

Synthesis of a New Photoactive Nanovehicle: A Nanoworm

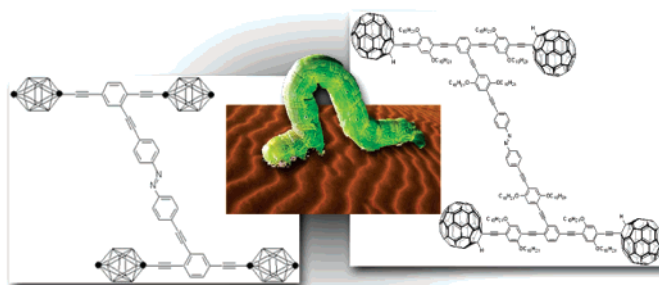
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ABSTRACT



A nanovehicle with a new photoactive moiety has been synthesized. The incorporation of the azobenzene chassis allows for potential wormlike movement accompanying the rolling behavior of the wheels. Two versions, the fullerene-wheeled and carborane-wheeled nanoworms, were synthesized to examine the solution-based photoisomerization yields of the chassis.

Advancements in the field of molecular machinery have afforded various bottom-up approaches toward performing macroscopic-like tasks at the molecular level.¹ In combination with imaging tools such as scanning tunneling microscopy (STM),² our group developed individually accessible nanocars, each bearing a chassis, axles, and fullerene wheels for a restricted rolling motion on a metallic surface.³ The movement is induced either thermally (surface heating) or electrically (STM-tip field). Recently, a nanocar with a light powered motor was introduced to provide a third source of

external stimuli.⁴ A cis–trans photoisomerization of azobenzene chromophores (Figure 1) to potentially generate inchworm-like motion on a surface is described. It is widely accepted that the photoirradiation step from trans to cis has a rotational pathway, whereas the heating step from cis to trans has an inversion pathway.⁵ The combination of these dissimilar pathways might help propel the nanoworm movement.

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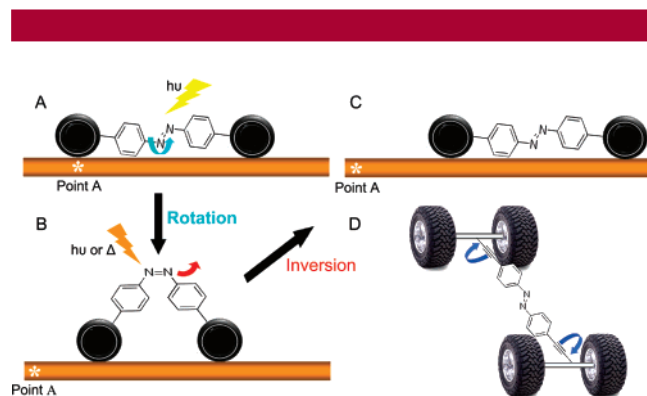


Figure 1. (A) Side view model of the nanoworm. The proposed photoactivated rotational pathway on a surface away from the reference point (noted by the star) by irradiating at 365 nm or 435 nm to convert A to B (trans to cis isomerization) by rotation. (B) Model of the nanoworm (cis) irradiated at >495 nm (or heated) to induce the inversion pathway to C which constitutes a cis to trans conversion, thus further propelling the nanoworm from the starred reference location. (C) The nanoworm again in the trans conformation, after completing the cycle of trans to cis to trans conversion, that is further displaced from the starred reference point. (D) Top view; rotation about the alkyne bonds is possible in order to achieve favorable conformations.

Two targets, fullerene-wheeled, and carborane-wheeled nanoworms, were synthesized (Figure 2). The latter was synthesized because the previous study of a motorized

