



Project no.  
**NMP4-CT-2004-013525**

Project acronym  
**Hy3M**

Project title  
**Hydrogen-bond geared Mechanically interlocked Molecular Motors**

Instrument  
**Specific Targeted Research Project**

Thematic Priority  
**Nanotechnologies and nano-sciences, knowledge-based multifunctional materials and new production processes and devices**

**Publishable Executive Summary second year periodic activity report**

Period covered: from 1.4.2006 to 31.3.2007

Date of preparation: 15.5.2007

Start date of project: 1.4.2005

Duration: 36 months

Project coordinator name: Wybren Jan Buma  
Project coordinator organisation name: UvA/HIMS

**Executive summary**

Hy3M seeks to create new types of synthetic molecular motors - fuelled by energy in the form of light, heat, electrons, *etc.* - that transmit the effects of mechanical motion from the *molecular* level through to the *macroscopic* world. To this purpose Hy3M has set out to (i) develop new methods and mechanisms for controlling sub-molecular translational and rotary motion through manipulation of hydrogen bonding interactions and (ii) find out how to link such movements to the outside world in order to do useful work. Primary objectives of the Project are to “*Design, Synthesize, Assemble, Characterize and Evaluate Functional Materials that act through Mechanical Motion at the Molecular Level*”. With this objective we aim to demonstrate the feasibility of exploiting molecular motion at the macroscopic level in general, using key strategic targets as particular examples.

Six workpackages are aimed at obtaining an assessment of both the static and dynamic influences of mechanical interlocking at the molecular level, the ability to assemble the structures into films or polymers which must be engineered into a useful material, and an understanding of how key proximity effects could be “designed in” to tailor specific properties. The knowledge generated from these workpackages is employed to produce materials that exhibit various types of macroscopic responses from mechanical motion at the molecular level (surface-property change, shape-change, movement of object) as well as a synthetic molecular motor coupled to the outside world to do work.

The contractors involved in Hy3M are given in the following Table:

<b>Partic. Role*</b>	<b>Partic. no.</b>	<b>Participant name</b>	<b>Participant short name</b>	<b>Country</b>	<b>Date enter project</b>	<b>Date exit project</b>
CO	1	Universiteit van Amsterdam	UvA-HIMS	NL	Month 1	Month 36
CR	2	University of Edinburgh	UniEd	UK	Month 1	Month 36
CR	3	Università di Bologna	UniBo	I	Month 1	Month 36
CR	4	University of Groningen	RUG	NL	Month 1	Month 36
CR	5	University of Angers	UniAn	F	Month 1	Month 36
CR	6	Consiglio Nazionale delle Ricerche	CNR	I	Month 1	Month 36
CR	7	Intertek ASG	ASG	UK	Month 1	Month 36

\*CO = Coordinator; CR = Contractor

The overall project management is in the hands of HIMS (Van 't Hoff Institute of Molecular Sciences) of the Faculty of Science of the Universiteit van Amsterdam. Prof. dr Wybren Jan Buma (1961) is the co-ordinator. Contact details of the co-ordinator are:

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At the start of the second year of the Project Hy3M has identified the following six secondary objectives to work on: (i) develop viable, high yielding synthetic routes to functional catenanes and rotaxanes, (ii) develop methods of shuttling/switching the positions of the mechanically interlocked components, (iii) determine properties of functional catenanes and rotaxanes, (iv) assemble ordered catenane and rotaxane arrays, (v) determine effects of shuttling on properties, and (vi) develop methods for engineering catenane and rotaxane-based materials. Objectives (i-iii) and vi have been a continuation of the first year work, objectives (iv-v) have been initiated in the second year period. During the reporting period all partners have been actively involved in the work on these objectives.

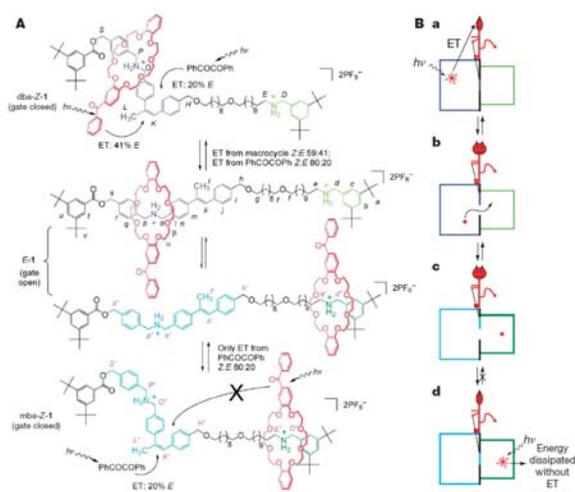


Figure 1. A photo-operated molecular information ratchet. A, Irradiation of rotaxane **1** (1mM) at 350nm in CD<sub>3</sub>OD at 298K interconverts the three diastereomers of **1** and, in the presence of benzil (PhCOCOPh), drives the ring distribution away from the thermodynamic minimum, increasing the free energy of the molecular system without ever changing the binding strengths of the macrocycle or ammonium binding sites. For clarity, the photoinduced energy transfer (ET) pathways are only illustrated on the Z- (gate closed) forms of **1** although the same processes occur for the equivalent E- (gate open) translational isomers. When the macrocycle is on the mba binding site (green), intramolecular ET from the macrocycle is inefficient and intermolecular ET from benzil dominates (the cross on the intramolecular ET arrow is used to indicate that it is a rare event compared to other relaxation pathways). When the macrocycle is on the dba binding site (blue), both ET mechanisms can operate efficiently. The amount of benzil present determines the relative contributions of the two ET pathways and thus the nanomachine's effectiveness in pumping the macrocycle distribution away from equilibrium. The mechanism requires the shuttling of the ring between the two ammonium groups in E-1 to be slow with respect to the lifetime of the macrocycle-sensitizer triplet excited state. B, Cartoon illustration of the operation of **1** in terms of a non-adiabatic Maxwellian pressure demon.

