

University of Groningen

Object Transportation System Mimicking the Cilia of *Paramecium aurelia* Making Use of the Light-Controllable Crystal Bending Behavior of a Photochromic Diarylethene

Nishimura, Ryo; Fujimoto, Ayako; Yasuda, Nobuhiro; Morimoto, Masakazu; Nagasaka, Tatsuhiro; Sotome, Hikaru; Ito, Syoji; Miyasaka, Hiroshi; Yokojima, Satoshi; Nakamura, Shinichiro

Published in:
Angewandte Chemie-International Edition

DOI:
[10.1002/anie.201907574](https://doi.org/10.1002/anie.201907574)

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:
2019

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

Citation for published version (APA):

Nishimura, R., Fujimoto, A., Yasuda, N., Morimoto, M., Nagasaka, T., Sotome, H., Ito, S., Miyasaka, H., Yokojima, S., Nakamura, S., Feringa, B. L., & Uchida, K. (2019). Object Transportation System Mimicking the Cilia of *Paramecium aurelia* Making Use of the Light-Controllable Crystal Bending Behavior of a Photochromic Diarylethene. *Angewandte Chemie-International Edition*, 58(38), 13308-13312. <https://doi.org/10.1002/anie.201907574>

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.



Crystal Motion Hot Paper

International Edition: DOI: 10.1002/anie.201907574
German Edition: DOI: 10.1002/ange.201907574

Object Transportation System Mimicking the Cilia of *Paramecium aurelia* Making Use of the Light-Controllable Crystal Bending Behavior of a Photochromic Diarylethene

Ryo Nishimura,* Ayako Fujimoto, Nobuhiro Yasuda, Masakazu Morimoto, Tatsuhiro Nagasaka, Hikaru Sotome, Syoji Ito, Hiroshi Miyasaka, Satoshi Yokojima, Shinichiro Nakamura, Ben L. Feringa, and Kingo Uchida*

Abstract: The design of an object transportation system exploiting the bending behavior of surface-assembled diarylethene crystals is reported. A photoactuated smart surface based on this system can transport polystyrene beads to a desired area depending on the direction of the incident light. Two main challenges were addressed to accomplish directional motion along a surface: first, the preparation of crystals whose bending behavior depends on the direction of incident light; second, the preparation of a film on which these photochromic crystal plates are aligned. Nuclei generation and nuclear growth engineering were achieved by using a roughness-controlled dotted microstructured substrate. This system demonstrates how to achieve a mechanical function as shown by remote-controlled motion along a surface.

Recently, molecular machines, in which one molecule or an assembly of responsive molecules exhibit a mechanical motion at the microscopic or nanoscale accompanied by three-dimensional structural changes due to external stimuli, have been actively studied.^[1] In nature, many animals and plants have specific micro/nanostructures at their surfaces exhibiting various dynamic functions.^[2] In particular, the responsive structures and cooperative effects in arrays, for example, the antireflection effect of the moth eye,^[3] strong adhesion and friction forces of the gecko foot,^[4] and cilia of the mammal's respiratory tract,^[5] have been studied and put to practical use. The cilia's functions include the transportation of food, body fluids, body waste, and reproductive products, and the cleaning of the respiratory tract. Especially,

those of *Paramecium aurelia* have attracted much attention, since the cilia's motion induces many complex movements of the body.^[6] Mechanical functions and responsive surfaces are very attractive;^[7] therefore, cilia-inspired functional materials have been designed.^[5] Chemoresponsive self-oscillating gels such as the artificial cilia-inspired actuator have been studied.^[5a-c] The spontaneous mechanical oscillation of the gel is induced by the Belousov-Zhabotinsky (BZ) reaction and propagates as a wave on the gel plate. The diffusion of this chemical wave affects the dynamic behavior of neighboring BZ gels. This diffusing dynamic behavior regenerates wave of cilia. These systems operate by no external stimuli; therefore, precise control of the gel's motion is difficult. On the other hand, other systems responding to external stimuli (e.g. light or magnetic field) have also been reported.^[5d-g] Jiang and co-workers reported the transportation of a microsphere by magnetically actuated fibers mimicking the cilia's bending motion.^[5d] The fibers consist of polydimethylsiloxane (PDMS) and cobalt magnetic particles (Co MPs). The bending motion of the fiber array was guided by a magnetic field. On the smart array, a PS microsphere was transportable by the magnetic field. In the other report, a water droplet was transported by the magnetic field.^[5e] However, in this system, a droplet moved not only because of the magnetic field but also because of longitudinal vibrations. Photoactuated cilia-inspired materials also have been studied.^[5f,g] Oosten and co-workers reported a light-driven miniature polymeric actuator mimicking the motion of natural cilia; the actuator was prepared by inkjet printing technology and self-organization

