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# Modification of graphite surfaces for the adsorption of molecular motors

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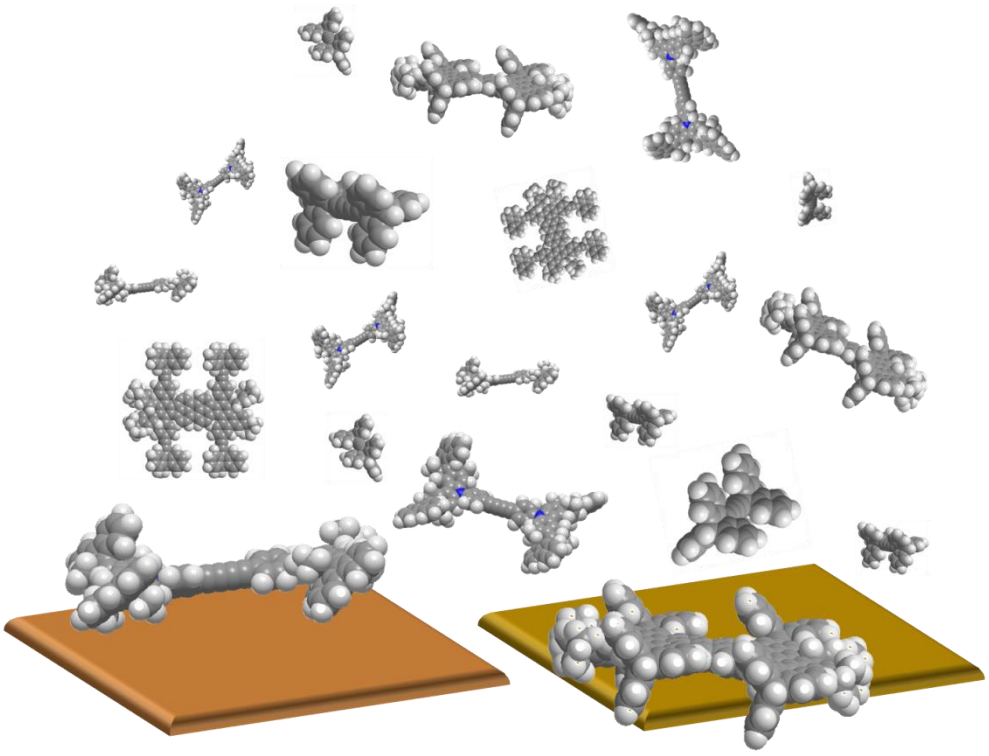
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# Chapter 1

## Introduction:
## Artificial Nanovehicles on Surfaces



*Over the past few decades, both physicists and chemists have worked on the rapid development of molecular machines, including the rise of new molecular vehicles. In this chapter, the design strategies and behavior of these molecular machines on surfaces is described and discussed.*

A key challenge in the field of nanoscience is to design molecular machines that are individually controllable on surfaces, i.e., converting external stimuli (light, electricity, heat or a chemical transformation) into unidirectional translational movement at the nanoscale. This chapter will report on the development and design of unidirectional moving artificial nanovehicles on surfaces.

## 1.1 Molecular motion on surfaces

In 1998 Gimzewksi et al. reported the high-speed rotation of hexa-*tert*-butyl decacyclene on Cu(100) driven by thermal energy. This was probably the first single-molecule observed on a dry surface exhibiting rotational motion and studied by scanning tunneling microscopy (STM).[1] Although the molecules therein act as passive elements, this work raised interest in the fabrication of functional molecular machines on surfaces. Pushing motion[2], lateral hopping motion[3] and single atom displacement[4] induced by using STM tips were already reported in the early nineties of the last century. Furthermore, the STM was used to power several anchored molecular motors on the surface.[5,6] These studies illustrated that STM is an important tool for the investigation of molecular machines at the nanoscale since it permits both visualization and manipulation of single-molecules on the surface. However, examination of rolling motion in nanomachines was required in order to mimic the directional motion of vehicles at the macroscale. The frequent non-directional hopping motion of surface-adsorbed molecules can occur in any direction towards the next adsorption site, whereas rolling motion of molecular wheels is expected to be directional. Grill et al. reported the first example of rolling motion of a single molecule equipped with two wheels on the surface and thereby, paved the path towards the bottom-up assembly of more complex nanovehicles.[7]

