

**MOLECULAR ROTOR WORKSHOP 2023**  
2.-3. NOVEMBER 2023, PRAGUE, CZECH REPUBLIC

# BOOK OF ABSTRACTS

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**IOCB PRAGUE**



# Molecular Rotor Workshop

PRAGUE, CZECH REPUBLIC  
NOVEMBER 2–3, 2023

ORGANIZER: JIŘÍ KALETA ([jiri.kaleta@uochb.cas.cz](mailto:jiri.kaleta@uochb.cas.cz))  
WWW: [kaleta.group.uochb.cz/en/mrw2023](http://kaleta.group.uochb.cz/en/mrw2023)

## Thursday 11/02/2023

### 8:30-8:45 CONFERENCE OPENING

8:45-9:35 Ben FERINGA Exploring Light-driven Rotary Molecular Motors

9:35-10:25 Ivan APRAHAMIAN Hydrazone-Based Functional Materials

### 10:25-11:00 COFFEE BREAK + POSTER SESSION

11:00-11:50 Angiolina COMOTTI & Piero Sozzani Controllable Rotors and Switches in Porous Materials: Their Interplay with Gases and Vapours

### 11:50-13:30 LUNCH BREAK

13:30-14:20 Alberto CREDI Supramolecular Pumps Powered by Light

14:20-15:10 Miguel GARCIA-GARIBAY Crystalline Molecular Rotor Arrays

### 15:10-16:00 COFFEE BREAK + POSTER SESSION

16:00-16:50 Nicolas GIUSEPPONE Using Artificial Molecular Machines to Drive Complex Chemical Systems Out-of-equilibrium

16:50-17:40 Grace HAN Solar Fuels Produced by Molecular Machines

17:40-18:30 Stefan HECHT Powering Molecular Systems with Photons: Prospects, Problems, Strategies

18:30 CONFERENCE DINNER (invited speakers)

## Friday 11/03/2023

9:00-9:50 Rainer HERGES Light-controlled Levitation and Switchable Aerogels

9:50-10:40 Jiří KALETA Photoswitchable Monolayers

### 10:40-11:10 COFFEE BREAK + POSTER SESSION

11:10-12:00 Nathalie KATSONIS Mechanochemistry of Molecular Rotors

### 12:00-13:40 LUNCH

13:40-14:30 Rafal KLAJN Supramolecular Machinery for Disequilibrating Azobenzenes

14:30-15:20 Eric MASSON Supramolecular Lego with Cucurbiturils and Lanthanides

### 15:20-16:00 COFFEE BREAK + POSTER SESSION

16:00-16:50 Zbigniew L. PIANOWSKI Photochromism in Cyclic Dipeptides

16:50-17:40 Gwénaél RAPENNE Biomimetic and Technomimetic Nanomachines: Molecular Motors, Vehicles and Gears

### 17:40-18:00 CLOSING REMARKS

18:00 CONFERENCE DINNER (invited speakers)



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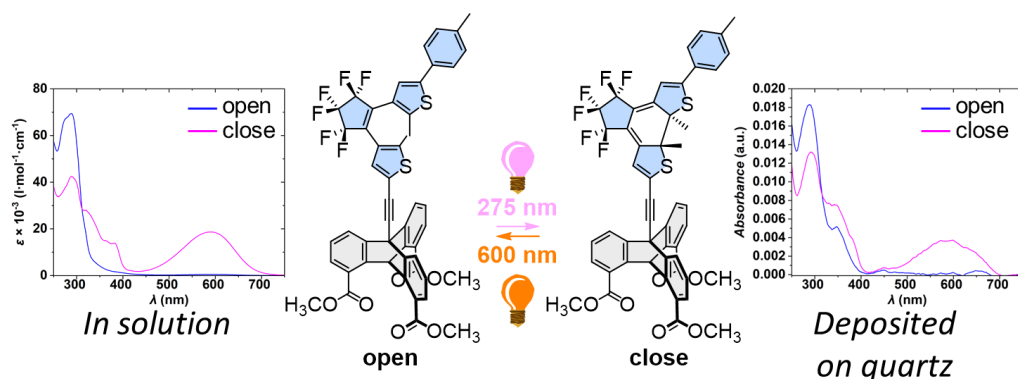
ORGANIZER: JIŘÍ KALETA ([jiri.kaleta@uochb.cas.cz](mailto:jiri.kaleta@uochb.cas.cz))  
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## Triptycene-Based Tripodal Stands For Organized Photoactives Films

Guillaume Bastien,<sup>a</sup> Lukáš Severa,<sup>a</sup> Carina Santos Hurtado,<sup>a</sup>  
Milan Mašát,<sup>a</sup> Eva Kaletová,<sup>a</sup> Ivana Císařová,<sup>b</sup> Jiří Kaleta<sup>a</sup>

<sup>a</sup> Institute of Organic Chemistry and Biochemistry of the Czech Academy of Sciences, Flemingovo náměstí 542/2, 160 00, Praha 6, Czech Republic. <sup>b</sup> Department of Inorganic Chemistry, Faculty of Science, Charles University in Prague, Hlavova 2030, 128 40 Prague 2, Czech Republic.

In our quest to form stimuli responsive smart materials, we recently developed a triptycene-based molecules which proved to be suitable for the formation of various photoactive films.<sup>1,2,3</sup> Tilting and bending of these originally straight and rod-shaped molecules were identified as an important factors determining the self-assembly properties. A new triptycene-based tripodal stands were developed in order to suppress these issues. These molecular pedestals are equipped either with carboxylic acid- (suitable for Langmuir-Blodgett depositions) or thiol-based (for adsorption on metallic surfaces) anchoring units and ethynyl moiety in the axial position allowing smooth interconnection with various functional units. UV-vis and NMR spectroscopies proved that photoswitches and molecular motors attached to this molecular pedestal retain their functionalities in solution. These molecules formed Langmuir-Blodgett films on the water/air interface, which were transferred to various substrates. Structural characterization of these films involved several techniques such as ellipsometry, phase modulation infrared reflection absorption spectroscopy (PM-IRRAS), atomic force microscopy, X-ray photoelectron spectroscopy. We demonstrate here that this approach allows the formation of densely packed films that can still respond to radiative stimulation.



