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Synthesis of a Porphyrin-Fullerene Pinwheel

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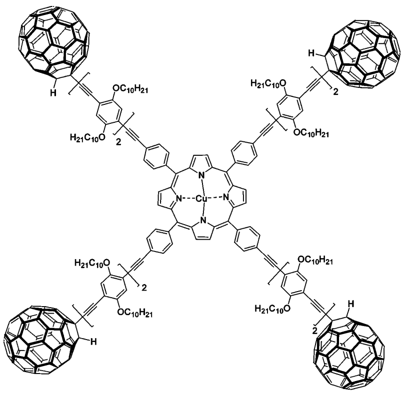
ABSTRACT



We disclose the synthesis of a porphyrin-fullerene pinwheel that was subsequently observed by scanning tunneling microscopy. The molecule was designed to further our understanding of fullerene-surface interactions, directional control, and surface-rolling versus pivoting capabilities of this class of nanomachines. The inner porphyrin provides the square planar configuration that might lead to realization of the pinwheel spiraling motion on surfaces.

There have been recent advancements in the field of imaging techniques, such as scanning tunneling microscopy (STM),[1] applied to the field of molecular machinery.[2] The two fields have inspired us to work with individually accessible single-molecular nanomachines. Of particular interest for our group is the development of nanocars.[3] In our design of the nanocars, fullerenes served both as molecular components easily identified by STM as well as wheels that enabled

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controlled rolling motion of the molecules on surfaces. Because of the friction-like (charge transfer at the molecular level) interactions between the fullerenes and the gold surface, a new motion mechanism was demonstrated for the first time, directionally restricted rolling instead of sliding on a surface. After establishing that rolling motion did occur, we directed our attention to the study of functionalized nanocars with varying properties that could produce different surface movements.[4] Here we report the synthesis and the initial images of a fullerene pinwheel molecule that was synthesized to further distinguish between translation and pivoting in molecular surface-rolling molecules.

The pinwheel **1** has four fullerene wheels, comparable to that of the nanocars (Figure 1), with copper inserted into the porphyrin core. Porphyrin-fullerene combinations have attracted a considerable amount of interest in the fields of solar cells,[5] photosynthetic antennas,[6] and nonlinear-optics[7] for their interesting photoinduced electron-transfer properties. The goal of this synthetic project, however, was solely directed at understanding nanocar directionality on metallic surfaces. Since porphyrins and metal-complexed porphyrins have been observed with STM,[8] it was thought that the addition of this feature to the nanocar design would make imaging more facile. With the wheels projecting from the body at 90° angles, the molecule is designed to show a different rolling behavior than that of the nanocar. The motion we predict may be similar to that of the trimer molecule (Figure 1), a control experiment from our past work in which the molecule rolled through pivoting about its central axis without any translational motion on gold surfaces.[3] Whether or not the porphyrin-based square conformation will permit this pivoting rolling motion is an area of intense interest in future STM experiments.