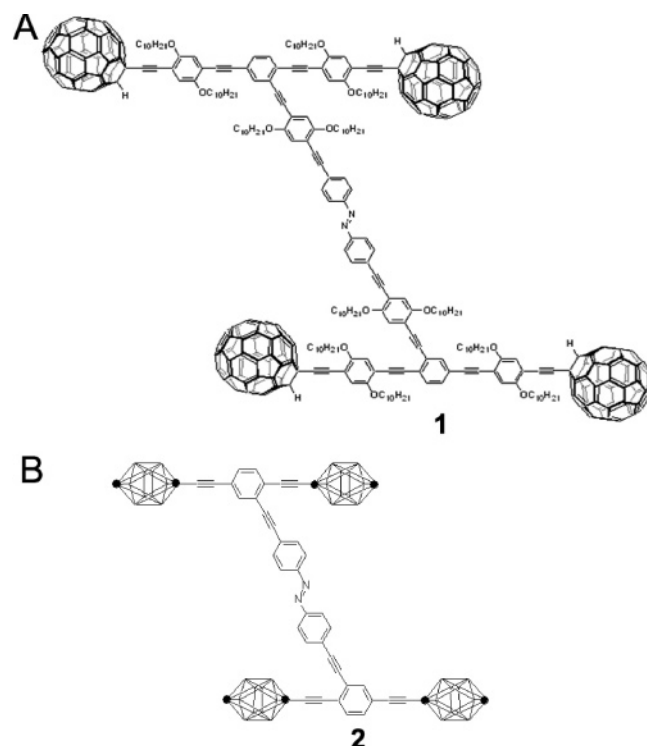
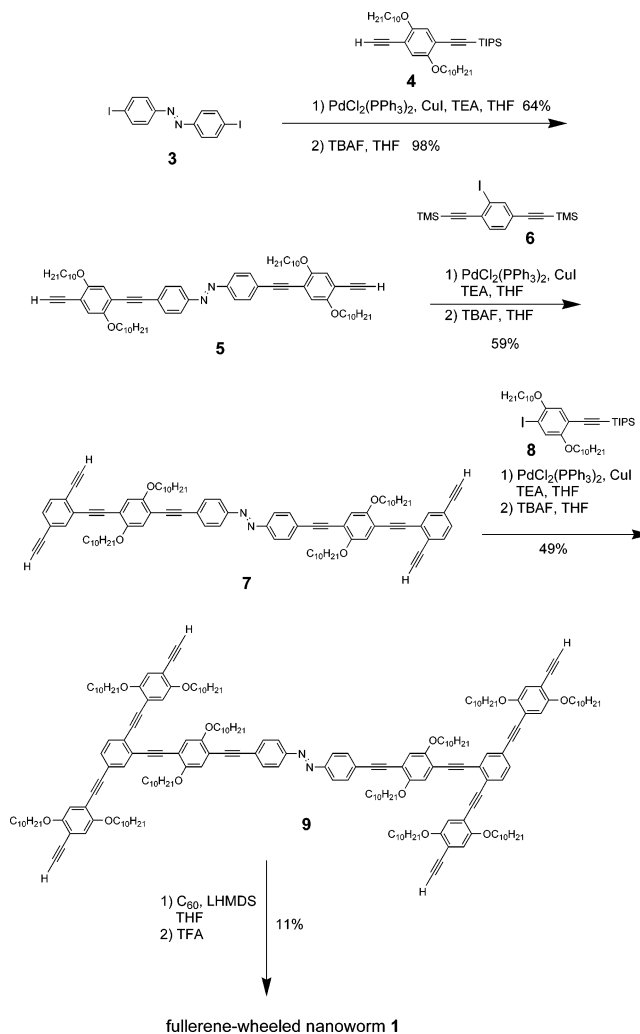


Figure 2. (A) C₆₀-wheeled nanoworm **1**. Extended dodecyl-substituted axes were added to ensure solubility. (B) *p*-Carborane-wheeled nanoworm **2**. The *p*-carboranes have BH at every intersection except at the points denoted by black spheres, which represent C and CH positions, ipso and para, respectively.

nanocar showed that the motor unit was inactive in the presence of fullerene.⁴ The rapid intramolecular energy transfer to the fullerene wheels quenched the photoexcited state of the motor. The photoisomerization of azobenzene has been studied extensively and used in devices and photoinduced systems for the large geometrical change accompanying the isomerization.⁶ However, there are few reports on the photoisomerization properties of azobenzene/fullerene hybrids.⁷ *p*-Carboranes have been used as wheels because they have three-dimensional, near-spherical structures⁸ that do not absorb at 365 nm. Other favorable properties from carboranes such as enhanced solubility and Pd-catalyzed compatible chemistry have allowed our group to produce several new-generation nanocars with this wheel.^{4,9}

