On conformational and configurational aspects of molecular motors
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Light-driven molecular motors based on overcrowded alkenes are molecules able to convert light energy into directional rotational motion. The first example of such a compound was reported in 1999 and since then many different variations have been developed. These motors can be categorized in three classes, or so called generations. A first generation motor has two stereogenic centers and two equivalent halves connected to the central alkene. A second generation motor has one stereogenic center and two different halves connected to the central alkene. The third generation motor has a pseudoasymmetric center and two sterically hindered alkenes. Although these motors all have different structural features, the overall mechanism for the unidirectional 360° rotation is in general the same. In the scheme below, the mechanism for the directional rotation is given for a second generation molecular motor.

Scheme 1: Mechanism for unidirectional 360° rotation for second-generation light-driven molecular motor.

In the synthesis of e.g. (R)-1 only two out of the four stereoisomers are obtained, i.e (R)-(M)-trans-1 and (R)-(M)-cis-1. These two isomers are thermally stable and are sometimes called stable cis and stable trans. The other two isomers are metastable, they undergo a thermal relaxation process called a thermal helix inversion (THI). When one of the stable isomers is irradiated, for example (R)-(M)-trans-1, a photochemical E–Z
isomerization is induced, giving rise to the formation of (R)-(P)-cis-1. Subsequently, this photogenerated metastable isomer undergoes a thermal helix inversion (THI), where the naphthalene moiety slips over the lower half in order to form the stable diastereoisomer (R)-(M)-cis-1. The result of the energetically uphill photoisomerization and thermodynamically downhill THI is a 180° rotation of the upper half relative to the lower half. Another photochemical step followed by a THI completes the unidirectional 360° rotation around the double bond. Repetitive unidirectional rotation is achieved upon continuous irradiation at high enough temperature. The stereogenic center plays a crucial role in the functioning of the motor. The presence of this center ensures unidirectionality of the rotation, while the configuration of this center dictates the direction of rotation. It is thus the interplay between the conformational (helical chirality) and configurational elements (point chirality) which lies at the basis of the functioning of overcrowded alkenes as unidirectional rotors. It is therefore vital to have control over the stereochemical elements of these compounds throughout their synthesis. However, up to date, only few methods exist to access these compounds enantiomerically pure. In chapters 2, 3 and 4, new ways are investigated to obtain motors as single enantiomers. Other conformational and configurational aspects of motors are discussed in chapters 5, 6 and 7.

In chapter 2, a method is described to synthesize first generation molecular motors asymmetrically in two steps. The developed strategy consists of an enantioselective protonation of a silyl enol ether derived from an racemic indanone precursor, followed by a McMurry coupling.

In chapter 3, a method is described to obtain hydroxyl-functionalized first generation molecular motors as single enantiomers. The process involves a short synthesis of three steps and a solvent-switchable chiral resolution using a readily available resolving agent. The obtained motor still functions as anticipated as was concluded from studies using 1H NMR and UV/Vis spectroscopy supported by DFT calculations.

The problem of the asymmetric synthesis of second generation molecular motors is the loss of optical purity during the formation of the diazo and thioketone precursors required for the Barton Kellogg coupling. In chapter 4, the design and synthesis of a new second generation type motor is described. The new design features a β stereocenter which enables the asymmetric synthesis without any loss of optical purity throughout the synthesis. On the basis of photochemical and kinetic studies using UV/Vis, CD, and 1H NMR spectroscopy, it was established that they still function properly as unidirectional molecular motors.

In chapter 5, a strategy to red shift the excitation wavelength of motors is described. To this end, a new motor with an extended aromatic lower core was designed and synthesized. From UV/Vis spectroscopy studies, it was concluded that the structural modification results in a red-shifted absorption spectrum but at the cost of the quantum
yield of photoswitching. Moreover it was show by DFT calculations that the designed motor show interesting conformational behavior upon isomerization.

In chapter 6, the focus is on transfer of chirality. The molecular motor is a unique molecule which not only show unidirectional rotation, but also exhibit switchable chirality. This feature was used to control the helicity of a dynamic helical polymer. It was found that a dicarboxylic acid functionalized motor can bind via non-covalent interactions to an ammonium functionalized poly(phenylacetylene). Binding of the motor to the polymer leads to a preferred helicity in the polymer backbone. Upon irradiation, the motor is able to photoisomerize which leads to the inversion of the overall helical chirality of the polymer.

In chapter 7, a method is described to control the rotational speed of the motor by chemical means. A motor functionalized with a 2,2''-biphenol moiety showed reduced rotational speed upon bridging of the two hydroxyl groups with a methylene spacer. Next to covalent modification, also the non-covalent binding of guests, induced a deceleration of the rotational speed. From titration studies it was concluded that a cyclohexane diamine derivative binds to the 2,2''-biphenol moiety. This proved to be an effective way to reversibly control the rotational speed, as the binding of the diamine could be undone by the addition of either methanol or acetic acid.