous in the design of molecular devices for future biomedical applications such as drug delivery and gene therapy, as well as sensing and computation.^{73,78–80}

Inspired predominately by biological motor proteins from the kinesin, dynein, and myosin families, clever DNA walkers have been designed to enable progressive movement along prescribed tracks.^{81–84} Numerous strategies have been employed to facilitate directional movement including the incorporation of Brownian ratchet and enzymatic “burnt bridge” mechanisms, asymmetric molecular design, and the use of chemically modified architectures containing azobenzene that initialize walking upon photoisomerization.^{85–88} These walkers may behave autonomously or require external intervention; the latter most often

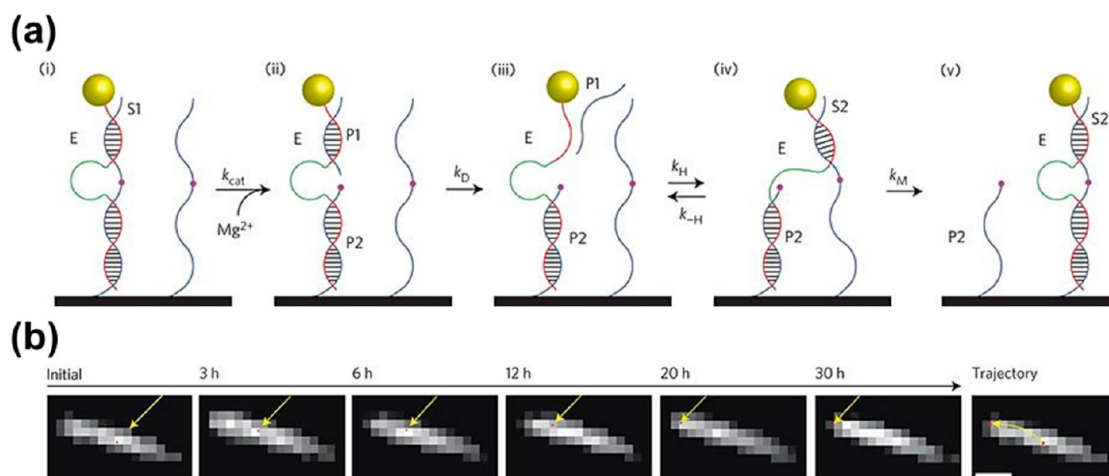


Figure 6. (a) Schematic of a DNA enzyme-based molecular machine that walks autonomously along a RNA-functionalized carbon nanotube track (black) carrying a CdS nanoparticle (yellow). The DNA enzyme (E) here is a synthetic oligonucleotide sequence that contains recognition regions (red) and a catalytically active sequence (green) that cleaves an associated RNA molecule (S1) in the presence of Mg²⁺. Upon cleaving S1, the DNA enzyme processes through a series of conformational changes to hybridize with another RNA molecule (S2) attached to the carbon nanotube, facilitating its movement along the track as the process is repeated. (b) Series of overlaid fluorescence microscopy images (to determine CdS position) and near-infrared nanotube images over 30 h in the presence of Mg²⁺. Scale bar, 2 μm. The DNA motor is capable of carrying inorganic cargo with a maximum velocity of ca. 0.1 nm s⁻¹. The noninvasive optical measurements used here are ideal for monitoring the real-time, *in situ* motion of cargo-carrying DNA walkers and may be applied to other systems for the characterization of various parameters that influence walker motility. Reproduced with permission from ref 91. Copyright 2014 Nature Publishing Group.

enables greater complexity in programmability. Some of the first remarkable reports of functional DNA walkers utilized stepwise mechanics to design systems capable of synthesizing organic molecules or donating cargo.^{89,90} In a more recent example, Choi and co-workers described the fueled, autonomous translocation of CdS nanocrystal cargo by a single-stranded RNA-cleaving DNA enzyme over 3 μm along a RNA-decorated carbon nanotube track while demonstrating robust control over stopping and starting the walker (Figure 6).⁹¹ These proof-of-principle designs for DNA walkers show promise for DNA-based circuits, nanorobotics, and cargo transport, supported by quantitative control over rates for complementary strand displacement reactions.^{92,93} Still, these complicated mechanical systems have generally been plagued by slow kinetics and poor overall performance. The operational yields of complementary strand hybridization or displacement reactions that facilitate the progressive and repetitive movement of many DNA walkers are generally lower than the elementary reactions that take place outside the context of complex DNA architectures.⁹⁴ Considerable effort has been directed toward improving the operational yield of DNA walkers to improve reliability, motility, and control by targeting various parameters that influence their mechanics.^{95,96} For example, Nir and co-workers recently demonstrated a two orders of magnitude increase in the operational yield of a DNA walking device through mechanistic investigation of oligonucleotide strand fuel removal and fuel addition reactions to prevent undesirable trapped states.⁹⁷ Nevertheless, further

improvements in walking speed, yield, and fuel optimization may be necessary for efficient and practical transport and assembly of molecular and nanoscale cargo. Maintaining autonomy with increasingly complex programmability in the design of walkers and tracks is a challenging task but will help DNA walkers move beyond the initial steps that have been taken to convert these nanomechanical devices into useful machines.^{98,99}

Nanostructure Functionalization. The intelligent functionalization of larger organic or inorganic nanostructures with small molecular switch and rotor components, as well as complex DNA assemblies, further expands the versatility of these dynamic systems for applications such as drug delivery and to tune the chemical and physical properties of the hybrid materials.^{100,101} Exemplary demonstrations of artificial molecular machinery that employ functionalized nanostructures are mesoporous nanocrystals modified with molecular nanoimpellers, valves, or gates for the capture and release of cargo with external control.¹⁰² Numerous switch motifs have been utilized as gatekeepers to control payload release from these versatile materials including rotaxanes,¹⁰³ pseudorotaxanes,^{104,105} DNA molecules,^{106,107} coumarins,^{108,109} and azobenzenes.^{110,111} Besides the necessity for biocompatibility, tissue specificity, and high loading capability, to implement these systems *in vivo* for biomedical applications such as controlled drug release, noninvasive actuation mechanisms are also required because some stimuli may be detrimental to biological environments.¹¹² In a recent example, a nanoimpeller system developed by

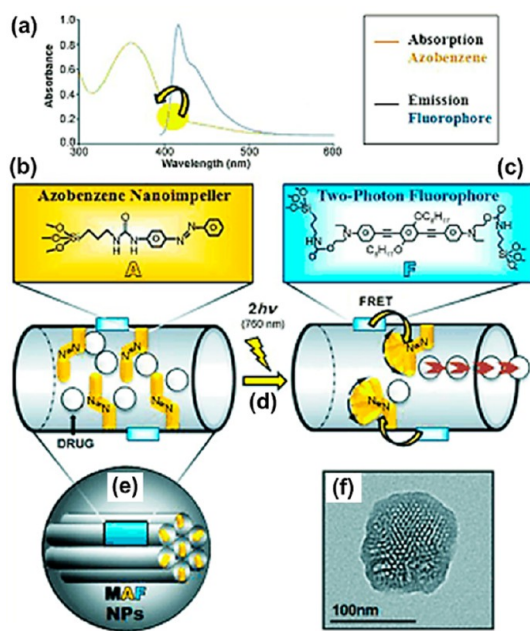


Figure 7. Two-photon excitation (TPE) of a fluorophore to facilitate Förster resonance energy transfer (FRET) to photoisomerize azobenzene nanoimpellers on mesoporous silica nanocrystals and subsequent cargo release. (a) Overlap of the emission spectrum of the fluorophore and absorption spectrum of the azobenzene nanoimpeller enables FRET. (b) Structure of the azobenzene moiety. (c) Structure of the two-photon fluorophore. (d) Photoisomerization of azobenzene using two-photon (760 nm) excitation of the fluorophore. (e) Schematic of the mesoporous silica nanocrystal. (f) Transmission electron microscopy image of a single nanocrystal. Light-activated nanovalves that utilize near-infrared irradiation such as this TPE-based mechanism show promise for targeted drug delivery applications and should be further explored to extend their scope. Reproduced with permission from ref 113. Copyright 2013 Wiley.

