

## Assembly and investigation of electrochemically triggered molecular muscles

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Mechanically interlinked supramolecular systems are of interest for the design of systems displaying shape alteration/adaption.<sup>1</sup> Particular appealing are systems reacting on an external trigger and thus, catenanes and rotaxanes comprising electrochemically addressable subunits have been assembled and displayed redox state dependant mechanical motions.<sup>2</sup> Immobilization of the macrocyclic subunits of rotaxanes comprising two rings on flexible cantilevers even allowed translating the electrochemically triggered molecular motion into the macroscopic bending of the substrate.<sup>3</sup> In order to assemble a molecular muscle, Sauvage presented the design concept of a pseudo-rotaxane.<sup>4</sup> By attaching the rotaxane axis at the macrocycle's periphery he obtained a system forming a supramolecular dimer in which the axis of one molecule is penetrating the macrocycle of the other. Functionalization of the subunits with different coordination sites allowed altering the expansion of the structure by varying the coordinating ion.

Inspired by the concept of Sauvage,<sup>4</sup> we investigated organic molecular structures potentially able to dimerize to pseudo-rotaxanes.<sup>5</sup> By functionalizing the periphery of a *Diederich*-type cyclophane<sup>6</sup> with a rigid OPE rod we obtained the ideal pseudo-rotaxane molecule **1** forming a dimer in polar solvents already at very low concentrations (e.g.  $10^{-7}$  mM in H<sub>2</sub>O/CH<sub>3</sub>OH: 3/2).<sup>7</sup> The pronounced tendency to form the mechanically interlinked dimer makes it to the ideal lead structure for the integration of pseudo-rotaxanes in molecular architectures. Here we suggest to further functionalize the molecular rod with an electrochemically addressable tetrathiafulvalen (TTF) subunit as displayed e.g. in the amphiphilic molecular rods **2** and **3** (Figure A). The attraction between the electron rich TTF and the positively charged cyclophane subunit will even further increase the dimerization tendency of the molecular structure. More interesting will be the redox chemistry of the pseudo-rotaxane dimer. The TTF subunit can be oxidized at a moderate applied potential (0.34 V for TTF vs. Ag/AgCl in CH<sub>3</sub>CN) creating the cation TTF<sup>+</sup>. Upon oxidation the positive charges of both TTF<sup>+</sup> cations and of the cyclophane subunits will repel each other resulting in a contraction of the pseudo-rotaxane subunit. The electrochemically triggered contraction of the system is sketched in figure C.

The amphiphilic rods **2** and **3** are terminally functionalized with a trimethylsilyl (TMS) protected acetylene to enable their integration in molecular architectures by click-chemistry.<sup>8</sup> As an example the reaction of the rod **2** with the triazine **5** provides the amphiphilic rod **4** comprising acetyl protected terminal anchor groups. While already the dimeric pseudo-rotaxane of **4** is very interesting as the interplay between electrochemistry and expansion of the structure can be analyzed in an electrochemically controlled AFM experiment (n=1 in Figure D), a more general integration strategy will be investigated. Numerous click-chemistry protocols in polar solvents (even aqueous conditions) are reported in which the amphiphilic molecular rods **2** and **3** are present as mechanically interlinked pseudo-rotaxanes. Performing click-chemistry with the mechanically interlinked structure allows to mechanically lock the system. As displayed in figure B, the bulky triazine **6** will act as a stopper providing the mechanically locked dimer structure **7** which is no longer exposed to a threading/de-threading equilibrium. Such locked pseudo-rotaxanes are no longer limited to polar solvents and thus the scope of potential reaction conditions for their integration will be considerably enlarged.

The modularity of these building blocks enables to easily vary the target structures and an equally interesting example will be the copolymerization with bifunctional linkers like **8** or **9** providing poly- and oligomers with electrochemically triggered dimensions. Figure E sketches the contraction of a cyclic hexamer upon oxidation resembling the action of a ring muscle.

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<sup>8</sup> C. R. Becer, R. Hooenboom, U. S. Schubert, *Angew. Chem. Int. Ed.*, **2009**, *48*, 4900.

This PhD program is geared towards the development of the synthesis of these interlinked supramolecular systems in the labs of the PI (Marcel Mayor, University of Basel). The investigation of the electrochemically triggered mechanical motions of these systems will be performed with mechanical controlled break junction and scanning probe experiments under electrochemical control at the Department of Physics of the University of Basel (Co-PI, Michel Calame) as well as in the Department of Chemistry and Biochemistry the University of Berne. The cooperating teams have a long standing tradition of joint research projects which resulted in numerous joint publications, guaranteeing the scientific exchange and feedback between both teams.