**Figure 1.** Example of tripodal triptycene-based molecular platform that is functionalized with diarylethene switch and corresponding UV-vis spectra in solution and on a quartz substrate.

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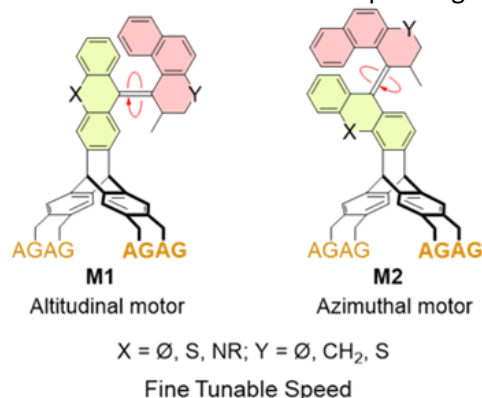


## Towards Tetrapodal Molecular Motors

Kateřina Bezděková,<sup>a,b</sup> Jiří Kaleta<sup>a</sup>

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Unidirectional light-driven molecular motors represent a unique class of organic molecules with a broad scope of applicability ranging from medicine, material science to informational technology.<sup>1,2</sup> These molecules already became an essential part of many sophisticated (supra)molecular systems mostly due to their well-defined four-stages 360° rotation cycles as well as fine-tunable physical properties.<sup>3–5</sup> Our current research is focused on development of a conceptually novel class of mostly surface-bound multiphotochromic molecular devices/machines consisting of two or more orthogonally interconnected photoswitches. Geometrically unique molecular motors with general structures **M1** and **M2**, that were recently developed in our research group, represent functional hearts of these complex organic systems. They consist of a rotor (red-marked structure in



**Figure 1:** General structures of altitudinal and azimuthal molecular motors.

Figure 1) capable of rotation around stator (green part of molecule in Figure 1) that is fused to a rigid triptycene-based pedestal, that is equipped with four anchoring groups (AG). They should secure immobilization of these devices on surfaces. Slight change in the molecular structure allows fine-tuning of not only the direction of rotation (altitudinal vs. azimuthal machines), but also the speed of rotation ranging from nanoseconds to million years at ambient conditions. All these parameters determine their use in our future molecular machines.

Herein we report a dozen of unidirectional light-driven molecular motors based on the **M1-2** and the progress on the characterization of their four-stages unidirectional rotation cycles.

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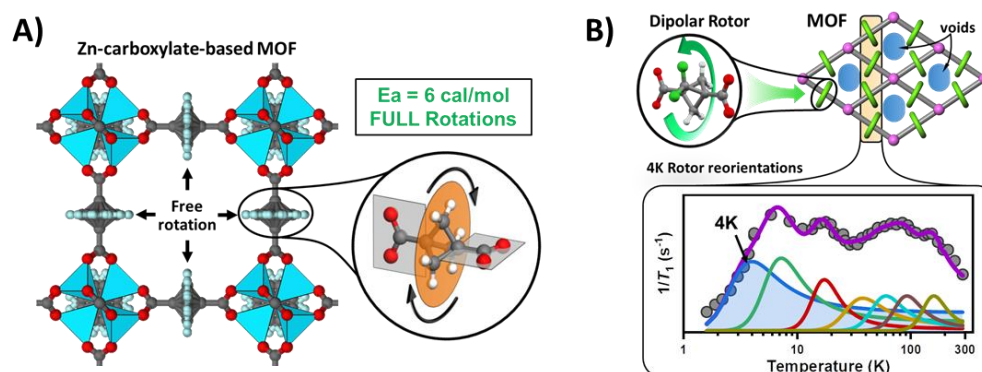
## MOF CONTAINING LAYERS OF DIPOLAR-ROTOR WITH VERY HIGH MOBILITY AT EXTREMELY LOW TEMPERATURES.

Charl X. Bezuidenhout, Jacopo Perego, Andrea Daolio, Silvia Bracco, Sergio Piva, Piero Sozzani,<sup>a</sup> Giacomo Prando,<sup>b</sup> Jiří Kaleta,<sup>c</sup> Angiolina Comotti<sup>a</sup>

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Metal-organic frameworks (MOFs) present a platform that allows the insertion of ligands in a wide range of structural and chemical environments, thus tuning the ligand's interactions with neighbouring moieties within the MOF. Conventionally, fast rotary dynamics is achieved by isolating molecular rotors, used as struts in MOFs, from their neighbours to reduce intermolecular interactions. Inserting bicyclo[1.1.1]pentandioate (FTR) rotors into a cubic framework yielded isolated rotors with a rotational energy barrier of only 6 cal/mol (Fig 1 A).<sup>1</sup>

The outstanding synthetic versatility of MOFs allows us to explore more dense arrangements of rotors to study the effect of cooperativity between the rotors. The FTR rotors were inserted into a pillar-and-layer Zn-MOF, and a geminal fluorinated FTR rotor into an Al-MOF. For the Zn-MOF, these rotors are still dynamic at very low temperatures through co-rotating pairs of rotors in a geared-like fashion. These geared molecular rotors have extremely low energy barriers for rotation (24 cal/mol) owing to the synchronicity of their rotation.<sup>2</sup> Furthermore, the dipolar FTR-F2 rotor in the Al-MOF forms layers of interacting rotors oriented in different configurations. Contrary to expectation, these rotors are extremely dynamic down to 4K through a cooperative reorientation cascade of the dipolar rotors with a barrier for reorientation of ca. 17 cal/mol (Fig 1 B).<sup>3</sup>



**Figure 1.** A) Zn-carboxylate-based MOF containing isolated (FTR) rotors (red). B) The dipolar molecular rotors in Al-FTR-F2 with dynamics down to 4 K, as shown by the <sup>1</sup>H relaxation rate spectrum.