Croissant *et al.* utilizes azobenzene photoisomerization as a driving force to release the anticancer drug camptothecin from mesoporous silica nanoparticles (Figure 7).¹¹³ Contrary to classic designs in which azobenzene *trans* to *cis* isomerization is triggered by ultraviolet (UV) light, which is harmful to living cells, this prototype system is based on two-photon excitation (TPE) of a fluorophore with near-infrared (NIR) light. The use of NIR light facilitates isomerization of the azobenzene moieties through Förster resonance energy transfer (FRET) from a nearby fluorophore. Isomerization of the azobenzene nanoimpellers subsequently kicks out the camptothecin cargo, leading to cancer cell death *in vitro*. Using TPE with NIR light to trigger drug release from mesoporous nanoparticles has not yet been extensively explored but offers the benefits of deeper tissue penetration in the biological spectral window (700–1000 nm) and lower scattering loss.^{114,115} The TPE-based designs illustrate how the actuated mechanics of photoswitches can be tailored by their immediate surroundings by coupling simple switches or rotors to their nanostructured environment, provided that the fluorophores have large two-photon

absorption cross sections and sufficient emission quantum yields (>0.5) for FRET.

The integration of switchable molecular systems with inorganic nanostructures and nanoparticle assemblies also enables the manipulation of the hybrid material's optical properties *in situ*. Two common methods to direct the optical properties of nanostructured materials are the active tuning of refractive indices at the surface of plasmonic nanoparticles functionalized with switchable molecules^{116–118} and physically modulating interparticle distances or orientations.^{119–123} Using the latter strategy, Willner and co-workers have designed a myriad of hybrid DNA-based tweezers, catenanes, and rotaxanes functionalized with gold nanoparticles or quantum dots, whose interparticle distances can be directly manipulated with stimuli including pH, metal ions, and oligonucleotide strands.¹²⁴ The switchable mechanical control over these hybrid assemblies is accompanied by unique spectroscopic features as a result of plasmonic coupling between gold nanoparticles, chemiluminescence resonance energy transfer between quantum dots, or the photoluminescent properties of attached fluorophores.^{125–127} Increasing the modularity and dimensions of DNA-based nanomechanical assemblies in this manner has enabled exceptional function; still, challenges remain as the increases in size and complexity of devices may be accompanied by lower synthetic yield and product heterogeneity.^{128,129}

INCREASING DIMENSIONALITY AND HIERARCHICAL ORGANIZATION

Linear Assemblies. The actuated inter- or intramolecular motion of small individual switch and rotor components occurs on the Ångström to nanometer scales. In order to perform macroscopic work, it would be useful to harness the synchronized mechanics of ordered ensembles of molecules in which the collective action translates into motion orders of magnitude larger than that of individuals. This hierarchical organization is exemplified by skeletal muscle tissue. Sarcomeres, the basic repeating units throughout muscle cells, are composed of interdigitated myosin and actin filaments. The sliding of actin along myosin is facilitated by the walking of globular motor proteins attached to cross-bridges between the filaments. This motion generates tension and is responsible for the linear contraction and expansion of each sarcomere. Analogously, MIMs exhibit practical architectures for the building blocks of synthetic molecular muscles due to their mechanostereochemistry.¹³⁰ In particular, bistable daisy-chain rotaxanes, which are composed of two interlocked cyclic dimers, display muscle-like contraction and expansion upon switching (Figure 8a). Many stimuli may be used to actuate motion in these efficient and versatile switches including pH, redox reactions, light, solvent, and ions.^{131–135} Efforts have

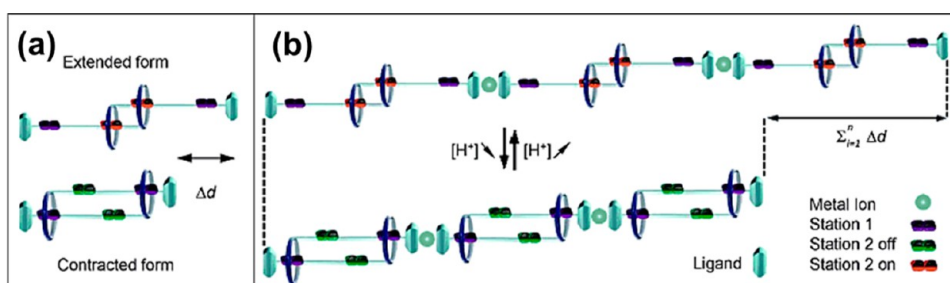


Figure 8. (a) Bistable daisy-chain rotaxane. (b) Metallo-supramolecular polymer of multiple pH-switchable daisy-chain rotaxanes. The culmination of contraction or extension by individual monomers results in global changes in large contour length of the polymer on the order of microns. Reproduced with permission from ref 138. Copyright 2012 Wiley.

been made to polymerize daisy-chain rotaxanes into linear assemblies with varying success.^{136,137} In one of the most remarkable examples, Giuseppone, Buhler, and co-workers demonstrated a metallo-supramolecular polymerization process to combine thousands of pH-switchable daisy-chain rotaxanes.¹³⁸ The polymers demonstrated global changes of contour length of approximately $6\ \mu\text{m}$ (Figure 8b). This contraction is on the same order of magnitude as that observed in sarcomeres. Subsequently assembling these chains into ordered fibers and bundles similar to the hierarchical assembly of sarcomeres in myofibrils and their attachment to surfaces will be a significant accomplishment toward enhanced engineering of artificial muscles from small switch components.