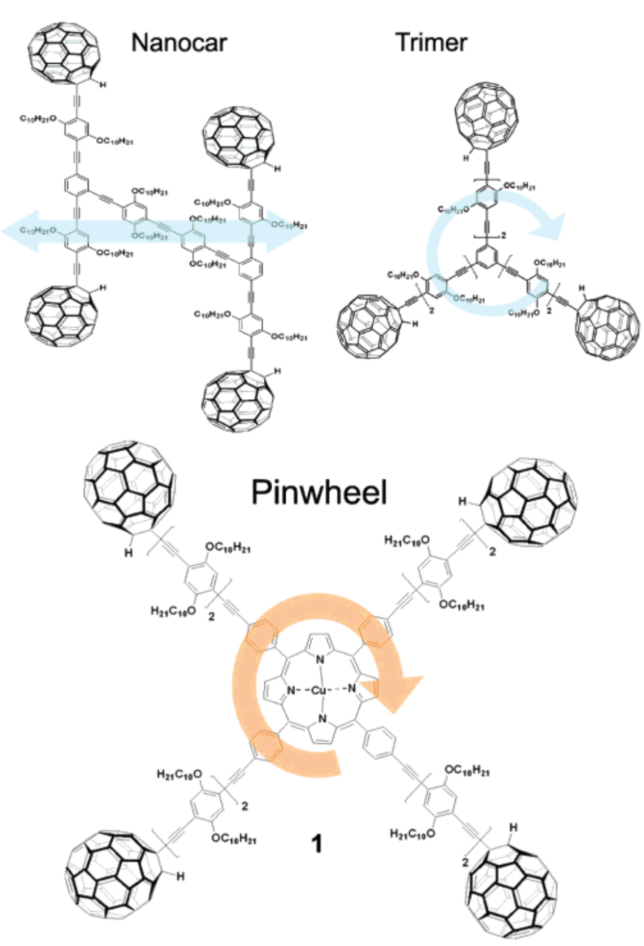
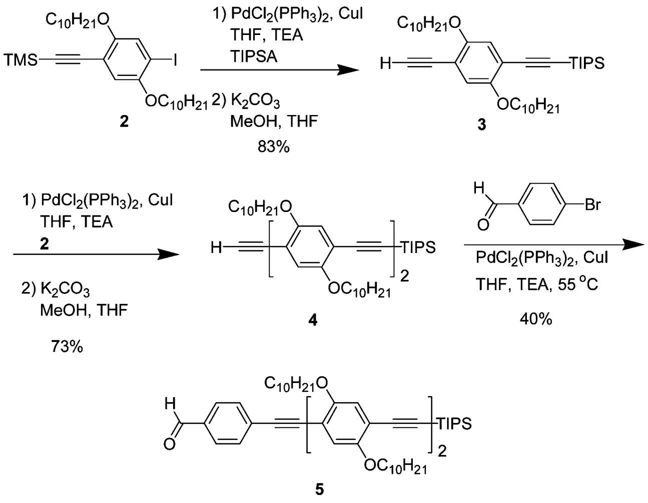


Figure 1. The nanocar showed directionally controlled translational motion on a surface while the trimer showed only pivoting. The pinwheel (**1**) prepared here, also bearing four wheels like the nanocar, should only undergo pivoting as observed with the trimer.

The synthesis began (Scheme 1) with three Pd-catalyzed Sonogashira couplings, the first two followed by the selective removal of the TMS-protecting group using K_2CO_3, to obtain **4**.[3,9] Note that for this design, long chain hydrocarbon

Scheme 1. Synthesis of Trimer **5**



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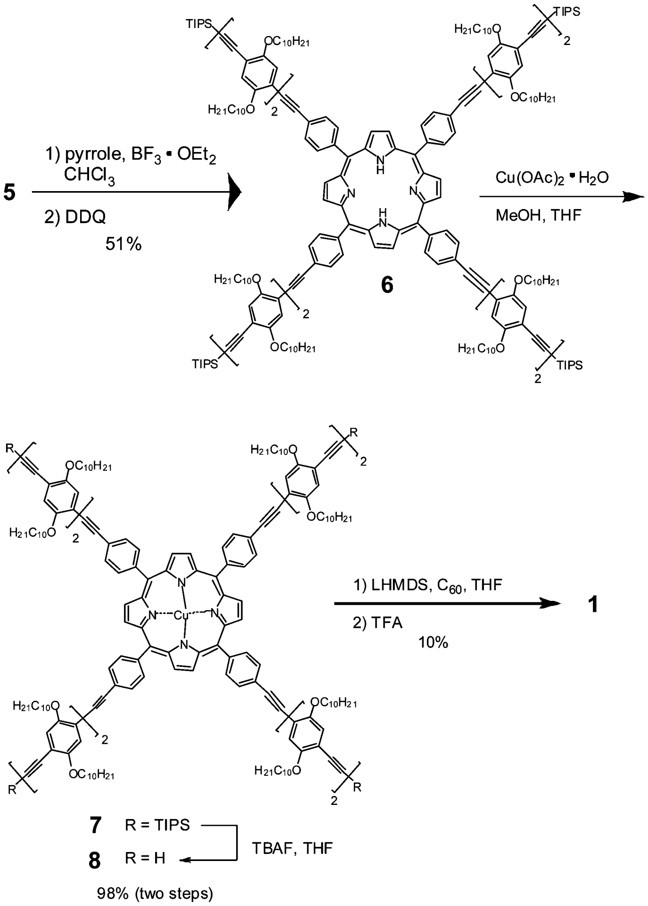
substituents were included to offset the low solubilities of the fullerene and porphyrin moeities. An extended dimer axle was used to increase the solubility of the final target. Compound **4** was coupled at elevated temperature with 4-bromobenzaldehyde to afford **5**, the precursor for the porphyrin reaction.[10]

