

University of Groningen

## Nanomotor rotates microscale objects

Eelkema, R; Pollard, MM; Vicario, J; Katsonis, N; Ramon, BS; Bastiaansen, CWM; Broer, DJ; Feringa, BL; Serrano Ramon, Blanca; Bastiaansen, Cees W.M.

*Published in:*  
Nature

*DOI:*  
[10.1038/440163a](https://doi.org/10.1038/440163a)

**IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.**

*Document Version*  
Publisher's PDF, also known as Version of record

*Publication date:*  
2006

[Link to publication in University of Groningen/UMCG research database](#)

*Citation for published version (APA):*

Eelkema, R., Pollard, MM., Vicario, J., Katsonis, N., Ramon, BS., Bastiaansen, CWM., Broer, DJ., Feringa, BL., Serrano Ramon, B., Bastiaansen, C. W. M., & Broer, D. J. (2006). Nanomotor rotates microscale objects. *Nature*, 440(7081), 163. <https://doi.org/10.1038/440163a>

### Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

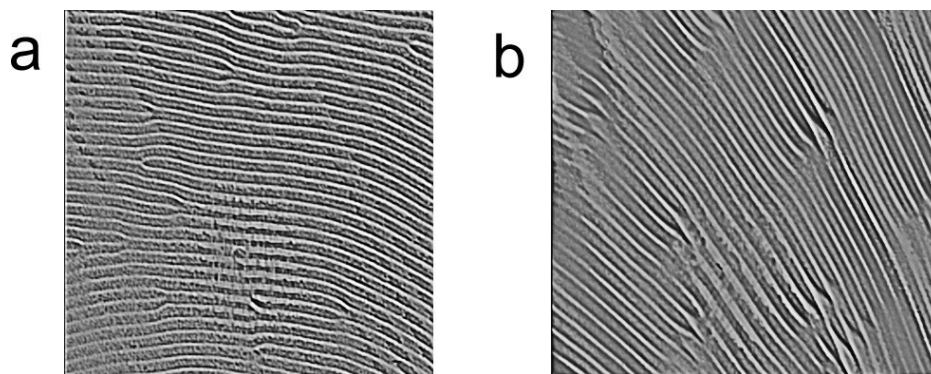
### Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

*Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.*

## Supplementary information

### Supplementary figure



#### Supplementary Figure 1

This picture shows the rotation of the surface relief of a reorganizing liquid crystalline film. **a** and **b** show optical profilometry images of the LC film doped with motor **1** (1% by weight), during the thermal step of the motor. The images were recorded at a 90 s interval, showing the counter-clockwise movement of the surface relief. The size of the images is  $240 \mu\text{m}^2$ .

### Supplementary methods

#### Materials

All solvents were HPLC or spectroscopic grade, and were used as received. The liquid crystalline material E7 was purchased from Merck, Darmstadt.<sup>1</sup>

#### Preparation of liquid crystalline films

A microscope slide was thoroughly cleaned, spin-coated with a commercially available polyimide (Optmer AL1051, JSR, Belgium) and allowed to harden overnight in a vacuum oven ( $170^\circ\text{C}$ , 200 mbar). The surface was then rubbed with a polyester fabric to induce parallel alignment in the liquid crystalline samples. A toluene solution of E7 and (*P*)-**1** (1

wt% (*P*)-**1** with respect to E7) was then deposited on this surface, the toluene was allowed to evaporate to give cholesteric phases with polygonal textures, which rotated when irradiated with 365 nm light.

## Particle rotation

All particles were placed on the LC film by sprinkling them on a freshly prepared LC film. Using the optical microscope they could be observed rotation during irradiation and thermal steps.