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## SWEET MOLECULAR MOTORS: SYNTHESIS, SELF-ASSEMBLY, LECTIN-BINDING

Adrien Combe,<sup>a</sup> Roberto Terracciano,<sup>b</sup> Marc C. A. Stuart,<sup>a</sup> Alexander Ryabchun,<sup>a</sup> Gokhan Yilmaz,<sup>b</sup> C. Remzi Becer<sup>b</sup> and Ben L. Feringa<sup>a</sup>

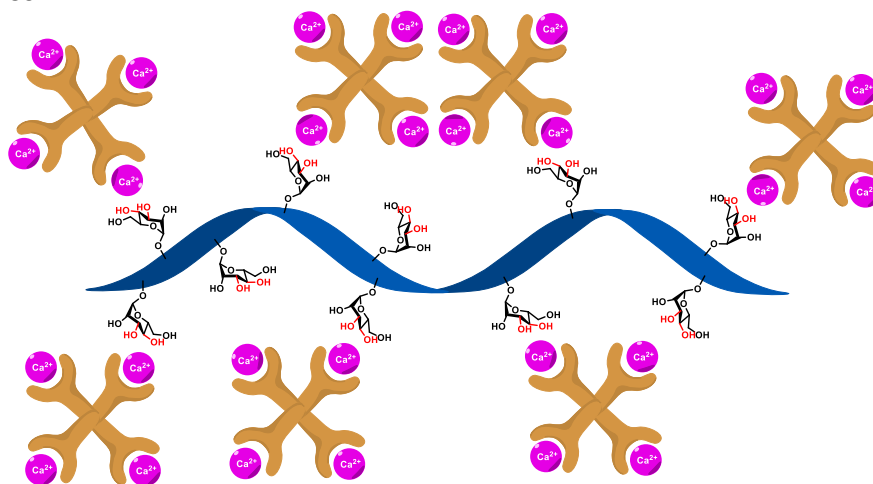
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<sup>b</sup> Department of Chemistry, University of Warwick, Coventry, CV4 7AL, United Kingdom.

Carbohydrates are indispensable moieties in many cell biological recognition processes. Because individual carbohydrates interact only weakly with their specific protein receptor, multivalency is a key for high affinity in such processes. It has been demonstrated that the conformation and orientation of carbohydrates moieties are decisive for an effective multivalent interaction with carbohydrate-binding proteins termed lectins.<sup>1</sup>

Among the different binding modes of multivalent interactions, chelation binding by a multivalent ligand, is assumed to make a major contribution to high affinity binding.<sup>2</sup> Due to rigidity of carbohydrates, control of the mode of presentation and orientation of sugar moieties provides a possible mode of regulation of these recognition processes both in biological and synthetic systems. A proven and widely applied method to induce changes in orientation of structures on demand in glycochemistry is the use of molecular photoswitches, such as azobenzene<sup>3</sup> and arylazopyrazole.<sup>4</sup>

However, these photoswitches are not perfect candidates due to a relatively poor thermostability, which can be resolved by a first-generation molecular motor. The aim of this project is to incorporate  $\alpha$ -D-mannose units on both sides of a simple first-generation motor, tethered by a long alkyl chain, and in a complementary approach, on only one side. The presence of a hydrophilic part and a hydrophobic part on the motor allow the motors to self-assemble in water in order to produce an aligned range of carbohydrates resulting in a perfect affinity binding with mannose-specific lectin such as ConA.



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## Out-of-equilibrium disruption of $\beta$ -amyloid fibrils using light-driven molecular motors

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A multitude of biomolecular machines perform advanced functions that sustain life processes (e.g., ATP synthase<sup>1</sup>). Taking inspiration from nature, scientists have developed artificial molecular machines able to transform energy in directional motion.<sup>2,3</sup>

To make use of the work generated by such molecular machines, our research group have recently integrated light driven rotary motors in covalent polymer networks.<sup>4</sup>

In the present work, we now take advantage of the active rotation of molecular motors in supramolecular gels. In this context, we have integrated light-driven artificial molecular motors in dipeptide supramolecular hydrogels forming  $\beta$ -amyloid fibrils. Interestingly, the actuation of the motors under UV-light results in reversible gel-sol transitions at the macroscopic scale.

This unique reversible gel-sol transition phenomenon was studied by rheology and several spectroscopic techniques (<sup>1</sup>HNMR, UV-Vis, CD, X-ray scattering...) proving that the sol state results exclusively from the work generated by the out-of-equilibrium rotation of the motor under UV light, and capable of disrupting  $\beta$ -amyloid fibrils.

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## Hemipiperazines As Novel Peptide-Derived Molecular Photoswitches

Peter Gödtel,<sup>a</sup> Susanne Kirchner,<sup>a</sup> Anna-Lena Leistner,<sup>a</sup> Angelika Seiwjorstow,<sup>a</sup>  
Zbigniew L. Pianowski<sup>a,b</sup>

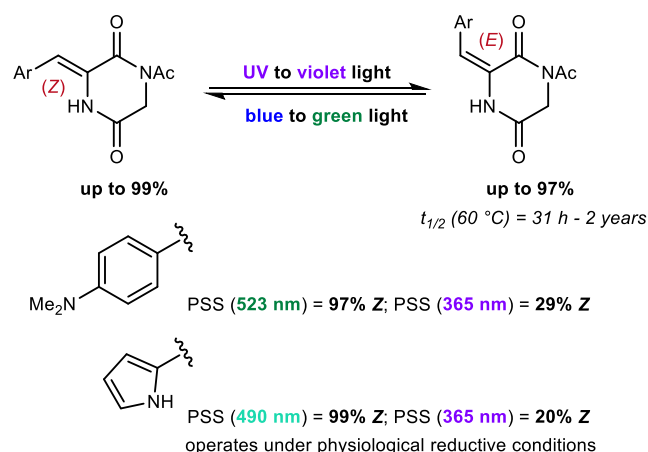
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<sup>b</sup> Institute of Biological and Chemical Systems – FMS, Karlsruhe Institute of Technology, Karlsruhe, Germany.

Employing molecular photoswitches as dynamically addressable bioactive compounds has been demonstrated numerous times to be a promising lead for ground-breaking pharmacological advancement.

One such example was the center point of our latest studies, which revolved around plinabulin and its previously unknown ability to photo-isomerize and thus reversibly change its anti-mitotic activity significantly. The photochromic structure within plinabulin, which we dubbed “hemipiperazine” (HPI), had thus far not been described as a reversibly photo-responsive motif and led us to investigate this new class of molecular photoswitches in more detail.