Compound **5** was condensed with pyrrole and then oxidized with DDQ to afford porphyrin **6**.[11] The copper metal was inserted using $Cu(OAc)_2 \cdot H_2O$,[12] to obtain porphyrin **7**.[13] The deprotection step with TBAF was carried out after the metal insertion to avoid possible homocoupling of the free alkynes with exogenous copper. In addition, copper was the metal of choice due to its stability in the porphyrin complex and to avoid destruction of the porphyrin molecule in the presence of excess lithium hexamethyldisilazide (LHMDS) that would be used in the next step. Four fullerenes were successfully coupled via the in situ ethynylation method to complete the synthesis of the fullerene pinwheel **1** (Scheme 2).[3,9] The solubility of **1** was sufficient in $CHCl_3/CS_2$ or toluene to enable dosing valve[14] deposition on a gold surface and subsequent STM analysis.

Scheme 2. Synthesis of Pinwheel **1**[a]



[a] TBAF = tetrabutylammonium flouride, DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.

Although some of the molecules were clustered together, clear images of individual pinwheel molecules were observed by STM (Figure 2).[14] From cross-sectional analysis, the diagonal distance from fullerene to fullerene was ∼4.8 nm. This is slightly smaller than ∼5.4 nm calculated in PC Spartan (relative structure was calculated using empirical molecular mechanics based on Tripos 5.1 force field). The discrepancy may have resulted from the long oligo(phenylene ethynylene) (OPE) legs bending normal to the surface due

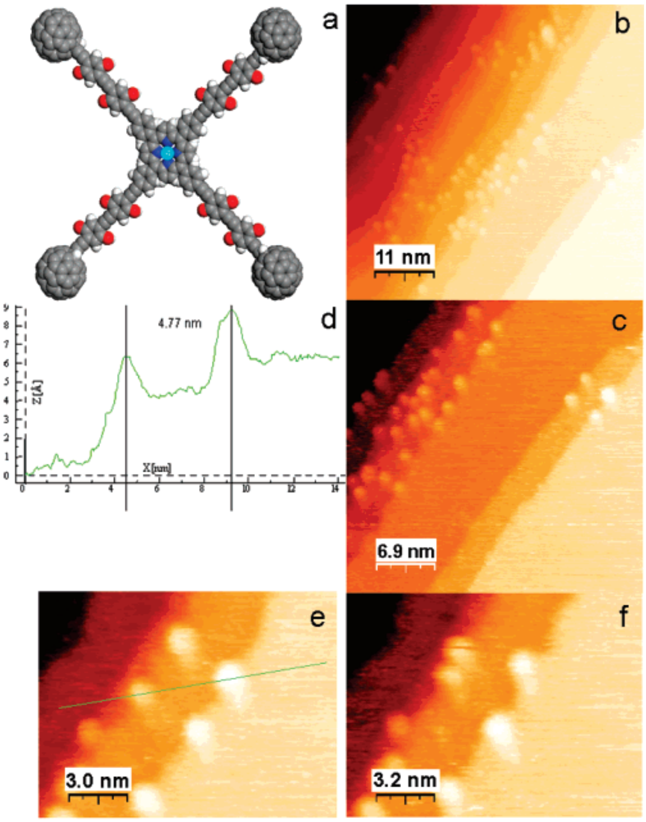


Figure 2. (a) Materials Studio (MS) modeling of C_{60}-poryphyrin pinwheel molecule **1**. The alkyl groups are ommitted for clarity. (b) STM image of scattered individual molecules **1**. (c,e,f) Higher resolution images with (d) cross-section analysis of **1** pictured in (e). (f) Lateral bend of OPE legs of **1** brings two fullerenes closer together on a step edge. (Bias voltage = −100 mV, tunneling current = 3 pA).