Another molecular switch motif that holds promise for artificial muscles through linear polymerization is the azobenzene chromophore. By incorporating azobenzene within the main chain of a linear assembly, the culmination of modest dimensional changes of merely a few Ångströms for each chromophore can result in dramatic changes in the contour length of the polymer. Utilizing this strategy, Gaub and co-workers demonstrated the capability of individual polyazobenzene peptides to perform mechanical work by tethering one end of the chain to a substrate and the other to a flexible cantilever to measure the force exerted by the contracting polymer upon photoisomerization.¹³⁹ The extent of polymer deformation, and thus the usefulness of the molecules for optomechanical applications, depends on both the conformational rigidity of the backbone and minimization of electronic coupling between azobenzene moieties.¹⁴⁰ The synthesis of rigid-rod polymers that include azobenzene within a poly(*para*-phenylene) backbone is one strategy to maximize photodeformation, enabling accordion-like compression and extension of chains upon cycling with UV and visible light (Figure 9a).¹⁴¹ Lee *et al.* demonstrated that these single-chain polymeric assemblies may even exhibit crawling movements when deposited onto an octadecylamine-modified graphite surface and imaged with scanning force microscopy (Figure 9b).¹⁴² Chemically or physically cross-linked supramolecular assemblies of these linear photomechanical polymers

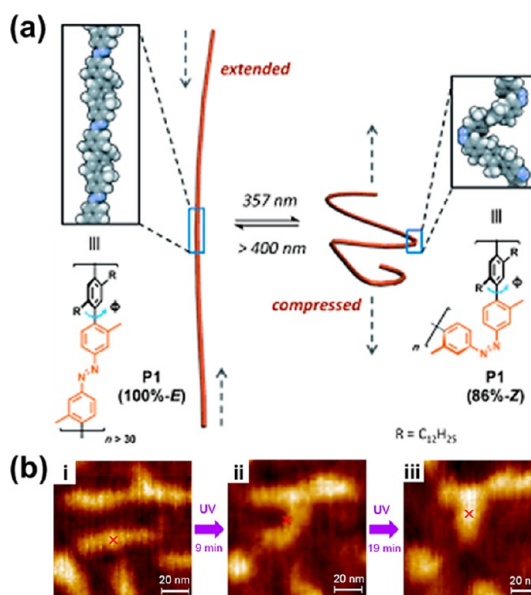


Figure 9. (a) Schematic of a main-chain azobenzene-containing polymer (P1; $R = \text{C}_{12}\text{H}_{25}$) with a poly(*para*-phenylene) backbone. Irradiation with UV or visible light facilitates photoisomerization of azobenzene and conversion to the compressed and extended conformations, respectively. Reproduced with permission from ref 141. Copyright 2011 Wiley. (b) Scanning force microscopy images of P1 deposited on a modified graphite surface. The polymer crawls along the surface as it contracts upon UV irradiation. Demonstrating control over movement direction, and the functionalization or tethering of the polymer strands to scaffolds may enable the macromolecules to perform work by lifting weights or transporting cargo. Reproduced from ref 142. Copyright 2014 American Chemical Society.

may be envisioned to behave as actuators, to lift weights, and to perform other types of work with greater resistance to deformation fatigue than individual strands.¹⁴³ For example, Fang *et al.* reported using a simple melt spinning method to fabricate hydrogen-bonded cross-linked fibers of azobenzene-containing main-chain polymers that were prepared *via* a Michael addition reaction (Figure 10).¹⁴⁴ The authors also investigated the photoinduced mechanical properties of the fibers, reporting a maximum stress generated by a single fiber of 240 kPa upon UV irradiation at 35 °C. This force is similar to the maximal tension forces of

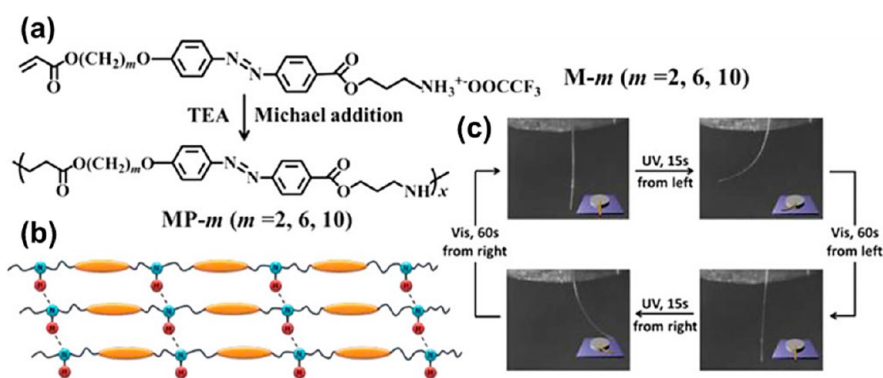


Figure 10. (a) Synthetic route and chemical structures of acrylate-type azobenzene monomers. (b) Supramolecular hydrogen-bonding interactions between main-chain polymers to facilitate physical cross-linking. (c) Photographs of a polymeric fiber fabricated by simple melt spinning. The fiber reversibly bends upon irradiation with UV and visible light. The fibers demonstrate robust photodeformation fatigue resistance and high thermal stability and show promise for applications as photomechanical actuators. Reproduced from ref 144. Copyright 2013 American Chemical Society.

some chemically cross-linked azobenzene-containing polymer fibers and even human striated muscles (ca. 300 kPa).¹⁴⁵

Two-Dimensional Assemblies and Surface Functionalization.

The aforementioned systems describe molecular switches, rotors, and motors in relative isolation. However, without a suitable frame of reference, even the contraction and extension over dramatic micron length scales by polymerized chains of functional rotaxanes is difficult to utilize for practical applications. Complicating matters, to leverage the mechanical motion of ensembles of molecules, some director is mandatory to overcome the chaotic application of force. Similar to Archimedes' need for a place to stand to move the Earth, a surface may be utilized to instill directionality to harness the power of large numbers of molecular machines. Two-dimensional coverage by molecular switches and rotors on planar surfaces provides advantages over isolated molecules or functionalized nanoparticles by facilitating the manipulation of physical and chemical properties of a material at the micro-, meso-, and macroscales. For example, through the amplification of collective molecular mechanical motion, the integration of small-molecule switches and rotors into ordered arrays has resulted in dynamic control over work function, refractive index, and surface wettability.^{146–150} In more obvious demonstrations of performing work, the cumulative nanoscale movements of stimuli-responsive rotaxanes assembled on metal surfaces have been harnessed to move liquid droplets uphill or to bend flexible microcantilever beams.^{151–155} Micropumps that are capable of establishing a steady flow of liquid or small particles may also take advantage of surface functionalization by molecular machines for microfluidics or drug delivery.¹⁵⁶ Molecular pumps based on host–guest interactions composed of cyclodextrin and azobenzene designed by Sen and co-workers perform such a function by external stimulation with light.¹⁵⁷ These hybrid systems are organized within gels or adsorbed