Here, we report in-depth photophysical investigations of HPIs, which have been shown to be water-compatible and able to withstand physiological reductive conditions over multiple switching cycles. Further, HPIs exhibit high selectivity in addressability of either isomer, in some cases even near-quantitative photostationary states, as well as very long thermal-half lives of the metastable isomers. In combination, these properties make HPIs very favorable candidates for chromophores in the field of photopharmacology.



**Figure 1:** General structural motif of HPIs, outline of their photophysical properties and two especially notable examples.

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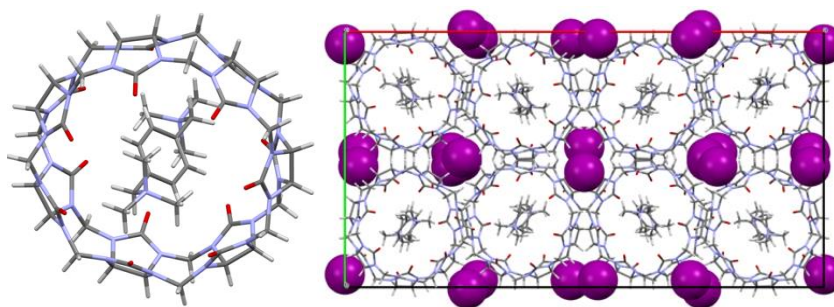
## Elucidating the $\mu$ -ED Structure and Molecular Dynamics of a Phenylene Rotor x Cucurbit[7]uril Complex using VT $^2\text{H}$ Spin Echo Solid-State NMR

Roberto Chavez,<sup>a</sup> Doroteja Lončarić,<sup>bc</sup> Krzysztof Konieczny,<sup>a</sup>  
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Cucurbit[n]uril macrocycles (**CB[n]**) have been established as excellent hosts for encapsulation of a variety of guests. The resulting host-guest complexes show high-affinity binding, the potential of acting as catalysts, and display interesting dynamic processes among several other properties.<sup>1</sup> Cucurbit[7]uril (**CB[7]**) has a much greater aqueous solubility compared to other members of the CB[n] family, exhibiting a water solubility of 30 mM compared to 0.01 mM for CB[8].<sup>2</sup> In this work, multiple host-guest complexes of 1,4-phenylenebis(methylenetrimethylammonium) diiodide (**DL**), with variable degrees of deuteration, and CB[7] have been successfully obtained from an aqueous solution.

Variable-Temperature  $^2\text{H}$  NMR spectroscopy is one of the most powerful techniques to investigate the internal dynamics of deuterium-enriched compounds in the  $10^3$ - $10^8$  Hz regime within the solid state. Careful simulation of the experimental spectra based on models derived from a  $\mu$ -ED crystal structure (shown below) can provide enough insight to characterize motions in solids since the line shape is sensitive to the trajectory and frequency of site exchange.<sup>3</sup> VT  $^2\text{H}$  spin-echo experiments were performed on samples of selectively deuterated guest DL and CB[7] to explore the complex dynamics of the phenylene ring, the methylene groups, and the methyl groups directly attached to the amine moiety in the crystalline solid-state.



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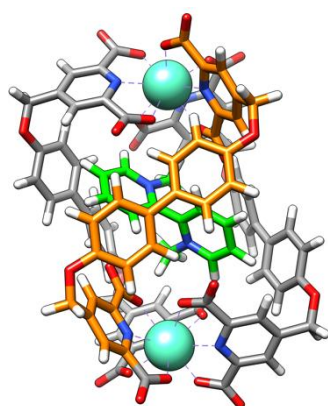
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## Designing Lanthanide-based Supramolecular Hosts

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Research into the molecular recognition and applications of metal-organic coordination cages has generated significant interest over the past few decades. These cages have been shown to encapsulate biorelevant guests, offer stabilization to guest molecules,<sup>1</sup> control reactivity, or catalyze reactions.<sup>2,3</sup> Water-soluble coordination cages are a particular subset of these supramolecules, and offer a unique advantage in furthering our understanding of biological processes, solution behavior in water, and mimicking other compartment molecules observed in nature.<sup>4,5</sup>



**Figure 1.** Self-assembly of a  $\text{Eu}_2\text{L}_3$  water-soluble cage, and encapsulation of a 2,2'-bipyridinium guest.

Lanthanide (Ln) ions in particular have seen relatively little use in the design of coordination cages and polynuclear complexes at large,<sup>6</sup> with the bulk of research focusing mainly on the use of rigid, branching ligands and metal ions with well-defined coordination preferences (namely, the transition or main group metals). In this project, we have synthesized a remarkably stable, water-soluble coordination cage utilizing two  $\text{Ln}^{\text{III}}$  ions bridged by three organic ligands. A series of dicationic guests were screened for geometric compatibility using semi-empirical methods and their affinity to the cage was quantified using UV-Vis spectroscopy and isothermal titration calorimetry. For an aqueous system with this amount of flexibility the binding affinities were very high, in the range of  $10^5 - 10^6 \text{ M}^{-1}$ . Cage formation and guest binding was studied with NMR spectroscopy and confirmed by high resolution mass spectrometry. To verify that guests were binding to the internal cavity, affinities were compared with a negative “half-cage” control and the mononuclear dipicolinate complex,  $\text{Eu}(\text{dpa})_3^{3-}$ .

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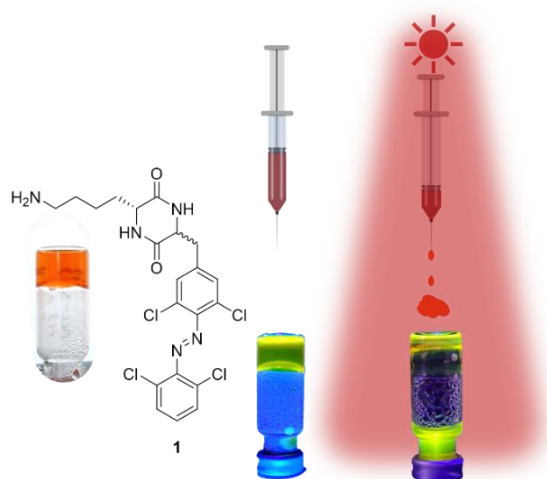