The wheel-dimer molecules (Scheme 1.1a), containing two triptycene molecules connected *via* a rigid butadiyne linker, were specifically designed to be individually guided on a surface by the tip of an STM.[8,9] The presence of the rigid linker allows independent rotation of each wheel around the central axle upon adsorption on a metal surface. Deposition of the wheel-dimer was achieved by sublimation at room temperature in an ultra-high vacuum (UHV) environment. Demobilizing the molecules by cooling the system down to 5 K allowed an extensive investigation of the displacement mechanisms upon STM manipulation. Upon manipulation of the wheel-dimer at larger tip heights, the current signals could be assigned to the rolling movement of one of the wheels. The periodicity of the signal was approximately 7 Å (Figure 1.1e), which corresponds to the displacement of a triptycene-wheel after a rotation of 120° around the molecular axle. The displacement of one of the triptycene wheels is depicted in Figure 1.1a-b, where the other wheel remained in its original position. In contrast, the lateral motion of the molecules caused by pushing at smaller tip heights led to typical periodic current signals as presented in Figure 1.1f. The 3.6 Å periodicity of these signals corresponds to the distance between two atomic rows on

the Cu(110) surface. Therefore, the molecule was hopping rather than rolling from one copper row to the next.

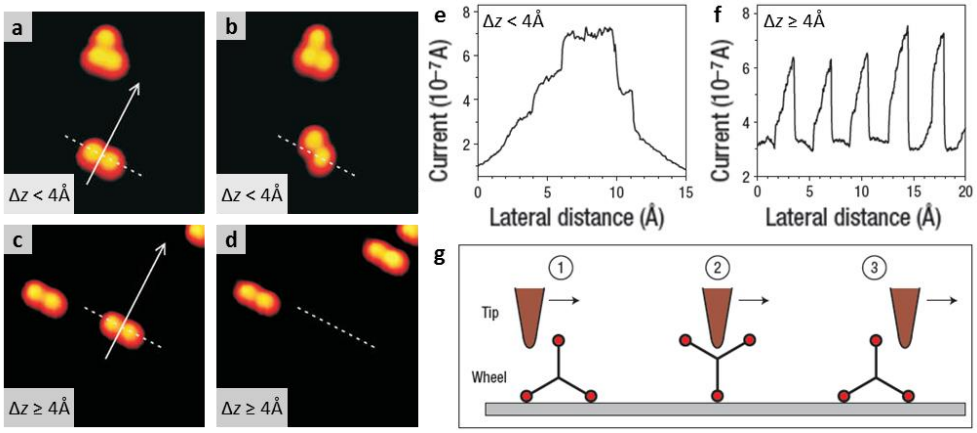
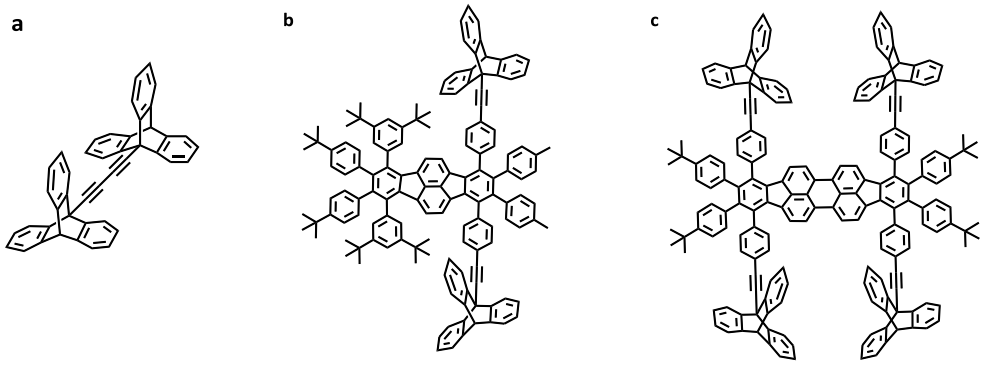



**Figure 1.1** Different lateral displacements according to rolling and hopping mechanisms. a-d) STM images of wheel-dimers (see Scheme 1.1a for structure) on a Cu(11O) surface in UHV at 5 K. a) Before, b) after manipulation with an STM tip ($\Delta z$ < 4 Å) showing rolling of one of the triptycene moieties. c) Before, d) after manipulation with an STM tip ($\Delta z \geq 4$ Å) showing hopping of the wheel-dimer molecule. The pathway of the tip apex during the manipulation is indicated by the arrow and the dashed lines indicate the initial position of the wheel-dimer molecules (all images 9 nm × 9 nm). e-f) Corresponding manipulation signals of the rolling and hopping mechanism, respectively. g) Schematic representation of the rolling mechanism. Tip heights ($\Delta z$) are represented with respect to the initial tip height of 7 Å. Reproduced with permission from reference [7]. Copyright © 2007, Springer Nature