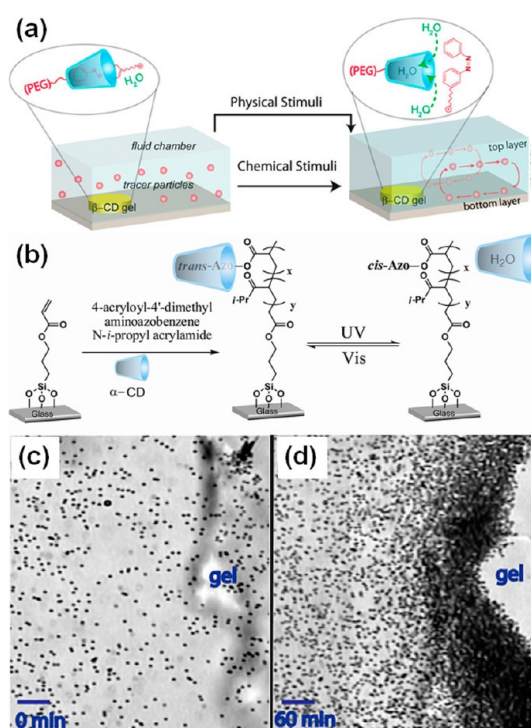


Figure 11. (a) Schematic of a dual-responsive micropump on a glass surface. Light or chemical stimuli may be used to induce fluid flow by a β -cyclodextrin–polyethylene glycol (β -CD-PEG) gel upon isomerization of the azobenzene moiety. (b) Schematic of the direct functionalization of glass surfaces by covalently tethering azobenzene-containing molecules. Reversible formation or disassociation of the host/guest complex with α -cyclodextrin results in fluid pumping. (c) Optical microscopy image of tracer particles in solution above a β -CD-PEG gel on a glass surface before irradiation. (d) Optical microscopy image of tracer particles accumulating at the edge of a β -CD-PEG gel after irradiation with UV light for 1 h. Scale bars, 50 μm . The reversibility of the host/guest interaction makes the design particularly appealing for rechargeable microdevices. Reproduced from ref 157. Copyright 2013 American Chemical Society.

directly on glass substrates (Figure 11a,b). Upon UV light absorption, azobenzene molecules isomerize and leave their cyclodextrin hosts. The created cavity is then promptly filled with water molecules. The amplified and

collective actions of the multitude of neighboring pumps creates a steady flow of fluid around the surface at the rate of *ca.* $2 \mu\text{m/s}$ (Figure 11c,d). The pump can also be activated by chemical stimuli and recharged by visible light irradiation. Despite these impressive examples, there exist few reports of integration of molecular switches and rotors in planar assemblies because of the challenging design rules that accompany surface functionalization, as described below.

Self-assembled monolayers (SAMs), Langmuir–Blodgett (LB) films, and layer-by-layer (LbL) assemblies are all well-understood organic thin-film technologies that can be utilized to fabricate nanoscale functional surfaces.^{158–160} Within SAMs, intermolecular distances, molecular orientation, and substrate–molecule interactions strongly influence whether assembled switches and rotors retain their functionality due to the varied chemistries of their interfaces.^{161,162} Physically and electronically decoupling these functional moieties from surfaces or from neighboring molecules is often necessary to avoid steric constraints or quenching of excited states.^{163–168} For example, molecular rotors can be tethered such that the axis of rotation is aligned parallel or perpendicular to the surface, in either altitudinal or azimuthal orientations, respectively. Feringa and co-workers reported the tunable and reversible wettability of gold surfaces modified with SAMs of altitudinal rotors based on light-driven overcrowded alkenes bearing perfluorinated alkyl chains (Figure 12a).¹⁶⁹ Taking advantage of unhindered rotation enabled by the superior altitudinal orientation of the rotor units dramatically modified the surface energy with resulting water contact angle changes of as much as $8\text{--}22^\circ$ owing to differences in the orientation of the hydrophobic perfluorobutyl group (Figure 12b). The photoconversion efficiency and rotation speed of these surface-bound rotors are still generally lower than for free molecules in solution, highlighting how proper spatial arrangement and sufficient room to rotate are necessary parameters to optimize for these dynamic molecular motifs to retain their large-scale functionality.¹⁷⁰

The design rules to retain functionality and to understand substrate–molecule and intermolecular interactions of MIMs that self-assemble on surfaces are not as well understood. Rotaxanes may be covalently modified with thiol or disulfide tethers to enable binding to noble metal surfaces, providing a platform for potential applications in diverse areas including molecular-scale electronics and nanoelectromechanical systems.^{152,154,155,171} However, many rotaxane and pseudorotaxane motifs have poorly defined orientations or conformations when tethered to surfaces due to their flexibility, making it difficult to predict conditions for reproducible self-assembly.¹⁶⁸ Heinrich *et al.* recently demonstrated that tight packing may be advantageous for the efficient switching of many

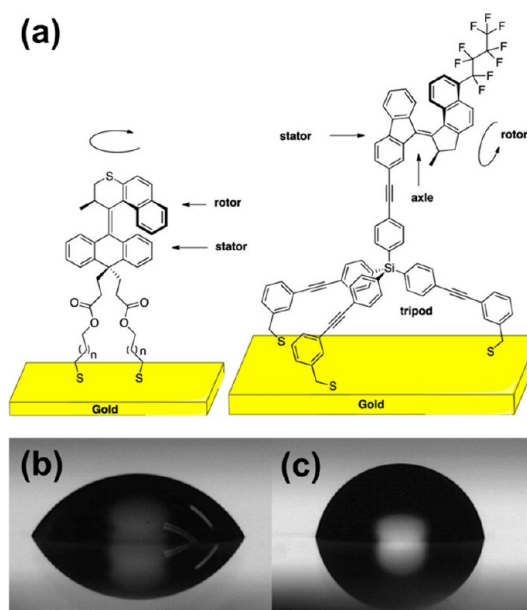


Figure 12. (a) Molecular rotors based on overcrowded alkenes attached to a gold surface in azimuthal (left) and altitudinal (right) orientations. (b) Water droplet on a gold surface functionalized with self-assembled monolayers of overcrowded alkenes in the *cis* conformation bearing perfluorinated alkyl chains. The hydrophobic perfluorobutyl group on the rotor is hidden from the interface, resulting in a contact angle of $60 \pm 1^\circ$. (c) In the *trans* conformation, the hydrophobic group is exposed to the interface, resulting in a water contact angle of $82 \pm 1^\circ$. The altitudinal orientation of the rotor and the tripod tethering unit are advantageous molecular structures that may be applied to other functional surfaces based on self-assembled monolayers of molecular machines. Reproduced from ref 169. Copyright 2014 American Chemical Society.

rotaxane molecules on the surface (Figure 13a).¹⁷² The authors used angle-resolved near-edge X-ray absorption fine structure (NEXAFS) spectroscopy to study cooperative effects in chemically switchable rotaxanes deposited on gold surfaces by LbL self-assembly. Linear dichroism effects in NEXAFS spectra reflect preferred ensemble molecular orientation, and therefore, the disappearance or enhancement of linear dichroism may be used to monitor conformational changes on surfaces. Densely packed monolayers of rotaxanes exhibited a pronounced increase in linear dichroism upon switching, indicating conversion of one ordered surface structure into another (Figure 13b). On the other hand, dilute monolayers in which the rotaxanes motifs were less densely packed displayed negligible linear dichroism effects both before and after application of chemical stimuli (Figure 13c). These results suggest that, in this system, properly designed densely packed rotaxanes can switch in a coupled manner, in contrast to previous reports of interference of proximal, randomly assembled surface-bound rotaxanes.¹⁶⁸ While inducing conformational change in a single rotaxane is unfavorable in the densely packed array, once a small number of molecules have converted to their isomeric forms, it becomes less sterically demanding for

