

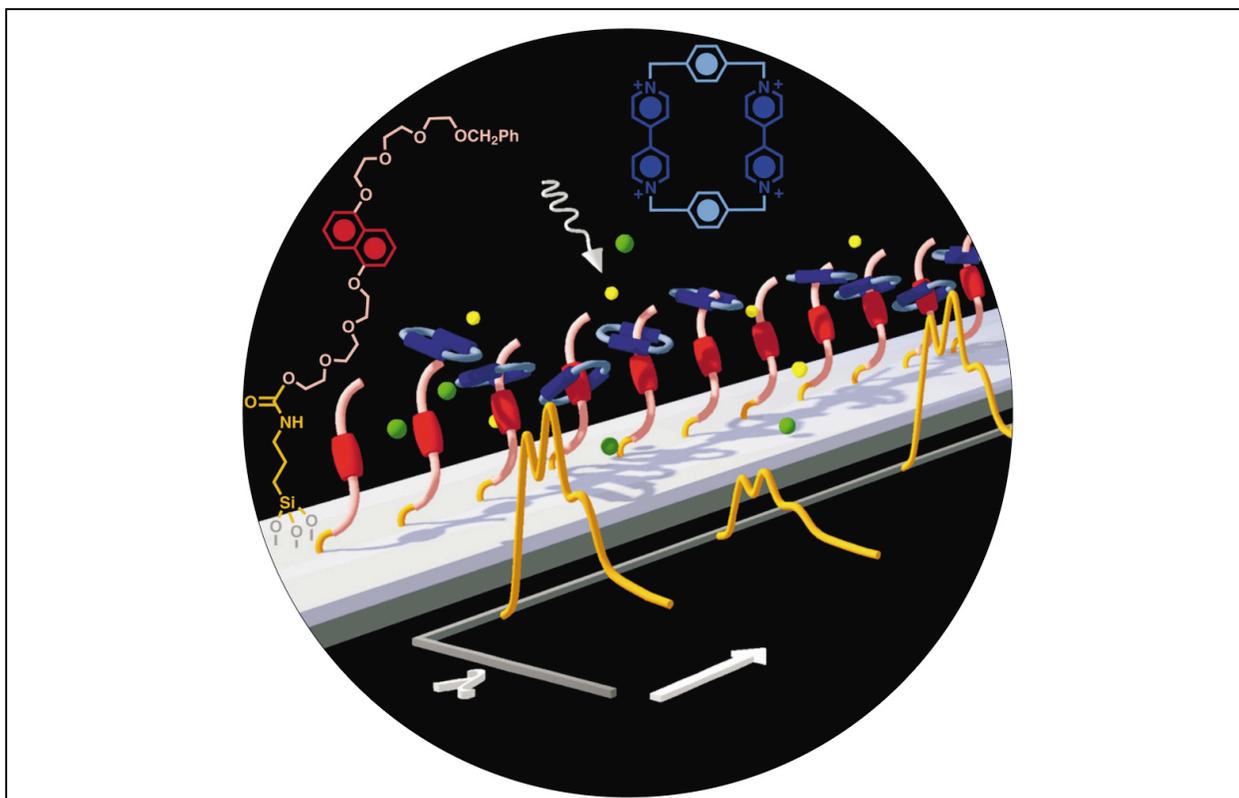
Artificial Molecular Machines and Devices

NSF NIRT Grant ECS-0103559

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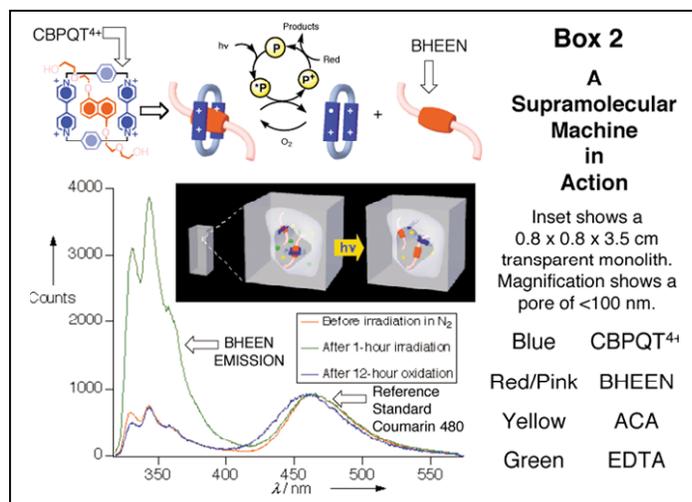
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The objectives of this program [1] of research are to demonstrate the transduction of force and motion from the relative mechanical movements of the components present in artificial motor-molecules into micro- and mesoscale mechanical motion. In order to realize these objectives, a coordinated effort that integrates a bottom-up approach based on the self-assembly and self-organization of artificial motor-molecules with a top-down approach, based on micro- and nanofabrication, is being pursued.