## Molecular Syringe for Cargo Photorelease - Red-light-triggered Supramolecular Hydrogel

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Hydrogels are soft but mechanically self-supporting materials, where a gelling agent - usually a covalent amphiphilic polymer (gelatin, agarose) – binds and cross-links large excess of water. Supramolecular hydrogels are formed either by low-molecular-weight gelators (LMWGs) or macromolecules in the presence of water, in a spontaneous and often synergistic manner by self-assembly through dynamic networks of intermolecular non-covalent bonds.<sup>1</sup> Hydrogels find application in biomedical context, and are well-known for their self-healing properties, thixotropy, on-demand reversibility and stimuli responsiveness, for example to light.<sup>2</sup> These light-triggered hydrogels, also known as photochromic hydrogels, are equipped with ‘photochemical switches’, which give reversible molecular responses, typically in the form of *E/Z*-photoisomerizations<sup>3</sup> or light-induced pericyclic reactions.<sup>4</sup> Such materials are excellent candidates for photo-controlled drug release.



Here we present a new red-light-responsive supramolecular low-MW hydrogelator **1** based on a cyclic dipeptide bearing *ortho*-chlorinated azobenzene as the light-sensitive component. This new hydrogelator forms supramolecular hydrogels already at 0.1 wt% loading.

The Hydrogel (orange) formed from **1** (here 0.3 wt%) in aqueous buffer can physically encapsulate cargo substances (yellow) and act as a molecular syringe. Irradiation of the hydrogels with biocompatible red light (660 nm) caused shrinking of the material with concomitant release of the aqueous buffer loaded with cargo. In darkness the composition remains stable.<sup>5</sup>

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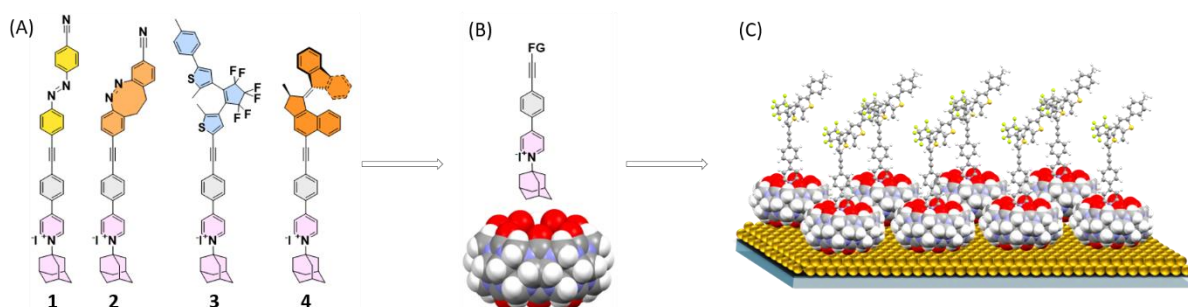
## Molecular Machines in Supramolecular Systems

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Two-dimensional arrays of molecular devices on various surfaces have been extensively studied in the recent decades. The interest is driven by their potential as new stimuli-responsive materials.<sup>1,2</sup> We propose that supramolecular host-guest complexation could offer a new perspective in preparation of single-layers of molecular devices. Cucurbit[7]uril (CB[7]) complexes with molecular devices are investigated on gold (111) surface. The bulky CB[7] macrocycle is intended to separate neighboring molecular devices, while supporting surface adsorption.

Rod-shaped molecular devices **1-4** containing adamantylated pyridinium-based binding sites<sup>3</sup> on one terminus were synthesized. The other terminus of synthesized rods carries either a photoswitch **1-3** or unidirectional light-driven molecular motor **4** (Figure 1). The kinetics of the switching process of devices, as well as their CB[7] complexes **1-4**·CB[7], was followed in solution by UV-Vis spectroscopy. As expected, complexation with CB[7] does not have significant impact on the functionality of such supramolecular assemblies. The next stage of the study involves exploration of self-assembly properties of these complexes on a gold (111) surface. These systems are analyzed by several techniques like PM-IRRAS, SERS, AFM, etc.



**Figure 1.** Structures of molecular rods **1-4** (A), general structure of supramolecular complex **1-4**·CB[7] (B), and an artistic visualization of surface-bound complexes (C).

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## DESIGN AND SYNTHESIS OF DIPOLAR LANTHANIDE(III) MONOPORPHYRINATES COMPLEXES WITH APPLICATIONS IN OPTOELECTRONIC AND NANOSCALE ROTORS

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Molecular architectures play a fundamental role in the quest to miniaturize electronic and mechanical devices.<sup>1</sup> In general, systems based on coordination compounds represent an attractive target for the development of molecular functional materials manipulable at the nanoscale due to their structural versatility, improved electronic properties due to the presence of the metal center, added to their high chemical and thermal stability.<sup>2</sup> The use of lanthanides(III) monoporphyrinates containing dipolar ancillary ligands, allows the access and study of novel coordination complexes with potential applications as technomimetic molecular design with respect to a propeller-type rotor. The porphyrin fragment is immobilized on a metal surface, *e.g.* Au(111), and it is possible to induce rotation of the auxiliary ligand around the metal center using Scanning Tunneling Microscopy.<sup>3</sup> In this regard, the dipolar moment due to the presence of electro-donor (D) and electro-acceptors (A) terminal groups linked by a  $\pi$ -conjugated bridge (D- $\pi$ -A) in the rotator ligand, orientates the molecules in the solid state allowing the synchronized manipulation of molecular arrays deposited on a surface.<sup>4</sup> In addition, the electronic nature of these molecular fragments (D- $\pi$ -A), will give access to chromophores with second-order nonlinear optical activity (NLO-2) in solution and the solid state by second harmonic generation (SHG).<sup>5</sup> Considering these points we present the synthesis and study of these molecular entities allows access to multifunctional molecular materials, with potential applications in optoelectronics and mechanical devices at the nanoscale. All molecular entities were studied and characterized by: UV-Vis, FT-IR, <sup>1</sup>H- and <sup>13</sup>C-NMR, ESI-MS and single-crystal x-ray diffraction.