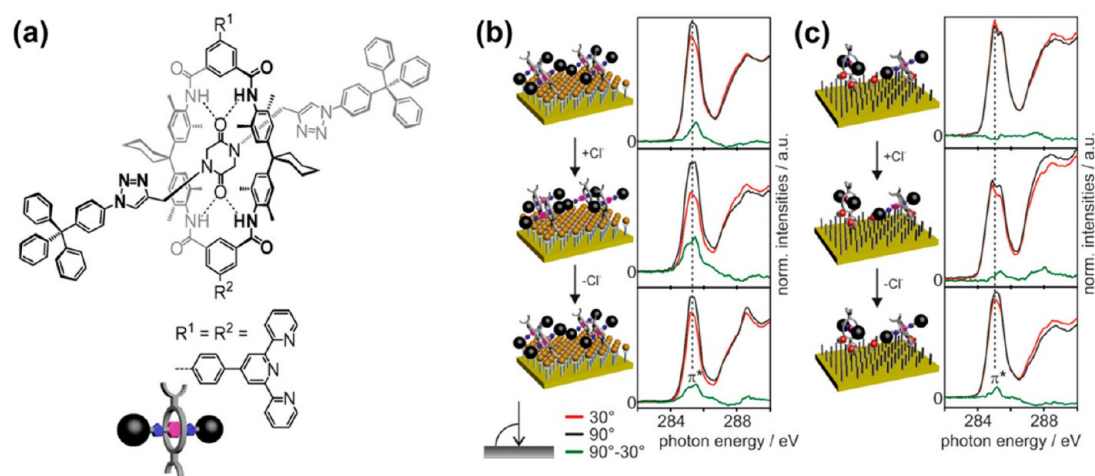


Figure 13. Molecular structure and angle-resolved near-edge X-ray absorption fine structure (NEXAFS) spectroscopy of layer-by-layer assembled switchable rotaxanes on gold surfaces. (a) Rotaxane molecule under investigation containing tritylphenyl stopper groups on the rod and terpyridine side chains attached to a functionalized tetralactam macrocycle. Angle-resolved NEXAFS spectra of (b) a densely packed rotaxane monolayer on a rigid pyridine-functionalized self-assembled monolayer (SAM) of (*E*)-4-(pyridin-4-yl)stilbenethiol (PST) and (c) a dilute rotaxane monolayer on a terpyridine-terminated dodecanethiol/decanethiol mixed SAM. The NEXAFS results are depicted from top to bottom: before chloride addition, after chloride addition, and after chloride removal. NEXAFS spectra were obtained for the incident synchrotron light beam at 30 and 90° angles (red and black lines). The difference between the two spectra is shown in green. Linear dichroism effects in (b) suggest the coupled motion of densely packed rotaxane monolayers, underscoring the advantage of lateral order and molecular alignment for functional surfaces based on large mechanically interlocked molecules. Reproduced from ref 172. Copyright 2015 American Chemical Society.

neighboring molecules to switch, resulting in rapid growth of newly ordered domains. This cooperative switching scenario is analogous to that observed in densely packed SAMs of molecules containing azobenzene headgroups.^{173,174} Applying similar design principles to other assemblies of switch and rotor motifs on surfaces to facilitate cooperative switching mechanisms would be advantageous for faster, more robust, and more energy-efficient molecular machines.

As described above, the design and fabrication of organic thin films of molecular switches or rotors on surfaces that retain switching yields comparable to those of free molecules in solution remain challenging tasks. Complicating matters, the favored molecular orientations, steric considerations, and intermolecular electronic coupling strengths are different for each system, whether the molecules are chemically adsorbed directly on surfaces or within polymeric assemblies. Nevertheless, the successful demonstrations of predictable surface attachment of molecular machines that give rise to directed and defined stimulus-induced function provide promising examples for applicability in the future. New directions may take advantage of combining bottom-up molecular assembly techniques with top-down patterning methods to design novel materials with controllable features from sub-100 nm to the centimeter scale.^{175–179} Patterning diverse switch and/or rotor components side-by-side with precise two-dimensional control may give rise to new surface functionality with molecular packing density gradients or multiplexed domains with various available actuation mechanisms.

Three-Dimensional Assemblies and Crystals. The integration of dynamic molecular switches and rotors into three-dimensional architectures is a natural and desirable extension of supramolecular assemblies, yielding dynamic materials with controllable properties in all directions. Some of the first three-dimensional molecular machines were fashioned from polymeric materials or photomobile crystalline arrays, such as light-powered walkers, rollers, and belt/pulley motors by Yamada *et al.*^{180,181} These examples utilized azobenzene moieties within liquid-crystalline elastomers, in which mechanical strain is strongly correlated with the characteristic orientational order of the mesogens. The incorporation of photoswitching molecules into liquid-crystalline polymer networks enables the amplification of, and greater control over, the reversible photodeformation of actuators. Notable advances in the field of photomechanical polymers include the development of more complex movement patterns, designs that respond to a broader range of stimuli, and better addressability and spatial precision.^{182–184} Katsonis and co-workers recently described impressive control over the helical motion of azobenzene-containing liquid-crystalline polymer springs, mimicking the extensile function of plant tendrils.¹⁸⁵ Unlike previous reports of twisting motion within photomechanical crystalline systems, in which the helical deformations are dictated by the facets that are irradiated with UV or visible light, the handedness and modes of coiling motion can be preprogrammed by including chiral dopants and controlling the relative orientation of the aligned liquid crystals within each spring, respectively.¹⁸⁶

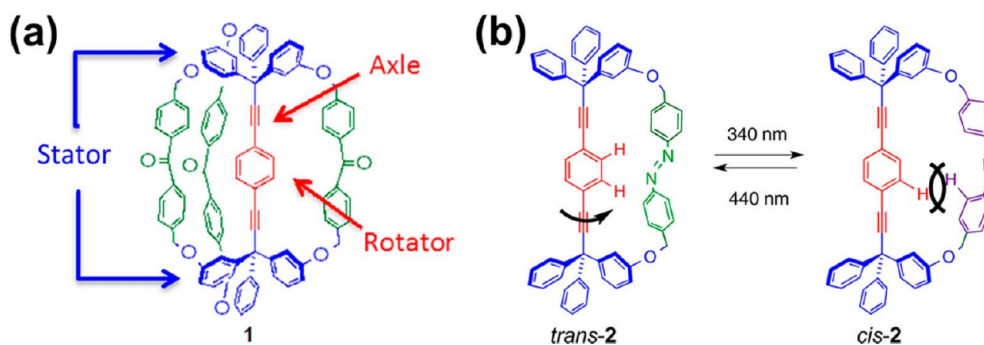


Figure 14. (a) Molecular gyroscope that contains benzophenone motifs (green) that bridge the structure from one stator to the other. (b) Azobenzene-bridged molecular gyroscope. In (a) and (b), the rotation of the central phenylene may be hindered by collapse of the bridge toward the rotor. The use of an azobenzene motif as a bridge enables control over the rate of rotation using UV or visible light to convert the switch, or brake, between *trans* and *cis* conformations. Reproduced from ref 203. Copyright 2014 American Chemical Society.