Box 1: Under the spotlight, tethered threadlike polyether chains (pink) intercepted by electron-donating naphthalene units (red) doff and don electron-accepting cyclobis(paraquat-*p*-phenylene) girdles (blue). Their risque actions are revealed by the luminescence of the naphthalene units when the girdles are removed. The temporal sequence (left to right) shows a bare thread donning a girdle then doffing it under the influence of light. The action is attentively monitored by the luminescence spectra. The intensity increases when the girdle is doffed and is quenched when it is donned.

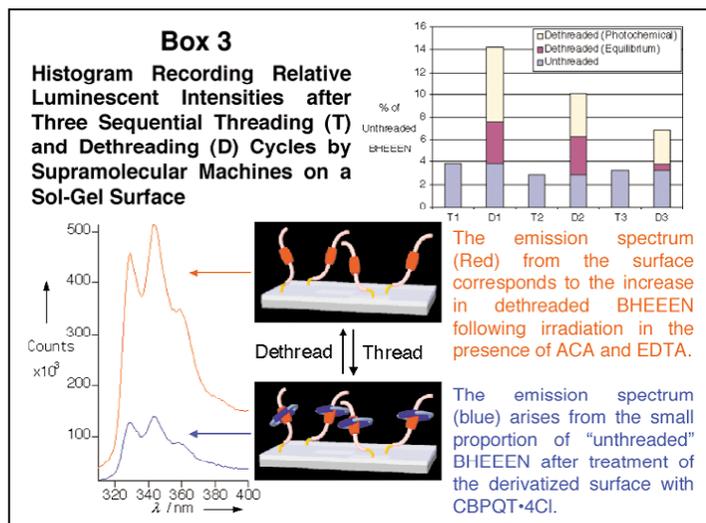
In one particular project [2], we aim to develop molecular valves at the entrances of suitably-sized container from which encapsulated molecules can be released controllably by application of chemical, electrical, or optical stimuli. The molecular valves are being constructed using supramolecular machines housed in porous silica sol-gel that provide a stable, transparent matrix for physically encapsulating the machine in a macroscopic solid. The nanopores filled with liquid will provide the light-driven supramolecular machines with a local solution environment in which they can perform their large mechanical movements. The silica framework provides the microscopic solid support and is transparent to visible light so that the machines can be driven by light.



We have demonstrated (**Box 1**) piston-like motion from a linear artificial motor-molecule that is directly attached onto the surface of a silica film. In this working supramolecular machine [2-9] mounted on a film surface, the piston in the form of a polyether chain, intercepted by a 1,5-dioxynaphthalene ring system, is tethered onto the surface of a sol-gel film and the ring in the shape of the tetracationic cyclophane, cyclobis(paraquat-*p*-phenylene), moves on and off the π-electron rich docking station. Under the cover of darkness, the π-electron deficient

cyclophanes are threaded on the chain, spontaneously forming surface-mounted pseudorotaxanes. The docking process quenches the fluorescence that is normally emitted by the 1,5-dioxynaphthalene station. The driving of the cyclophane off the docking station and along the chain can be photochemically driven (**Box 2**) using either UV light or chemical reagents. The restoration of the naphthalene fluorescence signifies the presence of a piston without a ring. Three consecutive strokes (**Box 3**) of the piston were recorded, illustrating the reversibility of this artificial supramolecular machine [10].

Nanoelectronic actuation requires the transfer under electrical control of the coherent and reversible nanoscale motions of molecular machines assembled on a surface to be actuated through to the micron scale and beyond. The observed piston-like motion augurs well for most of these requirements. Although the device is photochemically driven, light drives an electrochemical process in a manner which is akin to the electrical control that would be used to make most actuators work.



References

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