

Synthesis and Characterization of a light-driven molecular motor

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This project lies in the area of controllable dynamical nanodevices and involves the design, construction, and testing of a light-driven molecular motor. The motor is designed to exhibit unidirectional rotary motion upon the absorption of light, thereby converting electromagnetic energy into mechanical energy delivered to a nanoscale load. The motor consists of two essential parts: (1) a chiral base of C_3 symmetry that creates an dissymmetric force field that is the source of the unidirectional motion; and (2) a photochemically-activated rotor that is trapped in one of three equivalent configurations in its ground state, but free to rotate relative to the base when electronically excited. Among the key features of the molecular motor are: (1) the use of light to control and probe its motion; (2) flexible molecular design of the motor that allows one to adjust its physical properties and thereby enhance its power and directional specificity; and (3) detection of the motor's dynamics in both mobile and immobile environments.

The project has four phases that overlap in time:

Phase I: Synthesis and computational modeling of the basic motor structure

Phase II: Testing of the motor photochemistry and theoretical modeling of its photochemical dynamics

Phase III: Immobilization of the motor on surfaces and spectroscopic probing of its dynamics

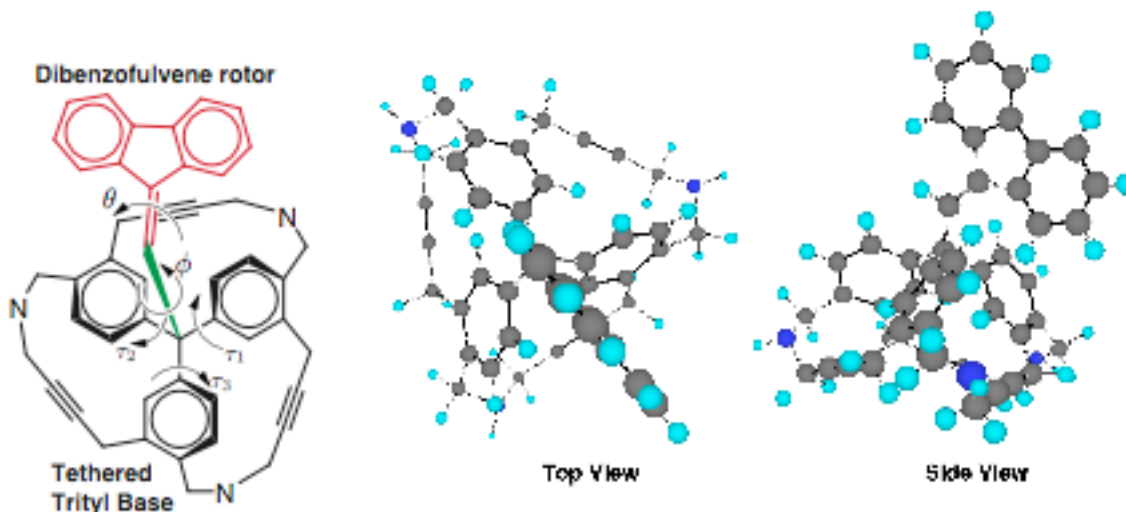
Phase IV: Insertion of the motor into a circular segment of DNA and use of spectroscopy and microscopy to detect supercoiling upon irradiation

Throughout the project, the Bell group will be involved in synthesis of different variations on the basic motor design and in functionalizing the motor for chemisorption to a non-metal surface and insertion into a DNA fragment. Computational modeling carried out by the Frederick group will aid in the design of motor variations to enhance unidirectional motion upon photoexcitation. The Cline group's laser spectroscopy laboratory will be used to measure the photoisomerization quantum yield of various motor prototypes and to polarized spectroscopic detection of surface-immobilized motor molecules. Finally, Cremo's group will undertake splicing the motor into circular DNA and will analyze the degree of supercoiling induced by the dynamics of the motor.

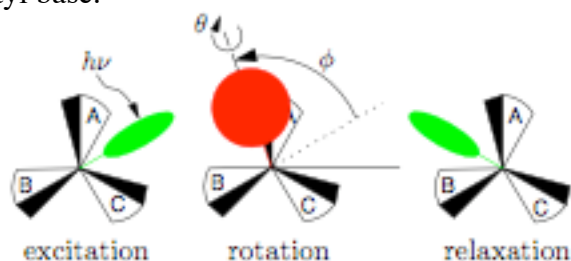
Among the key features of the motor are: (1) temporal control of actuation by pulsed laser light, (2) positional control of the motor using polarized light, (3) rotary frequencies potentially up to 100 MHz using intense laser light sources, (4) the ability to synthetically tailor the motor structure to emphasize specific performance characteristics, and (5) chemical functionalization of the motor for selective incorporation into specific sites of a nanostructure. The synthetic structure is robust over a wide range of thermal and chemical environments, including vacuum.

While a variety of chiral base and chromophore rotor structures are being investigated, most progress to date has been made towards the motor shown in the left panel below. This structure has two components linked by a C-C single bond: (1) a dibenzofulvene "rotor" and (2) a trityl (triphenylmethane) "stator" base. In its minimum energy conformation, the base has a chiral,

three-bladed propeller shape (C_3 symmetry) due to the attachments among its phenyl rings.



In the unenergized motor, rotation by ϕ about the C-C bond is hindered by the gearing of the rotor into one of the three, equivalent gaps between the phenyl ring “propeller-blades”, as depicted in the ball-and-stick models of the structure above. The cartoon below shows one cycle of motor operation as viewed from above the base. Photoexcitation of the rotor chromophore induces *cis-trans* isomerization about the *exo*-double bond of the rotor. The gearing of the rotor into the base couples ϕ -rotation about the double bond to ψ -rotation about the C-C linkage of the rotor to the base. The direction of the photoisomerization dynamics is biased by the C_3 chiral environment of the base. Ideally there is only one sense of rotation about the double bond, generating unidirectional migration of the rotor about ψ . Dissipation of the photon energy into the rotor load, and to vibrational relaxation (thermal loss), causes the rotor to relax into a neighboring gap in the trityl base.



In the first year of the project we have (1) performed computer simulations showing which parameters are required to generate a preference for sense of rotation of the rotor chromophore about the chiral base, (2) pursued a number of synthetic strategies leading to the motor design shown above, (3) performed photochemical investigations of the photoisomerization quantum yield as a function of excitation wavelength on a motor prototype structure, and (4) developed a technique for polarized excitation and probing of the immobilized motor with angular control. Preliminary spectroscopic evidence indicates we have succeeded in synthesizing the motor shown above in racemic form, however the synthesis needs to be optimized to produce large quantities of the optically pure motor suitable for testing.

References

- [1] For further information about this project email <ccline@chem.unr.edu>
- [2] "Bond angle vs. torsional deformation in an overcrowded alkene: 9-(2,2,2)-triphenylethylidene-fluorene", T.W. Bell, V. J. Catalano, M.G.B. Drew, and D.J. Phillips, *Chem. Eur. J.* **2002**, 8, 5001-5006.