The synthesis of nanoworm **1** consists of repetitive steps of Pd-catalyzed Sonogashira couplings and deprotection of alkynes. It begins with diiodoazobenzene **3**¹⁰ being coupled with **4**,^{3,11} followed by the removal of the triisopropyl protecting group to afford **5**.¹² Another coupling between **5** and **6**,^{3c,4,9} then deprotection, afforded the chassis **7**. The axles were then elongated via coupling of **8**^{3,11} to the chassis followed by desilylation to afford **9**, the backbone of the fullerene nanoworm. The four fullerene wheels were then

Scheme 1. Synthesis of Nanoworm 1



installed via the in situ ethynylation method^{3,11} to complete the synthesis of nanoworm **1** (Scheme 1).

Compounds **1** and **9** were subjected to photoisomerization experiments and monitored using UV–vis spectroscopy. As seen in Figure 3, the azo absorption peak was red-shifted

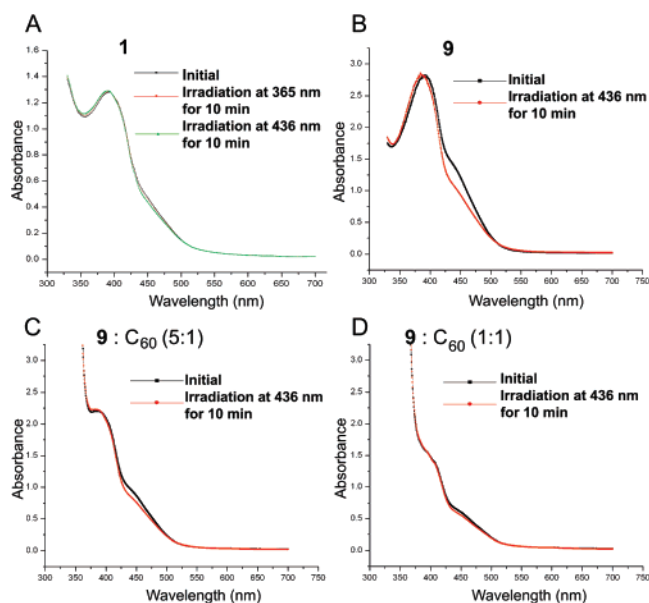


Figure 3. UV–vis absorption experiments of (A) nanoworm **1** in CHCl₃, 7.0 × 10⁻⁶ M, irradiated at both 365 and 436 nm for 10 min; (B) **9** in CHCl₃, 1.8 × 10⁻⁵ M, irradiated at 436 nm for 10 min; (C) 5:1, **9** in CHCl₃, 1.8 × 10⁻⁵ M, to C₆₀ in CS₂, 1.8 × 10⁻⁵ M, irradiated at 436 nm for 10 min (D) 1:1, **9** in CHCl₃, 1.8 × 10⁻⁵ M, to C₆₀ in CS₂, 1.8 × 10⁻⁵ M, irradiated at 436 nm for 10 min.

(when compared to the typical azo π – π^* absorption peak around 360 nm), due to the increased conjugation of the molecule; therefore the maximum concentration of cis isomer was obtained when **1** and **9** were irradiated at 436 nm rather than 365 nm.

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As summarized in Table 1, two noteworthy results were obtained. First, as expected, starting material **9** underwent

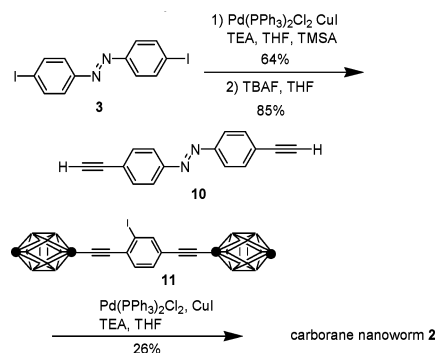
Table 1. Relative % Cis Yields^a with Irradiation at 436 or 365 nm for 10 min to Reach PSS Determined by UV–vis Spectroscopy