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to a strong gold-fullerene interaction (evidence of lateral bending is seen in Figure 2f). Another interesting feature of this molecule is the lack of imaging of its inner core. Our previous fullerene series[3,9] gave similar images via STM; however, with **1**, it was expected that the copper in the porphyrin would enable imaging of the core. The electronic nature of the fullerene-OPE interaction may be the reason for the unexpected failure to image the core; this aspect of the molecule is under investigation.[17] It should be noted, however, that the precise nature of the imaged moieties is highly structure dependent and is a topic that has generated much discussion.[18] Demetallation during the deposition process can be ruled out because of the mild dropcasting conditions used for the deposition technique, as previously reported by Yoshimoto et al., where metalloprophyrins were intact on similar Au(111) surfaces for imaging.[19]

The electronic absorption characteristics of the porphyrin-OPE-fullerene backbone were studied by UV/vis spectroscopy in chloroform of compounds **1**, **6**, and **8** (Figure 3). The peak observed for **1** at 319 nm is indicative of the fullerene peak.[9] The distinct λ_{max}, Soret band, is observed in all three compounds **1**, **6**, and **8**, indicating the presence of the porphyrin. The central molecular region (690 nm for **6**) is blue-shifted, consistent with metal insertion in **1** and **8**.[20] The distinctively enhanced absorption tail of **1**, above 450 nm, is due to the weak electronic interactions between fullerenes and the central OPE-porphyrin backbone. This is consistent with the periconjugation effect observed in our past fullerene-OPE hybrids.[3,9]

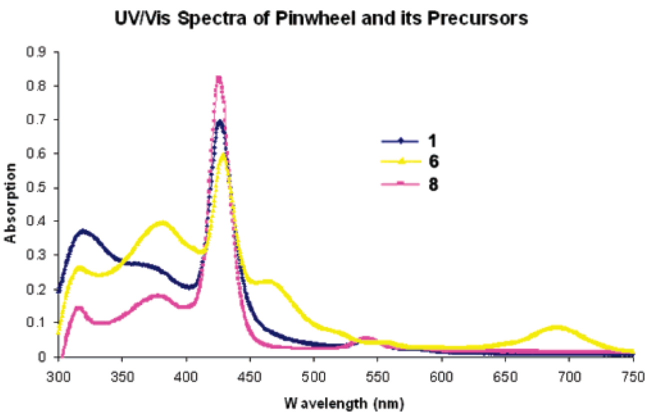

Figure 3. UV/vis spectra of compounds **1** (blue), **6**, (yellow), and **8** (pink).

In summary, we have successfully designed and observed a new fullerene-based molecule **1** for potential directional control of surface-pivoting nanomachines. Further study is currently underway using a heated substrate STM stage to observe the molecular motion.

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Supporting Information Available: Experimental details as well as spectroscopic data (FTIR, ^{1}H NMR, ^{13}C NMR, and mass spectrometry for compounds **5** and **6**; ^{1}H NMR, FTIR and mass spectrometry for **1**; FTIR and mass spectrometry for **7** and **8**). This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) **Sample Preparation and Data Collection for STM Study.** A toluene solution of pinwheel **1** (5 μM) was dosed in high vacuum using a fast-actuating, small orifice solenoid valve[15,16] onto argon-sputtered and annealed Au(111) on mica substrates and was imaged using an RHK variable temperature UHV-STM. A range of tunneling parameters (−1 to +1 V, 3−20 pA) was explored while attempting to resolve the inner structure. The dosing technique was chosen over sublimation in vacuum, as it appeared decomposition occurs at ~300 °C in thermal decomposition studies using a thermogravimetric analyzer in our previous work.[3] When imaging C_{60} and its derivatives with STM, their appearance is distorted by two effects, the first being the charge transfer between the fullerene and the underlying metal surface. Since STM is a reflection of both topography and electronic structure, the effect of the charge transfer causes the fullerenes to appear between 2.5 and 4 Å tall. The second effect is convolution with the finite size of the STM tip causing the lateral size of the fullerenes to appear much larger than expected. Thus, the combination of the two phenomenon results in the fullerenes being somewhat more flattened in their appearance than expected. For the case of bare fullerenes, this has been previously discussed by Yamachika, R.; Grobis, M.; Wachowiak, A.; Crommie, M. F. *Science* **2004**, *304*, 281.

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