## 1.2 Molecular designs of nanovehicles

Aiming for systems able to simultaneously undergo translational and rotational motions with two rolling wheels, a class of nanovehicles with triptycene wheels was designed. The first molecular nanovehicle came in the form of a molecular wheelbarrow.[9] Scheme 1.1b shows a molecular analogue of a wheelbarrow consisting of two triptycene wheels connected to a long rigid linker with a polycyclic aromatic hydrocarbon platform which was thought to be lifted from the surface via bulky 3,5-di-*tert*-butylphenyl legs. Even though they had to face many problems regarding the decomposition of these complex molecules upon sublimation, Rapenne and co-workers successfully imaged the molecular wheelbarrow on a Cu(100) surface.[10] However, the strong interaction between the molecular wheelbarrow and the metallic surface prohibited lateral motion upon manipulation with the STM tip at 5 K. The same group established also a molecular analogue of a car (Scheme 1.1c) with the presence of four triptycene wheels attached to a perylene-based chassis.[11] Based on the previous findings this molecule was expected to be unable to move across the surface.[12]




**Scheme 1.1** Chemical structures of triptycene-based nanovehicles. a) Wheel-dimer, b) Molecular analogue of a wheel-barrow. c) Molecular analogue of a car.

The strong physisorption of triptycene molecules on metallic surfaces prohibited any controlled movement of the molecular analogues of a wheel-barrow and car (Scheme 1.1).[12] A metal-semiconductor SmSi interface was introduced to change the molecule-surface interaction.[13] The periodic SmSi reconstructions led to the guided sliding of a new wheel-dimer (1,4-di-(9-ethynyltriptycenyl) benzene) along one surface orientation at room temperature. Their work demonstrated the importance of molecule–surface interactions in controlling the movement of molecules along a surface.

The need of a rolling motion mechanism in order to induce directional movement encouraged scientists to examine new types of molecular wheels. Nearly perfect spherical and robust $C_{60}$ fullerenes turned out to be good candidates. Tour and co-workers developed a whole series of Nanotrucks[14], -dragsters[15] and -cars[16–18] with $C_{60}$ fullerene-based wheels. Figure 1.2 shows two examples of nanovehicles with fullerene wheels, the fullerene-wheel based nanocar (FWBN) and the fullerene-wheel based trimer (FWBT). FWBN demonstrated to be stable and stationary at room temperature upon deposition *via* spin-casting from toluene on Au(111). This stability was ascribed to the strong adhesion force between the fullerene wheels and the underlying gold substrate. Thermally driven motion of the FWBN molecules began at temperatures above 443 K in two different directions. Translational motion occurred only in the direction perpendicular to the axles indicating that the molecules roll along the surface. The observed pivoting motion can be explained by the ability of the fullerene-wheels to rotate independently of each other. In contrast, the trimeric FWBT molecules only exhibited pivot motion since the geometrical shape of the axle inhibits translational rolling.[18] Event though the nanocars based on $C_{60}$ fullerene wheels successfully performed rolling motions on the surface, the electronic nature of the $C_{60}$ molecules means that those wheels would not be compatible with light-driven systems.