While polymeric materials offer ease of processing and fabrication, crystalline motifs offer a path to near-perfect three-dimensional arrangements of dynamic molecular building blocks, as well as a facile means to monitor the motion of the crystals using nuclear magnetic resonance (NMR) and X-ray diffraction. Furthermore, energy transduction in crystals is faster, and actuating motion is generally of larger magnitude compared to polymeric assemblies because rigidly packed molecules have to work as an assembly to function, whereas in a less-ordered medium, motion of the same molecular switches may be less directionally biased and ultimately less efficient. Often derided as a “chemical cemetery” after Leopold Ruzicka’s famous remark, crystal machines have witnessed a remarkable resurgence in recent years with discoveries of controlled or spontaneous actuation, reversible or irreversible movements, and reactivity.^{187–189} Research efforts toward molecular machines fashioned from crystals can be subdivided into two broad classes: one in which movable elements are present in the crystal lattice and the other where the entire crystal becomes a machine.

The former class of crystalline machines is composed of amphidynamic crystals that most often incorporate rotors into a lattice, thereby maintaining macroscopic order. If enough free volume is present, the molecules retain their rotational degrees of freedom and can spin with varying frequencies within the range of hertz to gigahertz. Such rotation demonstrates promise as a new class of mechanical switches, compasses, and gyroscopes.^{190–194} When the rotor units contain an electric dipole, amphidynamic crystals may also provide an avenue for tunable dielectrics.^{195–197} Solid-state NMR techniques are useful characterization methods to determine molecular order and the gyroscopic dynamics within amphidynamic crystals when rotors contain atoms that occupy multiple magnetically nonequivalent sites. As a molecule rotates, atoms may exchange positions between these sites, the rate of which is determined

by the rotational potential energy barrier and sample temperature.¹⁹⁸ Features in the NMR spectra at different temperatures provide information about ensemble exchange rates and, therefore, rates of rotation of rotors within the crystalline lattice. Spontaneous rotation is common in crystalline rotors with rotational activation energy barriers greater than $k_B T$ (the available thermal energy). Notable studies in this field have reported on engineering coupling between rotors^{199–201} and controlling the rate of motion by light or chemical input, similar to the design of synthetic brakes for noncrystalline rotors.²⁰² Recently, Commins and Garcia-Garibay developed a molecular gyroscope that utilized a photoactive azobenzene unit tethered on either side of a rotatable phenylene center block (Figure 14).²⁰³ The conformation of the azobenzene switch was shown to exhibit robust control over the rates of phenylene rotation. When the azobenzene brake was in the *trans* conformation, the crystalline assembly rotated 10 times faster than samples containing the *cis* isomer. Sozzani and co-workers demonstrated another sophisticated approach to engineer and to control crystalline rotors using porous molecular crystals.²⁰⁴ The authors demonstrated that permanently porous crystals that incorporate *p*-phenylene rotors were accessible to small-molecule guests such as CO₂ and I₂ in the vapor phase. In particular, the uptake of I₂ altered the molecular environment of the rotors dramatically: the exchange rate decreased by four orders of magnitude from 10⁸ to 10⁴ Hz (Figure 15). The same group also proposed using porous organic frameworks as hosts for molecular rotors due to their large surface areas and pore capacities.²⁰⁵ Comparable to the molecular cocrystals, diffusion of I₂ into the pores resulted in decreased rotation rates by three orders of magnitude at room temperature. Sensing or actuating applications may be envisioned that utilize the resulting influence of small-molecule guests on the rotation rates for the uptake and release of small-molecule guests by these amphidynamic crystals and organic frameworks.

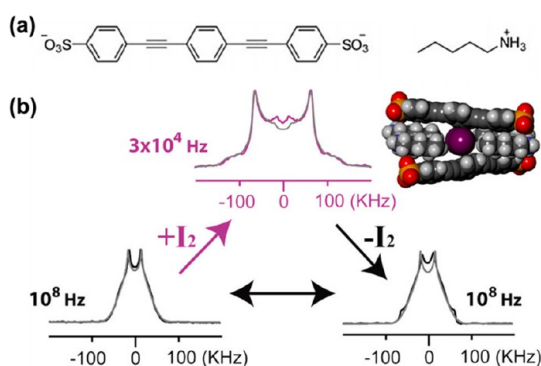


Figure 15. (a) Chemical structures of the components of a porous cocrystal: (left) 4,4'-bis(sulfophenylethynyl)benzene (SPEB) dianion and (right) *n*-pentylammonium (PA) cation. (b) Deuterium nuclear magnetic resonance (^2H NMR) spectra of porous cocrystals in the absence of molecular iodine, I_2 ; after exposure to I_2 in the gas phase; and following removal of I_2 from the crystals. Experimental and calculated spectra are displayed in black or violet, and gray, respectively. The exchange rate reversibly decreased by four orders of magnitude upon uptake of the small-molecule guest, suggesting the use of such crystals for gas phase sensing applications. Reproduced from ref 204. Copyright 2014 American Chemical Society.

While the previously described amphidynamic crystals possess sufficient free volume for rotation of essential structural elements, translational motion within a crystal is much less common. By incorporating rotaxane molecules as organic linkers within a metal–organic framework (MOF), Loeb and co-workers recently succeeded in facilitating the reversible translation of a molecular shuttle inside a solid-state material between two stable states.²⁰⁶ The system contains Zn_4O clusters as the nodes of the MOF and carboxylate struts as structural elements. Individual [24]crown-8 ether macrocycle shuttles could translate between degenerate benzimidazole stations on cross-bar linkers between struts at a rate of 283 Hz at room temperature. Future work to incorporate MIMs within highly dense, crystalline arrays with greater control over the actuation and speed of switching events will provide new potential applications for mechanically bonded host–guest systems with controllable physical and chemical properties in the solid state.

The second approach to fabricate crystalline molecular machines utilizes the entire crystal as an actuator and transfers the external stimulus such as light or heat into mechanical energy, categorized as (a) thermo- and photosalient or (b) photomechanical crystals.^{188,184,207} Thermo- and photosalient crystals most often exhibit spontaneous actuation (jumping) upon heating or irradiation. Thermo- and photosalient crystals developed by Naumov and co-workers harness the energy of polymorphic transformations that occur upon heating in crystals. The effect is driven by extremely rapid anisotropic expansion and contraction of the unit cell axes upon a phase transition that was

found to be 10^4 times faster than in regular crystal-to-crystal phase transformations.²⁰⁸ This class of crystalline compounds comprises a diverse range of materials, including brominated organic molecules, terephthalic acid, and organometallic complexes.^{209,210} Although there exists little directional control or foresight into which compounds will exhibit the effect, the explosive “popcorn” crystals nonetheless exhibit impressive centimeter-scale jumping movements that greatly exceed the crystal dimensions. Light-activated chemical processes within crystals, such as changes in the coordination sites of small ligands or [2 + 2] cycloaddition reactions, have also been shown to result in “popping” under ultraviolet irradiation.^{211,212} Similar to thermosalient materials, little control is possible over “popping” crystals, and thus their utilization as functional molecular machines is difficult to envisage. To circumvent this problem, Sahoo *et al.* developed smart hybrid materials that incorporate thermosalient microcrystallites on flexible sodium caseinate films to impart directionality to the crystals' movements.²¹³ The material represents a successful marriage of crystals with biocompatible polymeric films in one system, combining the benefits of the plasticity of soft polymers and the efficient, fast actuation of leaping crystalline solids.