	nanoworm 1	9	9 /C ₆₀ (5:1)	9 /C ₆₀ (1:1)	nanoworm 2
% cis	8	23	12	8	24

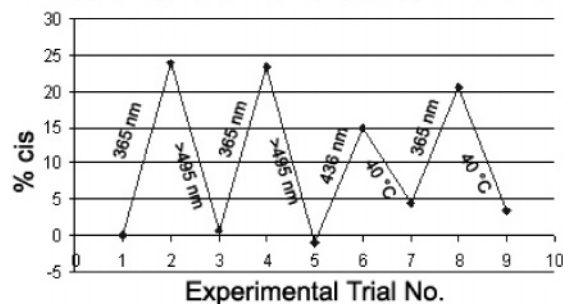
^a Change in absorption (Δ_{abs}) for the main absorption band of the trans isomer (π – π^*) (λ_{max} ~440 nm) reflects the minimum concentration of cis isomer at the PSS. Values are solely based on estimated yields due to limitations in UV–vis spectroscopy instrumentation as well as overlapping peaks.¹⁴ **1** and **9** were excited at 436 nm, and **2** was excited at 365 nm.

cis–trans isomerization with cis conversion ~23% upon irradiation at 436 nm for 10 min, at which time the photostationary state (PSS) was reached. The low conversion yields are due to steric interactions caused by the alkoxy groups and from the increased conjugation effect.¹² It was surprising that any switching behavior was observed from nanoworm **1**. Fullerenes attached via alkynes on conjugated systems introduce a weak electronic interaction called periconjugation,¹³ where the fullerene π -electrons communicate with the alkynyl π -electrons in a through-space p-orbital overlapping mechanism. This causes disruption in the electronic communication of the chromophore that has produced ~0% conversions in systems with two fullerenes in prior work.^{4,12} However, despite having four fullerene wheels, **1** showed slight conversion,¹³ a result that suggests that the distances between the azo and fullerene moieties are important despite their conjugated systems. Interaction of free fullerenes with compound **9** was also measured to illustrate the intermolecular effect of C₆₀ on photoisomerization yields. From the UV–vis spectroscopy data, a mixture of 5:1 of **9** to free C₆₀ decreased the cis conversion to 12%. Further addition of free C₆₀ to produce a 1:1 ratio decreased the cis conversion to 8%. This large intermolecular effect was not observed in the previous work.¹² The intermolecular photoquenching may be assisted through a supramolecular complex between free fullerenes and the flexible alkyl groups. Extensive studies on other factors such as relaxation

Scheme 2. Synthesis of Nanoworm **2**



Photochemical and Thermal Studies of Nanoworm 2



trial no.	experiment	duration (min)	% cis
1	Initial	0	0
2	365 nm	10	24
3	>495 nm	10	1
4	365 nm	15	23
5	>495 nm	5	0
6	436 nm	10	15
7	40 °C	15	5
8	365 nm	10	21
9	40 °C	15	4

Figure 4. Isomerization experiments of **2** in CHCl_3 , 1.4×10^{-5} M, at different wavelengths and temperatures.

rates and nonconductive linker energy transfers have recently been summarized.¹²

Because of the small switching activity observed with **1**, another wheel system was introduced in order to overcome the photoquenching effect, and as before,⁴ carboranes were chosen. The same starting material diiodoazobenzene **3** was coupled via Sonogashira coupling with trimethylsilylacety-

lene (TMSA) and then deprotected to afford **10**.¹⁵ The carborane axle/wheel system **11**^{3c,4,9} was then coupled to afford the target nanoworm **2** (Scheme 2).

From the photoisomerization experiment (Figure 4), the highest concentration of the cis isomer of **2** was obtained when the system was irradiated at 365 nm for 10 min, at which time the PSS was reached. Cis to trans switching occurred both photochemically when irradiated at >495 for 5 min (the temperature increase was <5 °C) as well as thermally when heated at 40 °C for 15 min.

In summary, two new photoactive nanovehicles with azobenzene chromophores have been synthesized. Preliminary solution-based photoisomerization showed conversion of trans to cis in nanoworm **2** and slight changes in nanoworm **1**. The results obtained from both spatially distant intramolecular interactions as well as intermolecular effects produced insights on chromophore–fullerene interactions. Studies are underway to image these nanoworms by microscopy and thereby study the photoactivated motion on surfaces. This might further necessitate nonconductive surfaces and or a switch to AFM or confocal microscopies.

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Supporting Information Available: Experimental details as well as spectroscopic data (FTIR, ¹H NMR, and ¹³C NMR) for compounds **1**, **2**, **7**, and **9**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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