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## ON COMMAND GAS SORPTION MODULATION AND MULTI-STIMULI RESPONSIVITY IN POROUS SWITCHABLE ARCHITECTURES

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Dynamic building blocks such as molecular switches and motors engineered in permanently porous solids provide fascinating opportunities to modulate properties with external stimuli and achieve complex behaviors beyond those exhibited by the individual components. Highly porous, yet stable architectures, denominated porous switchable frameworks (PSFs), were engineered to sustain the effective isomerization of molecular switches in the solid state.

We fabricate Porous Aromatic Frameworks (PAFs) with bistable molecular switches based on overcrowded alkene incorporated in the backbone of the materials. Dibrominated molecular photoswitches were copolymerized with porogenic building blocks, thus generating highly porous 3D frameworks which display BET surface areas as high as 3950 m<sup>2</sup> g<sup>-1</sup> and provide large free volumes that enable the conformational changes associated with the photoisomerization process.<sup>1</sup> Indeed, upon U.V. light irradiation, solid-state <sup>13</sup>C NMR spectroscopy demonstrates the quantitative isomerization of the light-responsive switches. Moreover, the local isomerization induced by light irradiation affects the overall porosity of the framework and modulates the bulk gas sorption properties. We extend our strategy engineering a hexadentate monomer containing an overcrowded alkene photoswitching core.<sup>2</sup> Yamamoto homocoupling reaction yields swellable and hierarchical micro- and mesoporous architectures with densely integrated photoswitches, that can switch between stable and metastable state upon selective light irradiation. Upon light and chemical stimuli, the flexible framework endowed with hierarchical porosity can explore three unique and distinct porosity states that can be accessed in sequence.

*In-situ* construction of spiropyran moieties with tailored functionality and precise responsivity produces highly porous dynamic materials which undergo reversible transformation of spiropyran to zwitterionic merocyanine by chemical and physical stimulation.<sup>3</sup> These materials show potential for pH active control, responsive gas uptake and release, ions removal, and water harvesting.

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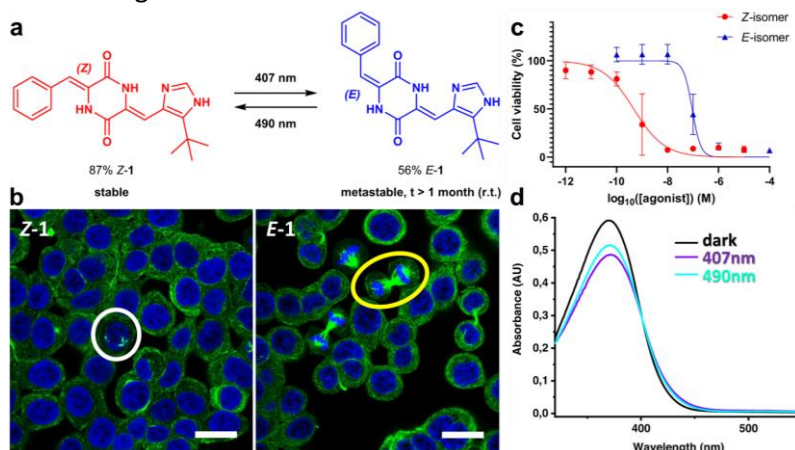
## Photomodulation of plinabulin – a tubulin polymerization inhibitor with low-nanomolar toxicity

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Photopharmacology has attracted growing interest in recent years. In this research area, molecular photoswitches are attached to bioactive agents to precisely control their activity both temporally and spatially. For example, the severe side effects of chemotherapy may be significantly reduced by local activation of a photomodulable drug in tumor tissue. However, modulation of the structure of a bioactive agent with a photoswitch often suffers from drastic reduction in its activity or biostability. Plinabulin is a tubulin polymerization inhibitor with low-nanomolar activity<sup>1</sup> that is in the third phase of clinical trials against non-small cell lung cancer (NSCLC) and chemotherapy-induced neutropenia (CIN).<sup>2</sup> In contrast to other photopharmacological agents, we found that plinabulin itself is capable of photomodulation without further modification. Thus, plinabulin does not suffer from loss of activity due to structural changes and furthermore exhibits pronounced thermal stability and compatibility with aqueous media. In addition, the difference in toxicity between the two isomers is significant, being 85-fold (unidirectional) and 11-fold (bidirectional), respectively.<sup>3</sup> Due to its many attractive properties, plinabulin represents a unique structure for the study and optimization of photomodulable bioactive agents.



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## Hemipiperazine-Based Photochromic Sensors and Nanomaterials

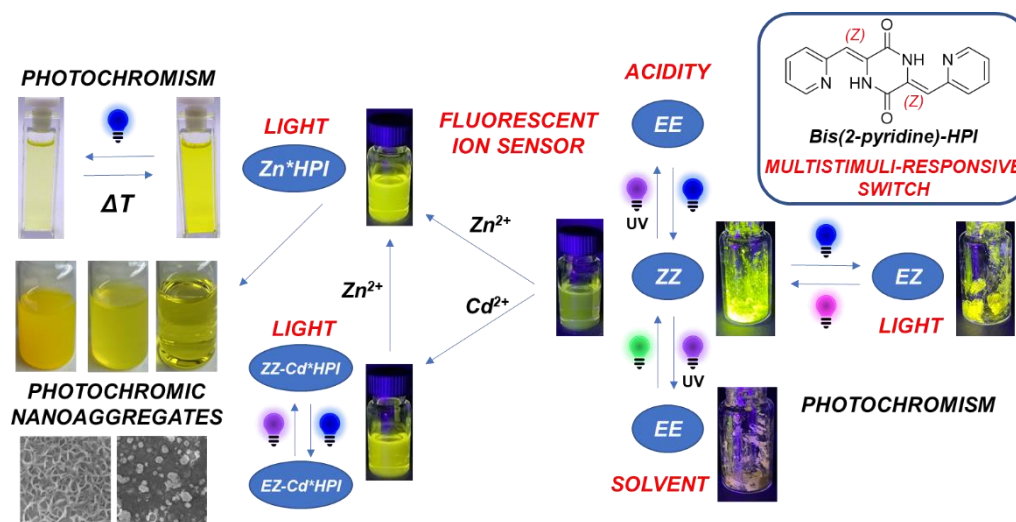
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Our group has recently reported a novel class of molecular photoswitches based on cyclic dipeptides – hemipiperazines (HPI) – which photochromism is based on *E/Z*-photoisomerization of an arylidene substituent attached to a 2,5-diketopiperazine ring. HPIs display a variety of favorable photophysical properties, as well as a broad applicability scope, e.g. water compatibility, bioactivity photomodulation and photoswitchable fluorescence.<sup>[1,2]</sup>