Alternatively, photomechanical materials move, bend, twist, or curl when exposed to light. Some of the most promising photomechanical crystalline systems for converting light into mechanical work have been proposed by Irie and co-workers and are based on diarylethene photoswitches.²¹⁴ Light absorption triggers pericyclic ring-opening and ring-closing reactions of this photoswitch throughout the crystal and is responsible for expansion and contraction, respectively, of the unit cell that consequently leads to photomechanical bending of the crystal. Structural studies on crystals of diarylethene derivatives link the initial speed of curvature change to crystal thickness.²¹⁵ The bending behavior is also dependent on the crystallographic face that is irradiated, which is attributed to differences in molecular packing. While the geometric change that occurs during the isomerization of a single diarylethene photoswitch is modest, the collective action of arrays of molecules in the crystal lattice can produce macroscopic motion. Cleverly engineered, such actuating crystals can perform work by pushing or lifting objects many times their weight,^{214,216} rotating gears,²¹⁷ or acting as an electrical circuit switch (Figure 16).²¹⁸

Other commonly studied photomechanical crystalline architectures are composed of anthracenes or salicylidene-phenylethylamine molecules. Bardeen and co-workers investigated the [4 + 4] dimerization reaction of anthracenes where the photoreaction results in reversible or irreversible twisting of crystalline microribbons.^{219,220} The curling and twisting motion may be attributed to strain between spatially distinct

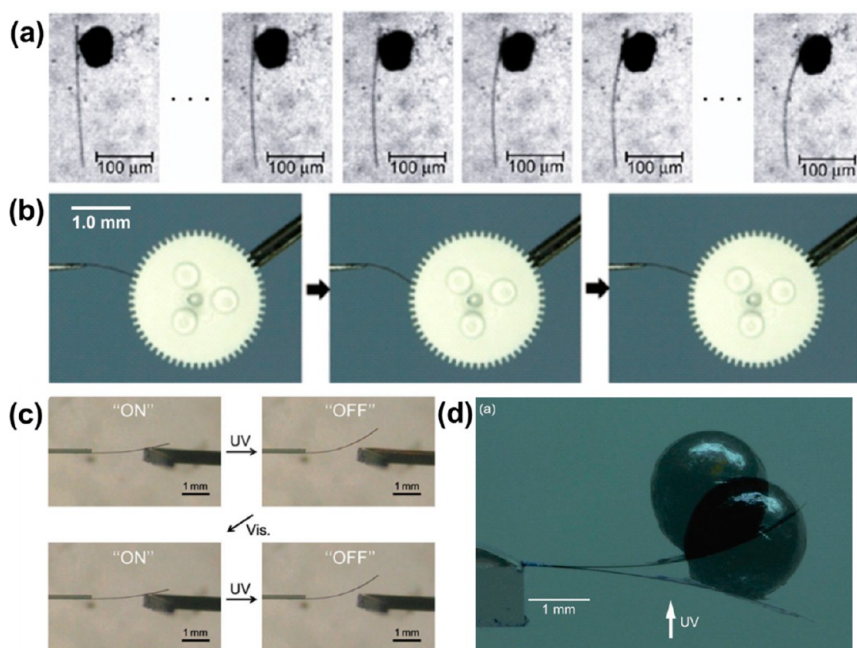


Figure 16. Photomechanical systems based on diarylethene crystals that convert light into mechanical work. (a) Rod-like crystal pushes a gold microparticle that is 90 times heavier than the crystal when irradiated with UV light. Bending of the crystal pushes the microparticle up to $30\ \mu\text{m}$. Reproduced with permission from ref 214. Copyright 2007 Nature Publishing Group. (b) Rotation of gears facilitated by the reversible bending of a crystalline actuator upon UV and visible irradiation. Reproduced with permission from ref 217. Copyright 2012 Wiley. (c) Irradiation of gold-coated diarylethene crystals with UV and visible light enables the ON/OFF photoreversible current switching of an electric circuit. Reproduced with permission from ref 218. Copyright 2015 Royal Society of Chemistry. (d) Superimposed photographs of a crystal cantilever lifting a lead ball with a mass 275 times larger than the crystal upon irradiation with UV light from the underside of the actuator. Reproduced from ref 216. Copyright 2010 American Chemical Society.

reactant and product domains as a result of differential absorption by different regions of the crystal or intrinsic solid-state reaction kinetics.²²¹ Another crystalline molecular machine was proposed by Koshima *et al.* based on photomechanical action in platelike crystals of salicylidenephenylethylamine (Figure 17).²²² These actuators are capable of lifting weights up to 300 times the crystal weight. The motion is linked to geometric changes in the molecules produced upon tautomeric transformation triggered by light absorption and consequent proton migration. Collective reorganization of the molecules within the lattice leads to small uniaxial cell expansion, which in turn results in bending of the crystal.

While the workhorse of many photomechanical studies, the azobenzene chromophore, has been extensively probed as isolated molecules, on surfaces, in polymers, and within liquid crystals, it has been far less studied by the crystalline photomechanical community.^{223–227} This is due, in part, to the sterically demanding *trans* to *cis* isomerization process which may be impeded in a crystal. Surprisingly, Koshima *et al.* demonstrated reversible photomechanical bending of thin *trans*-4-(dimethylamino)azobenzene plates upon ultraviolet irradiation, concluding that isomerization can still occur inside the crystal.²²⁸ That report was followed by a study of thin crystalline plates and needles of pseudostilbenes (azobenzenes with short-lived *cis* states),

which were capable of submillisecond bending and relaxation upon irradiation with visible light.²²⁹ Pseudostilbene bending crystals offer the fastest speed of bending—relaxation cycles as the whole event can take less than a second and is the only system that completely circumvents the need for ultraviolet light to induce isomerization. More recent reports have focused on elucidating the mechanistic aspects of azobenzene isomerization in crystals focusing on *in situ* X-ray diffraction studies of irreversible *cis*–*trans* isomerization in crystals²³⁰ and cocrystals²³¹ of the molecule (Figure 18). These reports demonstrated that *cis* to *trans* isomerization in crystals is mediated by a transient amorphous state. While the sterically demanding azobenzene isomerization reaction requires considerable free volume to occur and is rarely possible in a single-crystal/single-crystal fashion, an amorphization mechanism enables the photochemical reaction to proceed despite the constraints of the crystal lattice. Amorphous intermediates in the crystal were corroborated by the loss of diffraction spots upon irradiation with visible light at low temperature. Remarkably, isomerization within the crystals of azobenzene represents a topotactic process in which the orientation of the resultant *trans*-crystal phase is dependent on the initial crystal orientation and effectively represents template crystal growth directed by light.