The second year of the project has gone extremely well with several important breakthroughs reflected in accomplishing **deliverables D4, D8, and D9**. We showed that information about the location of a macrocycle in a rotaxane can be used, on the input of light energy, to alter the kinetics of the shuttling of the macrocycle between two compartments on the axle. The selective transport of particles between two compartments by Brownian motion in this way bears similarities to the hypothetical task performed without an energy input by a ‘demon’ in Maxwell’s famous thought experiment. Our observations demonstrate that synthetic molecular machines can operate by an information ratchet mechanism, in which knowledge of a particle’s position is used to control its transport away from equilibrium (see Figure 1).<sup>1</sup> We have developed new synthetic routes and prepared a host of new molecules.<sup>2,3</sup> In addition to using many new techniques to characterize the signatures of these compounds<sup>4-6</sup>, we have developed methods to electrochemically, photochemically, thermally, and mechanically switch rotaxane molecules. The material acquired from the synthetic and spectroscopic studies have formed a major input for an extensive review.<sup>7</sup> Great progress has been made in assembling arrays of catenanes and rotaxanes. Contrary to other reports, we have demonstrated that ordered acid-terminated self-assembled monolayers are obtained with the same preparation conditions as those of the methyl-terminated ones, without any additional treatment.<sup>8</sup> When a local mechanical perturbation is applied to the surface of a thin film of a rotaxane, it has been shown that the molecules self-organize into periodic arrays of discrete dots or lines<sup>9</sup> (Figure 2). The phenomenon can be exploited as a bottom-up nanofabrication method.

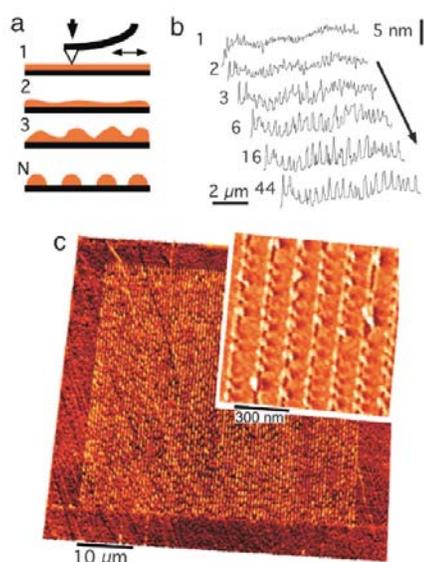


Figure 2 Patterning of rotaxane films by AFM triggered self-organization. (a) Scheme of the process. (b) Sequence of topography line scans recorded at the threshold force. (c) Array of dots fabricated by individual line scans of the AFM tip. Large area pattern of dots is shown. (Inset) An example of a high-resolution pattern.

The results illustrate that the major developments world-wide over the past 12 months on hydrogen bond-assembled molecular machines have occurred as part of the *Hy3M* Project. It is therefore not surprising that the *Hy3M* Project has attracted considerable attention in the form of highlights and commentaries in Journals like *Nature*, *Science*, and *PNAS*, as well as radio interviews, and innumerable newspaper articles, and that its participants are frequently invited to give their expert opinion on new results in this exciting field.

[1] V. Serreli, C.-F. Lee, E.R. Kay and D.A. Leigh, *Nature* **2007**, *445*, 523-527. [2] S. Djurdjevic, D.A. Leigh, H. McNab, S. Parsons, G. Teobaldi, F. Zerbetto, *J. Am. Chem. Soc.* **2007**, *129*(3), 476-477; [3] J. Brna, A.M. Brouwer, S.M. Fazio, N. Haraszkiewicz, D.A. Leigh and C.M. Lennon (nee Keaveney) *Chem. Commun.* **2007**, 1910-1912; [4] [P. Bodis, R. Timmer, S. Yeremenko, W.J. Buma, J.S. Hannam, D.A. Leigh, and S. Woutersen, *J. Phys. Chem. C* **2007**, *111*(18), 6798-6804 (2007); [5] C.M. Whelan, F.G. Gatti, D.A. Leigh, P. Rudolf, S. Rapino and F. Zerbetto, *J. Phys. Chem. B* **2006**, *110*(34), 17076-17081; [6] J. Niziol, K. Nowicka and F. Kajzar, in “*Nonlinear optical properties of matter: From molecules to condensed phases*”, M.G. Papadopoulos, J. Leszczynski and A.J. Sadlej, Eds, Berlin: Springer, 2006 - s. 609--643 - ISBN: 978-1-4020-4849-4; [7] E.R. Kay, D.A. Leigh and F. Zerbetto, *Angew. Chem. Int. Ed.* **2007**, *46*, 72-191; [8] S.M. Mendoza, I. Arfaoui, S. Zandarini, F. Paolucci, and P. Rudolf, *Langmuir* **2007**, *23*, 582-588. [9] F. Biscarini, M. Cavallini, R. Kshirsagar, G. Bottari, D.A. Leigh, S. Leon, F. Zerbetto, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 17650-17654.