## General procedure for determination of the cholesteric pitch

The pitch of the liquid crystalline (LC) phases was determined by Grandjean-Cano technique,<sup>ii</sup> using plane-convex lenses of known radii ( $R = 25.119$  or  $30.287$  mm, Linos Components; Radiometer), and an optical microscope. LC films were prepared as described above, and a plane-convex lens of known diameter was applied. Grandjean-Cano lines could be observed, and the pitch could be determined indirectly by measuring the distances between the consecutive lines. The helical twisting power of the stable form of **1** is  $+90 \mu\text{m}^{-1}$  ( $\beta_M$ , E7), the helical twisting power of the photostationary state (365 nm, E7) is  $> -59 \mu\text{m}^{-1}$  ( $\beta_M$ , E7). We were unable to quantitatively determine the amount of the unstable form of **1** in the photostationary state of the motor in the LC, as the lifetime of the unstable form of this motor is very short at room temperature, making it impossible to analyse by high performance liquid chromatography. Reported helical twisting powers are determined in mol dopant per mol LC, assuming an average molecular weight of  $271.2 \text{ g/mol}$  for E7.<sup>i</sup> The sign of the helical pitch was determined with a contact method.<sup>iii</sup> Mixed samples with a doped cholesteric liquid crystal of known negative screw sense were used, consisting of dopant ZLI-811 (Merck, Darmstadt, Germany) in E7.

## Microscope

Images and movies of the moving particles were recorded in transmission using an Olympus BX 60 microscope, equipped with polarizers and a Sony 3CCD DXC 950P

digital camera, attached to a personal computer with Matrox Inspector 2.1 imaging software.

## **Lamp**

For irradiation a Spectroline model ENB-280C/FE lamp was used at 365 nm. The lamp was held at an angle of 45° with respect to the sample plane, to allow irradiation under the microscope. The distance between the lamp and the sample was approximately 15 cm.

## **Optical profilometer**

Surface structures were determined using a Fogale Nanotech Zoomsurf 3D, with samples prepared as described above, using monochromatic red light. After irradiation with 365 nm UV light (5 min), the surface structure of the LC film was observed to rotate in optical profiles taken during the thermal isomerization step of the motor (see Supplementary Figure 1). Red light optical profilometry was found to overestimate the height of the measured relief structures. Therefore, a series of control experiments were performed to correlate the corrugation heights observed by AFM with those observed by optical profilometry. Through cross correlation of the liquid crystalline samples and reference solid samples measured by both AFM and optical profilometry, the corrugation height was determined to be between 20 and 50 nm. After optical profilometric measurement the samples were examined in an optical microscope. In all cases the periodicities determined by optical profilometry corresponded with those determined with the optical microscope.

## **AFM**

AFM measurements were performed with both a Dimension 3000 AFM and a Nanoscope IV (Digital Instruments, Santa Barbara, CA) at room temperature and under ambient conditions. Heavily doped silicon cantilevers with a resonance frequency of ~300 kHz were used for imaging in non-contact mode. Experiments were performed in several sessions using different tips to check for reproducibility and to avoid artefacts. The 3D

surface plot was drawn with Matlab. The textures observed by AFM showed the same horizontal periodicity as observed by optical microscopy on the same sample.

## **Characterization and enantioresolution of compound **1****

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Varian Mercury Plus, operating at 399.93 MHz, respectively, for the  $^1\text{H}$  nucleus, and at 100.57 MHz for the  $^{13}\text{C}$  nucleus, in  $\text{CDCl}_3$ . Chemical shift values are denoted in  $\delta$  values (ppm) relative to residual solvent peaks ( $\text{CHCl}_3$ ,  $^1\text{H}$   $\delta = 7.26$ ,  $^{13}\text{C}$   $\delta = 77.0$ ). Preparative HPLC was on a preparative Gilson HPLC system consisting of a 231XL sampling injector, a 306 (10SC) pump, an 811C dynamic mixer, an 805 manometric module, with a 119 UV-VIS detector and a 202 fraction collector, using a ChiralPak AD chiral column.