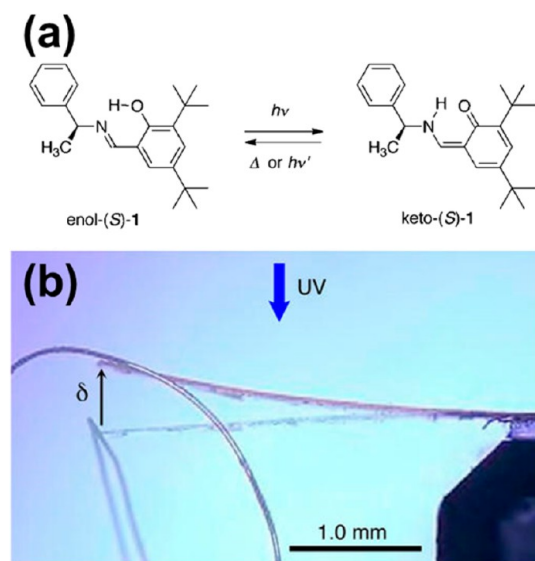


Figure 17. (a) Photoinduced proton transfer in the *S*-enantiomers of chiral salicylidenephenylethylamines upon keto–enol tautomerism. (b) Superimposed photographs of a chiral enol-(*S*)-1 crystal before and after irradiating the top of the crystal actuator with UV light. The crystalline cantilever achieved 26 nJ of work by lifting a 4.00 mg metal ring a height, δ , of 0.65 mm. Various photomechanical lifting work was achieved with different enantiomeric compositions within the crystal: the racemic crystal, enol-(*rac*)-1, achieved 59 nJ of work by lifting a weight with mass 300 times larger than the crystal (not shown). Reproduced from ref 222. Copyright 2013 American Chemical Society.

The growing number of investigations on dynamic molecular crystals that can perform as actuators demands new theoretical models. Various models have been reported in the context of polymer films, rods, or plates, such as the analysis by Warner and Mahadevan on photodeformation of nematic elastomers.²³² However, careful structural and kinetic considerations based on the spatial density and uniform orientations of photoactive molecules must be taken into account for these models to be fully applicable to crystalline systems. While the molecular motifs responsible for crystal motions are diverse, an attempt to unify photomechanical processes was done by Nath *et al.*, who proposed a mathematical treatment of photomechanical crystal bending by accounting for the gradual profile of the product in the crystal, irradiation time, direction and power using the azobenzene dye, Disperse Red 1, as a model compound.²³³ The model is applicable for any photomechanical crystal system and allows an easier comparison between the different platforms for efficiency, modulus, stress, and other parameters critical for optimization of the process for practical use. Ultimately, with the help of theoretical frameworks and empirical data, the goal of future development of photomechanical systems needs to be directed toward robust and fatigue-resistant designs capable for even faster and reliable actuation over thousands of cycles.

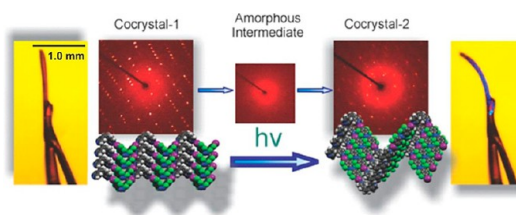


Figure 18. Amorphous phase-mediated azobenzene isomerization and photomechanical bending in a cocrystal ($1.2 \text{ mm} \times 90 \mu\text{m} \times 20 \mu\text{m}$). The cocrystal contains a 1:1 ratio of a halogen-bond acceptor (*cis*-1,2-bis(4-pyridyl)ethylene) and halogen-bond donor species. Bromine or iodine atoms on perfluorinated azobenzenes act as halogen-bond donors, forming a linear interaction with the pyridine nitrogen atoms on the halogen-bond acceptor. Irradiation of the cocrystals with a 532 nm laser facilitates *cis* to *trans* isomerization of the halogen-bond donors, *via* amorphous intermediates, determined by X-ray diffraction. Reproduced with permission from ref 231. Copyright 2014 Royal Society of Chemistry.

CONCLUSIONS AND OUTLOOK

In the quest to synthesize and to assemble genuine molecular machines, the efforts of the scientific community have evolved from mere observation and design of dynamic molecular building blocks to understanding the mechanisms of their function. A necessary advance is the intelligent combination of the available building blocks to prepare useful and functional molecular-driven machines. Thus far, a wide variety of systems have been proposed that perform some kind of action on their environment, and the initial demonstrations of the application are promising. While their size and scope are dramatically different, the underlying mechanisms of action are remarkably similar. Whether linear motion, rotation, bending, or twisting is involved, they are all powered by stimulus-driven reversible chemical reactions. In some cases, like photoactive catalysis, the work is performed at the single-molecule level. However, controllable and measurable macroscopic effects such as changes in surface energy or the bending of crystalline films can be achieved through the collective, amplified motion of many molecules. It should be kept in mind that it is not a simple act of preparing a binary switch or a bending, expanding, or contracting material that constitutes a machine; the efforts should rather be directed toward the reversible execution of a deliberate function.

In combination with the continued efforts in the design, synthesis, and assembly of novel molecular architectures, the characterization and analysis of stimulus-driven motion by new systems should include an assessment of the efficiency and reproducibility, and thus the viability, of a molecular machine as an invention.^{234,235} Molecular machine designs must be highly resistant to degradation over long periods of time and/or numerous actuation cycles, and objectively addressing these requirements is critical for analyzing performance. This robustness is important, for example, for *in vivo* application of DNA-based

assemblies that are susceptible to biodegradation by nucleases or repetitive UV irradiation cycles of crystal actuators. Measuring the efficiency at each step of energy transformation, from that of elementary switches and rotors to the entire assemblies, would also be highly beneficial, and results should be disseminated as a normal part of reported research findings. In photoinduced processes, this can be easily determined by calculating quantum yield or photoisomerization cross sections. Quantitative assessment of the forces generated by stimulus-induced motion by individual molecules or hierarchically more complex assemblies is also desirable where applicable.

The most glaring question that remains in the field is in what environments, or at what length scales, molecular machines will find truly impactful applications. While the hierarchical assembly of small switch and rotor components may provide more opportunities for externally controlled motion at greater length scales, will they be able to compete with other materials? For example, the impressive performance of electrochemically or thermally driven shape-memory polymer fibers and hybrid carbon nanotube bundles may make those materials more viable alternatives for commercial artificial muscles than linear chains of molecular switches.^{236,237} Likewise, the combination of mechanical actuators or sensors with integrated circuits based on microelectromechanical systems (MEMS) offers advantages over crystalline molecular machines due to the compatibility of microfabrication processes with complementary metal–oxide semiconductor (CMOS) technology on the scale of 1 μm to millimeters. To find their niche in similar applications, molecular machine designs must take advantage of alternative actuation mechanisms and offer more efficient energy transduction. Ultimately, the candid assessment of the potential applicability for leveraging the stimulated motions of molecules is more important than ascribing the label of a “machine”. With this admission in mind, the necessity to demonstrate applications that harness the power of molecular machines to perform work on their environment presents an exciting and unique opportunity for researchers. Understanding the chemistry and physics that govern this motion will be a continuous challenge as designs become increasingly complex. Nevertheless, the future of this field will benefit from the impressive diversity and creativity of individual molecular and assembly motifs that may be used to direct motion from the nano- to the macroscale.

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