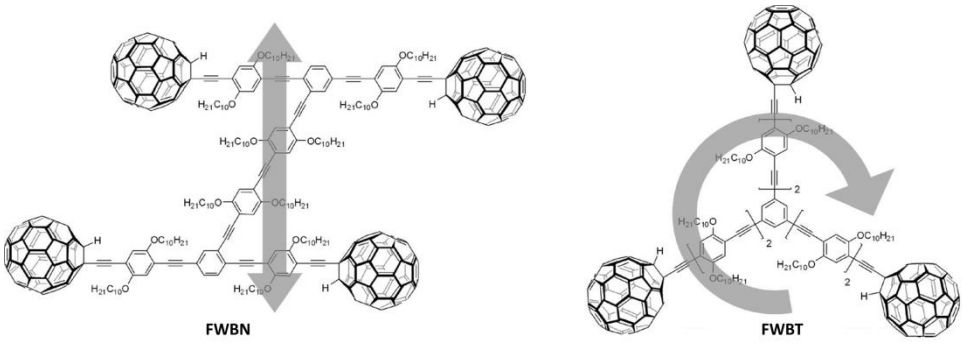


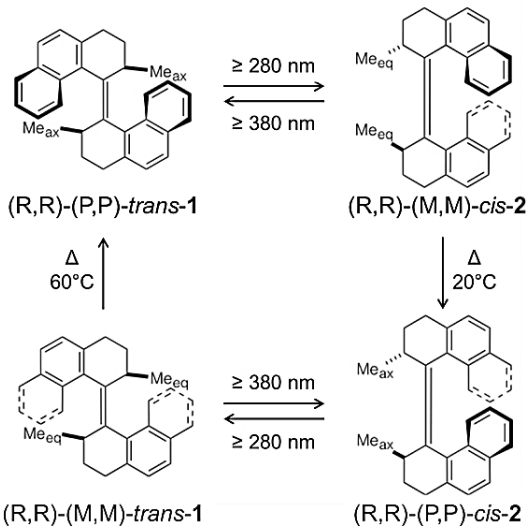

**Figure 1.2** Fullerene wheel based nanovehicles based on oligo(phenylene ethynlene) linkers. The arrows indicate the predicted direction of rolling motion on surfaces. Reproduced from reference [19]. Copyright © 2009, American Chemical Society.

In the quest for molecular wheels suited for rolling light-driven nanovehicles, two new types of wheels were introduced in the form of *p*-carboranes[20–24] and organometallic complexes[25]. The rolling motion of *p*-carborane wheels, however, has never been established. It is synthetically difficult to modify the *p*-carboranes unsymmetrically to, for example, install a tag which would help to investigate the movement mechanisms. Attaching organometallic ruthenium complexes as wheels to the nanovehicle might conceivably cause problems during the deposition, and the difficulty of clean deposition of these complexes might explain the lack of reported STM studies. An alternative design for molecular-wheels to improve the mechanical abilities of nanovehicles was introduced by the group of Rapenne.[26] They presented bowl-shaped boron–subphthalocyanine fragments coupled to an ethynyl-axle. This molecule should have a low affinity to the surface compared to the previous reported triptycene wheels because of the non-planarity of the three iminoisoindole-lobes of the structure. The rolling motion of the molecule on the surface could be studied by desymmetrizing one of the wheels with a nitrogen-tagged fragment. These double-wheel molecules were successfully sublimed on an Au(111) surface and subsequently imaged at 5 K. In a few cases, rolling a double-subphthalocyanine-wheel molecule on the surface over a short trajectory has been established. However, in most cases the molecules only slid over the surface after pushing or pulling with an STM tip due to the too-flat Au(111) surface.[27] To determine whether the subphthalocyanine-wheels are suitable for incorporation in nanovehicles, their rolling motion should be studied on more corrugated surfaces.

## 1.3 Molecular motors based on overcrowded alkenes

Previously reported examples described the motion on surfaces of intrinsically inert molecules, meaning that the molecule itself could not perform independent motion

without being either thermally-driven or mechanically manipulated with an STM tip. A drawback of STM manipulation, i.e. pushing, pulling and pulsing, of these inert molecules is that it only addresses one molecule at a time. One solution to this limitation are light-activated systems, since many of those systems can simultaneously be actuated *via* irradiation. Incorporating a molecular motor that is able to respond to external stimuli as light or electric pulses in the chassis of a nanovehicle would be a significant improvement to the design of unidirectional molecular nanovehicles. Promising candidates for the development of autonomous nanomachinery are the molecular motors based on overcrowded alkenes.




**Scheme 1.2** Rotary cycle of the first generation light-driven molecular motor. Reproduced from reference [28].

The first molecular motor based on an overcrowded alkene was developed in 1999 in the Feringa group.[28] This first-generation molecular motor has two identical halves on each side of a C-C double bond, featuring as the rotary axle, and features two stereocenters. The two methyl substituents of the stereogenic center adopt a pseudo-axial orientation in the thermodynamically stable isomers. The steric interactions in the *fjord* region of the motors cause the halves to twist out of plane resulting in a helical structure (Scheme 1.2). Upon irradiation of (P,P)-*trans*-**1** with UV light, a photochemical *cis*-*trans* isomerization occurs resulting in an isomer with opposite helicity ((M,M)-*cis*-**2**). The reversible character of this isomerization step means that there is no full conversion of the (P,P)-*trans*-**1** isomer into the (M,M)-*cis*-**2** isomer, instead, a photostationary state (PSS) is reached under continuous irradiation. For the motor depicted in Scheme 1.2, the *cis* to *trans* PSS ratio is found to be 95:5. After this isomerization, the two stereogenic methyl substituents ended up in an energetically less favorable pseudo-equatorial orientation. In order to adopt their energetically