Currently we investigate further applications for these novel photoswitches, with one of them being stimuli-responsive smart materials. Here we report that certain HPI derivatives can be used as phototunable fluorogenic metal ion sensors, thereby combining a reversible response to light with a metal induced fluorescence increase. For example, ion-dependent photoisomerization of the ligand could be used to distinguish different metal ions that usually display similar complexation properties. In a further step, it has been demonstrated that these complexes self-assemble into nanostructures, giving rise to complex multi-stimuli responsive systems.<sup>[3]</sup> Our discovery paves the way to a new family of peptide-derived metal sensors and quantum confined materials. Future applications of HPI in other stimuli-responsive molecular architectures are feasible, i.a. due to extreme thermostability, robustness, and modular synthesis typical to the novel photochrome, as well as its compatibility with polar and aqueous environment.



**Figure 1.** Schematic summary of the novel HPI-based multi stimuli-responsive system.

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## Photoinduced Supramolecular Morphing In Molecularly Motorised Langmuir Monolayers

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Two-dimensional matrices are interesting to study the functioning of molecular machines because their mechanical actuation can be more accurately controlled than in three-dimensional spaces like solvents, gels, or crystals.<sup>1</sup> An attractive 2D-medium is the air-water interface thanks to the possibility of enhanced molecular interactions and shifted equilibria.<sup>2</sup> Langmuir films with photoswitchable surfactants have been extensively studied and show pronounced and reversible differences in molecular packing, orientation and surface pressure upon switching between states and geometries.<sup>3</sup>

Our group has recently developed a series of approaches in which molecular motors can influence their surroundings, not as a function of their state, but because of the work produced during their continuous rotation.<sup>4</sup> In the present study, we now show that the movement of rotation of amphiphilic molecular motors can be used to induce large changes in the compressibility and in the supramolecular structuration of Langmuir monolayers. These dynamic phenomena were followed by compression isotherms, optical measurements and imaging techniques to prove that the self-organized structures observed under UV irradiation result from the rotation of the amphiphilic motors.

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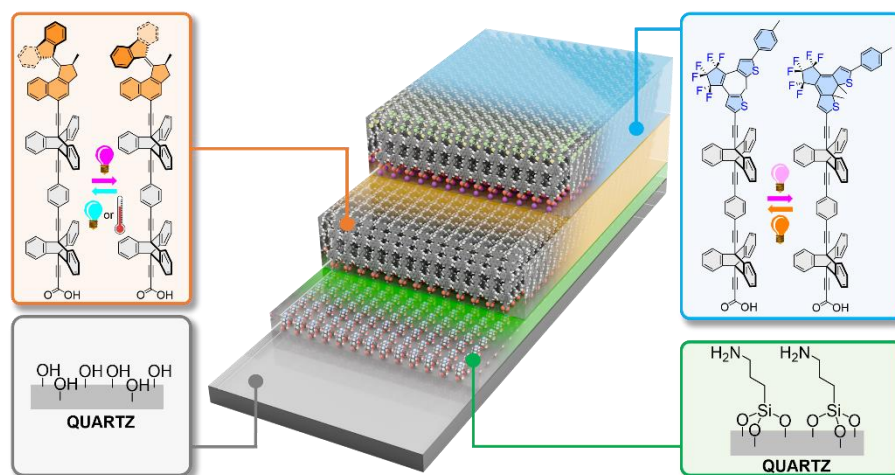
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## Regular Arrays of Rod-Shaped Molecular Photoswitches

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Our desire was to develop a robust methodology allowing smooth production of nearly infinite sheets made of photoresponsive 2-D arrays that can be deposited not only as single layers, but also well-defined multilayered systems to almost any substrate. To that purpose, a modular synthesis of different rod-shaped molecular photoswitches was developed. These triptycene-based rods carrying carboxylic acids were used to form sturdy Langmuir-Blodgett films on the water/air interface that can be transferred to various substrates. In depth structural analysis of these films was performed and experimental results were correlated with extensive density functional theory simulations to confirm the arrangement of the films. The photoswitching capabilities in monolayers, but also in multilayer materials adsorbed on a quartz surface were explored using UV-vis spectroscopy. It was found that molecules operating either on a solid/gas interface (upper layers) or in “solid-state” (photoswitches on interlayers) retained their functionality compared to isolated molecules in a solution. We also clearly demonstrated that individual layers made of the same molecules can be selectively switched using properly chosen monochromatic light.



**Figure 1.** Idealized visualization of multilayer system consisting of modified quartz surface that is covered with two different photoactive Langmuir-Blodgett films.

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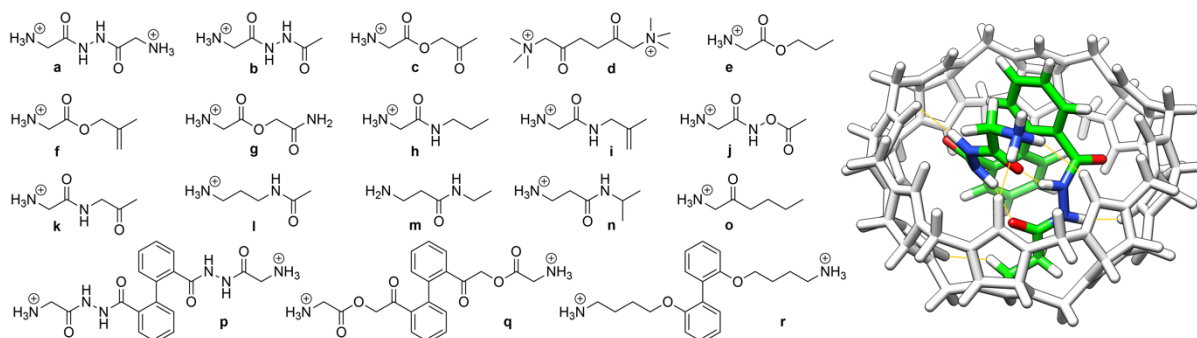