### **9-(2-Phenyl-2,3-dihydro-cyclopenta[a]naphthalen-1-ylidene)-9H-fluorene **1****

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.21 (d,  $^2J_{\text{HH}} = 15.0$  Hz, 1H,  $\text{CH}_2$ ), 3.98 (dd,  $^2J_{\text{HH}} = 15.0$  Hz,  $^3J_{\text{HH}} = 6.6$  Hz, 1H,  $\text{CH}_2$ ), 5.37 (d,  $^3J_{\text{HH}} = 6.6$  Hz, 1H, CH), 6.80 – 6.88 (m, 2H), 7.11 – 7.27 (m, 7H), 7.31 (t,  $^3J_{\text{HH}} = 7.7$  Hz, 1H), 7.41 – 7.53 (m, 4H), 7.77 (d,  $^3J_{\text{HH}} = 7.7$  Hz, 1H), 7.80 (d,  $^3J_{\text{HH}} = 7.7$  Hz, 1H), 7.87 (d,  $^3J_{\text{HH}} = 8.4$  Hz, 1H), 7.94 (d,  $^3J_{\text{HH}} = 8.1$  Hz, 1H), 8.00 (d,  $^3J_{\text{HH}} = 8.1$  Hz, 1H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  44.1 ( $\text{CH}_2$ ), 56.5 (CH), 119.1 (CH), 119.5 (CH), 123.7 (CH), 124.4 (CH), 125.5 (CH), 125.8 (CH), 126.1 (CH), 126.4 (CH), 127.0 (2CH), 127.2 (3CH), 127.6 (CH), 128.7 (CH), 128.8 (CH), 129.0 (C), 131.1 (CH), 132.7 (C), 133.0 (C), 137.0 (C), 137.6 (C), 139.5 (C), 139.8 (C), 140.1 (C), 143.9 (C), 146.2 (C), 146.4 (C).  $m/z$  (EI, %) = 406 ( $\text{M}^+$ , 84), 328 (100), 273 (35), 241 (43), 196 (68), 165 (32). HRMS (EI): calcd. for  $\text{C}_{32}\text{H}_{22}$ : 406.1721, found 406.1735; UV (*n*-hexane):  $\lambda_{\text{max}}$  ( $\epsilon$ ) 219 (64218), 238 (41105), 264 (23217), 387 (21119); CD (*n*-hexane):  $\lambda_{\text{max}}$  ( $\Delta\epsilon$ ) 208 (+65), 234 (-129), 273 (+72), 286 (+48), 321 (+11), 383 (-6.2); Enantioresolution of **1** was accomplished by preparative chiral HPLC (ChiralPak AD, *n*-heptane:IPA = 96:4, 1 ml/min.). Retention times: 5.1 ((2'*S*)-(P)-**1**) and 8.3 min ((2'*R*)-(M)-**1**). The absolute configuration of molecular motor (2'*S*)-(P)-**1** was determined by comparison of its circular dichroism (CD) spectra to the CD spectra of a similar motor of known configuration.<sup>iv</sup> The synthesis, structural analysis, photochemical and thermal isomerisation processes in solution of (2'*S*)-(P)-**1** will be reported elsewhere.

---

<sup>i</sup> For the composition of E7, see: Lee, H.-K., Kanazawa, A., Shiono, T., & Ikeda, T. All-optically controllable polymer/liquid crystal composite films containing the azobenzene liquid crystal. *Chem. Mater.* **10**, 1402-1407 (1998).

<sup>ii</sup> Dierking, I. *Textures of Liquid Crystals* (Wiley-VCH, Weinheim, 2003).

<sup>iii</sup> Isaert, N., Soulestin, B. & Malthète, J. Determination of absolute torsion direction of cholesteric and smectic c chiral phases. *Mol. Cryst. Liq. Cryst.* **37**, 321–333 (1976).

<sup>iv</sup> ter Wiel, M. J. K. *Ph.D. Thesis*, University of Groningen, 2004.