favored (pseudo-axial) position again, the motor undergoes a thermal relaxation step in which both halves slide alongside each other (helix inversion), resulting in (P,P)-*cis*-**2**. In this newly formed isomer, with inverted helicity, the methyl groups re-adopted their preferred pseudo-axial orientation. Hence, the isomers that are prone to undergo the thermal helix inversion (THI) have often been referred to as 'unstable' or 'metastable' state isomers. The second part of the cycle proceeds in a similar fashion: photoisomerization of (P,P)-*cis*-**2** to the unstable (M,M)-*trans*-**1** occurs with a PSS ratio of *trans* to *cis* of 90:10 and is followed by a second thermal helix inversion resulting in the reformation of (P,P)-*trans*-**1**. The THI step is an important step in the rotary cycle of the motor, since the energy difference between the two isomers is so large that this step can be considered as an irreversible step which eventually allows for 360° unidirectional rotation around the carbon-carbon double bond.

Among the overcrowded-alkene based molecular motors, the second-generation molecular motor[29] is the most suitable candidate for the incorporation in a molecular nanovehicle. This asymmetric motor with non-identical upper and lower halves and only one stereogenic center allows for a broad scope of functionalization. Several systems with second generation molecular motors anchored on surfaces *via* functionalization of the lower half have been already reported, demonstrating that the motor is able to perform unidirectional rotational motion under ambient conditions upon light irradiation on different substrates, e. g. on gold nanoparticles[30], gold[31], quartz[32,33] and Si/$SiO_2$ substrates.[34] Moreover, it is possible to synthetically modify these systems to adjust the rotational speed.[29,35–39]

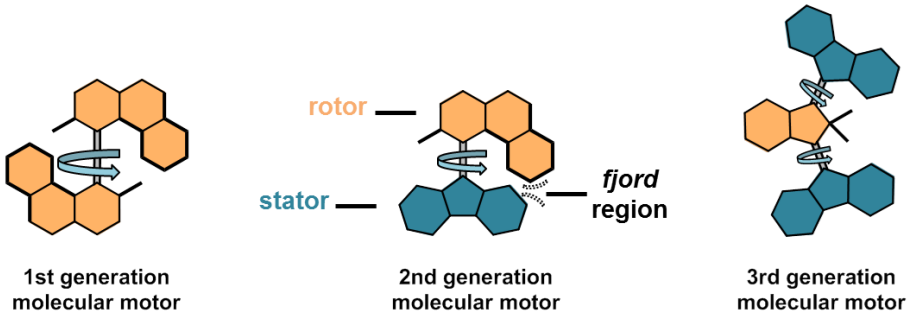



**Figure 1.3** Schematic representation of the three different generations of overcrowded alkene based molecular motors. The arrows indicate possible rotary motion around the double bond axle in an arbitrary fashion.

Development of the third-generation molecular motor revealed insight in the role of the stereogenic center on the unidirectional rotation. Whereas two stereogenic centers are responsible for the unidirectional rotation in the first-generation molecular motor, this has been reduced to a single stereogenic center in the design of the second generation molecular motor. In the latest design, the third-generation molecular motor, there is no stereogenic center present; this symmetric achiral motor bears two rotor units and has only a pseudo-asymmetric center. However, rotary

motion around both axels was found to occur in a unidirectional fashion when the pseudo-asymmetric center has two groups of distinct different sizes attached to it. [40,41]

## 1.4 Motorized nanovehicles

The first motorized nanovehicle was realized in 2006 in the group of Tour.[42] With an unidirectional overcrowded alkene based rotary motor incorporated in the chassis of their nanovehicle, they expected to enforce directional motion on the surface *via* a propulsion mechanism (Figure 1.4a). However, with a half-life of the unstable state of the motor unit of 101 hours at room temperature this design was not compatible with further STM investigations. Attempts with the previously used fullerene wheels did not fare as well due to intramolecular quenching of the photoexcited state of the motor unit.[42] In an ameliorated version of their motorized nanocar, a faster second-generation molecular motor was implemented in the chassis with a half-life of the unstable state of approximately $10^{-7}$ seconds.[39,43]