## Counterintuitive Encapsulation of Hydrophilic Guests Inside Water-Soluble Hosts: An exploration of the Hydrogen-Bond Driven Process in Cucurbit[n]urils

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Cucurbit[n]urils are known to encapsulate the hydrophobic portion of positively charged guests, often with extreme affinity<sup>1,2</sup> (up to  $7 \times 10^{17} \text{ M}^{-1}$ ). Each interaction between positively charged substituents and the carbonylated rims of CB[n]s enhances binding affinities, typically by 1000-fold.<sup>3,4</sup> CB[n]s form tight complexes with *hydrophobic* guests, as those suffer less desolvation penalty upon encapsulation.<sup>5</sup> Using 15 small tailor-made guests and 3 biphenyl derivatives, we show here that CB[n] can also encapsulate very *hydrophilic* guests, as long as a proper driving force is created. As the cavity of CB[n]s is very non-polar and non-polarizable, we show that hydrogen bonds from hydrophilic portions of the guests are greatly stabilized inside CB[n], both intramolecularly and intermolecularly with the carbonylated portals of the host.<sup>6</sup> Encapsulation is thus favorable when the stabilization of the hydrogen bonds inside the cavity is greater than the high penalty for the desolvation of the hydrophilic guest.



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## Activating a Light-Driven Molecular Motor by Metal Complexation

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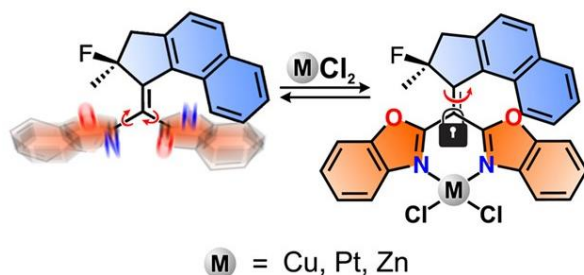
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- *In situ* activation of well-defined motor function
- *In situ* modulation of absorption wavelength and rotary speed
- On-demand coupling of molecular motions

Designing increasingly complex, responsive, and dynamic molecular systems of which the actions can be controlled by a combination of cooperative stimuli is a key challenge towards the development of more advanced functional molecular machines.<sup>1–4</sup> We designed and synthesised a novel light-driven molecular motor, based on a bis(benzoxazole) ligand.<sup>5</sup> Coordination of the ligand to a metal salt leads to the *in situ* activation of a well-defined motor function which can be deactivated in the presence of a competing ligand. The absorption wavelength and the energy barriers in the thermal part of the rotation cycle strongly depend on the choice of metal and the resulting geometry around the metal center. To better understand these observations, we performed DFT calculations to elucidate the mechanism of the thermal part of the rotation cycle. These calculations show how the geometry of the metal center influences the rotational barriers and the possibility to couple the rotary motion with the wagging movement of the metal center. We anticipate that this approach will open new avenues towards more complex, dynamic and coupled molecular systems.

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## Surface Mounted Molecular Motor Based on a Chiral Tripodal Scaffold Driven by Angular Momentum Transfer

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Ensuring unidirectional motion is a long-standing challenge in the design of molecular motors for future molecular technologies. Molecular motor is a nanoscale machine that consumes energy to produce work via the unidirectional and controlled movement. When mounted on metal surfaces (e.g. gold), scanning tunneling microscopy (STM) is a powerful technique to characterize the molecular motors due to the atomic-scale resolution coupled with its ability to track the motion of molecular motor over time. Furthermore, the molecular motors can be powered by STM tip through injecting tunneling electrons. Here, we present the properties of the helical chiral rotor perpendicularly mounted on the gold surface by a tripodal stator in theory and experiment. Our approach to achieve both the perpendicular and spatial arrangement of a protruding chiral rotator on gold is based on a rigid extended tripod terminated with three anchoring groups [1, 2]. On the top of such a tripodal stator, propan-2-on-1,3-diyl bridged biphenyl is mounted via ethynyl linker, which acts as a chiral “Geländer”-type rotator. At the low temperature of the STM experiment the molecular motion is reduced to a level suppressing atropisomerization, such that the helical chiral nature of the rotator is fixed. The proposed mechanism to drive the directed motion is based on the chiral-induced spin selectivity (CISS) effect. This effect causes the electron spin of an injected current to be polarized after passing through a chiral electric field [3]. Low temperature STM experiment with fixed tip position not only demonstrate the preferred rotation directions of individual rotators, but also shows that the rotation direction is maintained upon inverting the applied current direction. However, the experimental studies of the rotation on the dependence on the lateral tip position, voltage and current indicate that the CISS effect is unlikely to cause the preferred rotation direction. The unidirectional rotational motion of the molecule solely relies on the transfer of orbital angular momentum from the driving current to the rotator due to chiral orbitals in the current path, i.e. by orbital currents, as confirmed by theoretical studies. The combination of theoretical hypothesis with corroboration by experimental results is a significant step towards the qualitative comprehension of the microscopic mechanisms that control dc-current-driven molecular rotors.

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## Redox Active Polymers Containing Bisthioxanthylidene Switches

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Bisthioxanthylidene (BTX) switches are known to undergo switching both electrochemically and photochemically. [1] Upon oxidation, BTX readily forms a stable dication, which is accompanied by a large color change (colorless to red/purple). When incorporated in a polymer, the ability to undergo redox switching from a neutral state to a dication can influence the material's properties. When incorporated in a polymer hydrogel, oxidation and reduction should cause the material to swell and shrink, respectively, in a reversible manner. In the future, this could be used to make more complex redox-actuated smart materials. A special feature of BTX is that it is both photoactive and redox-responsive, which could introduce unique properties to BTX-materials. In this project, BTX-crosslinkers and side-chain functionalized monomers are synthesized to determine the difference between using the switch as a crosslinker or as a pendant group. The monomers are then photopolymerized with polyethylene glycol acrylate comonomers in different formulations and the resulting materials are studied. To determine the potential for actuation in water, we look at swelling and deswelling upon oxidation and reduction. We aim to find the optimal crosslinking density, material composition, polymerization solvent and conditions to make a redox actuator.

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