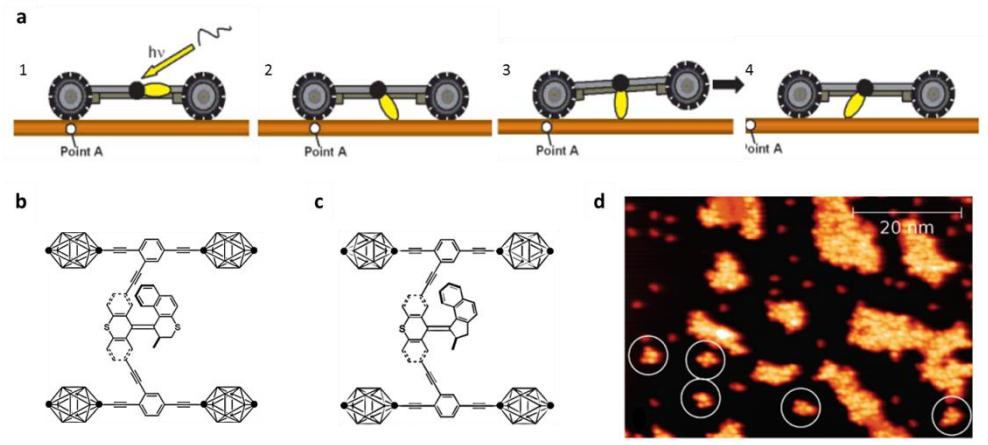



**Figure 1.4** Motorized nanocars with *p*-carborane wheels. a) Proposed propulsion scheme for the motorized nanocar **1** where (1) illumination with 365 nm light would induce (2) rotation of the molecular motor and subsequent (3-4) translational motion across the surface. b) First motorized nanocar with second-generation overcrowded alkene based molecular motor in the chassis. c) Motorized nanocar with a faster second-generation molecular motor in the chassis. d) STM image after adsorption of the structure depicted in c. The five-lobed protrusions in the white circles represent single nanocars. Smaller protrusions can be assigned to decomposed molecules. Images a-b are reproduced from reference [40], images c-d are reproduced from reference [43]. Copyright © 2012, American Chemical Society.

Even though the deposition on a Cu(111) surface was successful and the motorized nanovehicles could be imaged, it was not possible to induce translational motion upon light irradiation or STM tip pushing due to the strong interaction between the nanovehicle and the surface.[43] In 2011, the first example of directional motion of an electrical-driven motorized nanovehicle across a surface was reported by Feringa and

co-workers.[44] Instead of using any of the previously depicted wheels, i.e. triptycenes[7–11], fullerenes[14–18,23], organometallic complexes[25], *p*-carboranes[15,20–24,42,43] and subphthalocyanine moieties[26,27], they incorporated molecular motors based on overcrowded alkenes in the axles in such a way that they can function as molecular wheels (Figure 1.5a). The proposed paddling movement of the four molecular motor-based wheels on the surface should propel the nanocar forward upon applying external stimuli. After sublimation on a Cu(111) surface at 7K, the nanocars were imaged with STM under mild conditions so that no changes were induced upon scanning. Applying voltage pulses larger than 500 mV with the STM tip positioned directly above an individual nanocar resulted in movement of the molecule. A 6 nm long trajectory across the surface was travelled after ten excitation steps (Figure 1.5b). Even though the motion of each separate motor unit is unidirectional, the overall displacement was not, as achieving simultaneous excitation of all motor units was not possible.

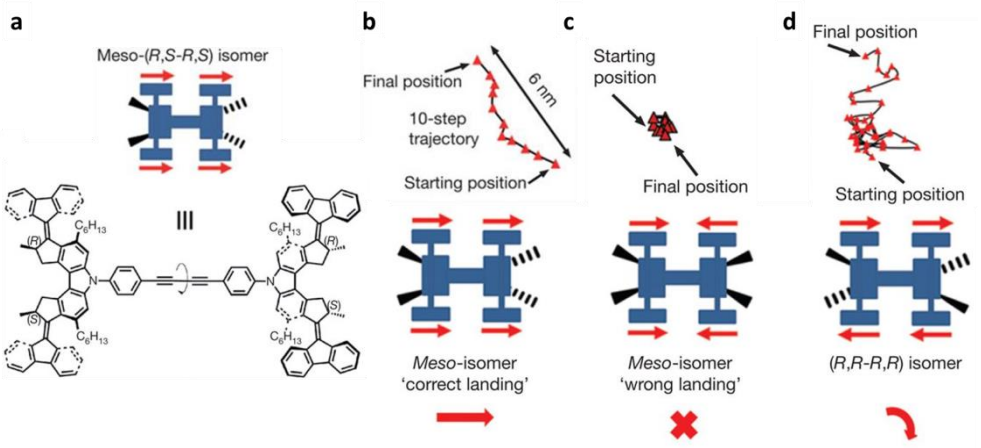



**Figure 1.5** First electrically driven unidirectional nanocar. a) Chemical structure of the *meso*-(R,S-R,S) isomer. b) Trajectory of the 'correct landed' *meso*-isomer after 10 excitation steps. In the lower part, the cartoon depicts the geometry and the proposed direction of movement of the molecule. c) Trajectory after 10 excitation steps of the 'wrongly landed' *meso*-isomer, showing no net displacement. d) Trajectory after 40 excitation steps of the (R,R-R,R) isomer, showing random motion. Reproduced from reference [44].

Additional evidence for the occurrence of electrically-driven motion of the nanocar came from the experiments probing the impact of the chirality of the motor units on the motion of the nanocar. Only the R,S-R,S isomer performed directional motion along the surface, provided that it 'landed' in the correct way. Free rotation around the bisalkyne C–C single bond led to two possible orientations of the *meso*-isomer on the surface. In a 'wrong landed' molecule the front and back wheels rotate in opposite direction prohibiting translational motion (Figure 1.5c). The diastereomers of the *meso*-isomer, the (R,R-R,R) and (S,S-S,S)-isomers were found to show pivoting and

random motion on the surface as the opposing motors in those isomers rotate in a disrotatory fashion (Figure 1.5d).

The first example of light-induced movement of a motorized nanovehicle was reported in 2016 by the groups of Tour and Grill.[45] Their NanoRoadster (NR) consists of a rigid axle with two adamantane wheels and in the middle of the axle an overcrowded alkene based molecular motor, attached *via* a Sonogashira coupling. Upon irradiation, the groups observed enhanced diffusion speeds of the NR on Cu(111) at temperatures above 150K (Figure 1.6). Although, the observed motion occurred in a random fashion, their results demonstrated the possibility of light-induced motion of nanovehicles on surfaces.

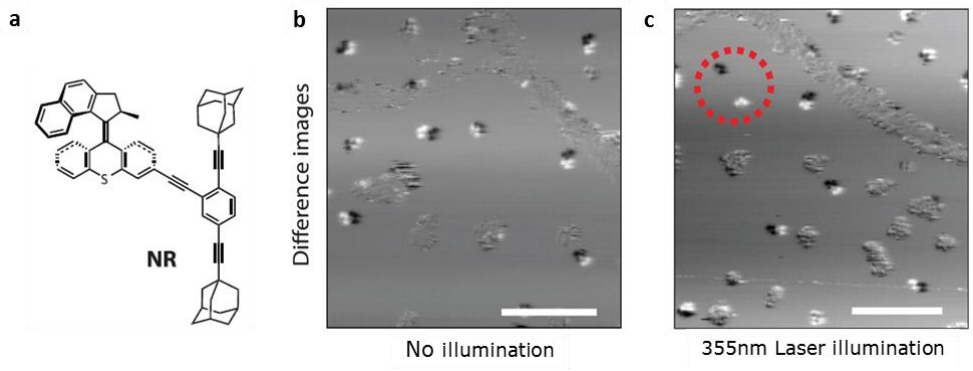



**Figure 1.6** a) Chemical structure of the NanoRoadster. b-c) Two overlaying STM images (the time between the images is approximately 1 h) of NR on Cu(111) acquired at 161K (scale bar: 20 nm). The dark spots refer to the NRs in their initial position. b) The white spots correspond to the NRs after thermal diffusion. c) The white spots correspond to the NRs after irradiation with 355 nm. Reproduced from reference [45]. Copyright © 2016, American Chemical Society.

However, it remains challenging to design a nanovehicle that can be propelled in a controlled manner along a surface. The previous paragraphs illustrated that the design of nanovehicles is a rather complex matter. First of all, the molecules need to be able to be placed on the surface without decomposition during the deposition. Secondly, the interaction with the surface should not be too strong so that motion is inhibited. Furthermore, directional motion on the surface of autonomous nanovehicles requires that molecules can convert light, chemical or electrical energy into translational motion. Moreover, it is desired that the design of the nanovehicles allows for rolling motion over the surface rather than hopping or slide-slip movements.

## 1.5 Aim of this research and thesis outline

It is necessary to have the molecular machines operating under ambient conditions in order to make a step towards possible applications, e.g., data storage, molecular transport and drug delivery. The research will be more feasible since expensive vacuum chambers and cryostats would no longer be needed. Furthermore, when working outside UHV, the molecular machines can be functionalized with groups that normally decompose upon sublimation, giving rise to a broader scope of functional nanomachines. The drawback of working under ambient conditions is the high probability of diffusing molecules due to the thermal energy available at room temperature and it will therefore be difficult to adsorb and immobilize the nanovehicles on the surface. On the other hand, in an ultra-clean UHV environment, the molecular machines could be trapped and immobilized on the surface at very low temperatures. Therefore, new molecular systems need to be designed such that the interactions between the molecular machines and the surfaces are carefully balanced. The interactions have to be strong enough to trap the molecular motors on the surface to overcome Brownian motion but must be dynamic enough to be able to induce translational motion of the nanovehicles along surfaces. Furthermore the systems need to be compatible with the preferred analysis technique, namely the STM, since this allows for elaborated analysis at the sub-molecular scale. In this thesis several design strategies are described for the adsorption of light-driven molecular motors on surfaces. The systems are studied under ambient conditions by STM. In this thesis, the focus is on the development of modified surfaces to control the interactions between the adlayer and adsorbates.

Chapter 2 outlines the basic working principles of the STM and describes the preparation methods used prior to the excecuted measurements discribed in the upcoming chapters.

Chapter 3 addresses the design of supramolecular surface-infrastructures from N,N'-bis(*n*-alkyl)-naphthalenediimides (NDIs) for the adsorption of molecular motors on a HOPG surface. The synthesis of NDIs with discrete long alkyl chains (28 or 33 carbons in the linear chain) was described followed by the analysis of thorough STM measurements to determine the influence of internal double-bonds present in the alkyl chains. The results presented in this chapter envision the possibility of creating long-range ordered and robust 2D self-assemblies by the insertion of an internal double-bond in the alkyl chains.

Chapter 4 focuses on the influence of multiple unsaturations in the long alkyl chains (≥39 carbons in the linear chain) on the self-assembly. This chapter complements the previous study on the long-range supramolecular order of alkyl substituted NDIs. The results herein described, show that assemblies with longer alkyl chains do not necessary lead to the formation of larger domains. However, the introduction of two

or three unsaturations in the alkyl chains improved significantly the local ordering of the self-assembled monolayers. The large separation between two NDI lamellae due to the presence of long alkyl chains might eventually pave the way towards more facile imaging of the potential adsorbed molecular motors.

In chapter 5 the possible use of these surface assemblies from N,N'-bis(*n*-alkyl)-naphthalenediimide (NDI) molecules as molecular highways was explored through adsorption experiments with pyrene derivatives. The NDI adlayer served as an adsorption template to facilitate the binding of alkoxy-pyrenes with short alkyl chains, which paved the way towards new adsorption strategies for molecules which could not be easily assembled on a bare HOPG substrate. In the last part of this chapter, the attempts to trap third generation molecular motors functionalized with two alkoxy-pyrene legs on the surface via the NDI template was described.

Chapter 6 explores the ability of the 5-(octadecyloxy)isophthalic acid (ISA-O-C18) adlayer to serve as an adsorption template for molecular motors with pyridine moieties under ambient conditions. STM experiments in 1-phenyloctane and *n*-octanoic acid revealed that the ISA-O-C18 adlayer serves as a successful template for the adsorption of second generation molecular motors with pyridine moieties in the lower-half of the motor. The formation of nanocorrals by nanoshaving in 1-phenyloctane allowed for controlled positioning of the molecular motors on the surface at the nanoscale.

Chapter 7 focusses on the synthesis of alkylated third-generation molecular motors for surface adsorption under ambient conditions. The molecular template in this chapter was fabricated from *n*-pentacontane. Preliminary results hint to the adsorption of bis(alkylated) third-generation molecular motors. However, the molecular design has to be optimized in the future to determine the reliability of this method.

In chapter 8 was the design of bis(urea)-substituted molecular motor tapes employed in order to get well aligned and operating molecular motors on the surface under ambient conditions. This strategy includes the use of support molecules to separate the motor units from each other allowing for free rotation of the motors. The results presented in this chapter demonstrate the effectiveness of this promising design strategy.

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