[*] R. Nishimura, A. Fujimoto, Prof. Dr. K. Uchida
Department of Materials Chemistry
Faculty of Science and Technology, Ryukoku University
Seta, Otsu, Shiga 520-2194 (Japan)
E-mail: uchida@rins.ryukoku.ac.jp
ryonishimura1019@yahoo.co.jp

Dr. N. Yasuda
Diffraction and Scattering Division
Japan Synchrotron Radiation Research Institute
1-1-1 Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5198 (Japan)

Prof. Dr. M. Morimoto
Department of Chemistry and Research Center for Smart Molecules
Rikkyo University
3-34-1 Nishi-Ikebukuro, Toshima-ku, Tokyo 171-8501 (Japan)
T. Nagasaka, Dr. H. Sotome, Dr. S. Ito, Prof. Dr. H. Miyasaka
Graduate School of Engineering Science, Osaka University
Toyonaka, Osaka 560-8531 (Japan)

Prof. Dr. S. Yokojima
School of Pharmacy, Tokyo University of Pharmacy and Life Sciences
1432-1 Horinouchi, Hachioji, Tokyo 192-0392 (Japan)

Dr. S. Nakamura
RIKEN Cluster for Science, Technology and Innovation Hub
Nakamura Laboratory
2-1 Hirosawa, Wako, Saitama 351-0198 (Japan)

Prof. Dr. B. L. Feringa
Stratingh Institute for Chemistry, University of Groningen
Nijenborgh 4, 9747 AG, Groningen (The Netherlands)

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:
 <https://doi.org/10.1002/anie.201907574>

of a liquid crystal network.^[5f] They introduced two different azobenzene units in the polymer as the photoresponsive moieties. By assembling two different photoactuated polymers to the substrate and irradiating with UV and visible light, they realized the complex asymmetric motion of cilia. The other example also realized the complex motion of cilia and transported the object by flow generated by fiber motion.^[5g] In the above examples, the complex motions of natural cilia were achieved. However, on-demand directional transportation of an object was not achieved.

Diarylethenes, a highly promising class of thermally stable photochromic compounds, show reversible cyclization and cycloreversion reactions upon alternating irradiation with UV and visible light, even in the crystalline state.^[8] The most commonly observed crystal behavior has been photoinduced bending, rolling, and twisting,^[9] resulting in the elegant demonstration by Irie and co-workers of an iron ball being lifted on a bending crystal.^[9b] Previously, we have shown the reversible photoinduced bending behavior of a crystal of a diarylethene **1o** that takes advantage of intermolecular hydrogen bonding (Figure 1 a).^[9d] The thin crystal of **1o** bent away from the incident UV light, and reverted to the original shape upon visible-light irradiation from any direction.

Herein, we report a unique surface-confined transportation system using the bending behavior of an **1o** crystal which is controlled only by photoirradiation (Figure 1 b). This system has the possibility to transport an object in any desired direction upon a change in the direction of incident UV light.

A key requirement in the design of the microobject transportation system is that the crystals bend in any direction in response to the incident UV light. Following the preparation of the platelet crystals of diarylethene derivative **1o**, we confirmed the bending behavior by irradiating with UV light from different incident directions.^[9d] At first, upon UV light ($\lambda = 254$ nm) irradiation of the (001) surface (the wide face), the crystal bent away from the incident UV light (Figure S1a, Supporting Information movie 1). Subsequently, UV light ($\lambda = 254$ nm) was applied to the (100) surface, the narrow face, and the crystal also bent slowly away from the incident light (Figure S1b, Supporting Information movie 2). Irie and co-workers reported the mechanism of the photoinduced crystal-bending behavior of the photochromic diarylethene.^[9b] When the short axis (height) of a diarylethene molecule in the crystal is parallel to the long axis of the unit cell, the crystals exhibit a bending motion away from the incident UV light,^[9b] due to the elongation of the height of the assumed triangle shape of the molecule (Figure 2).

The X-ray crystallographic analysis of the **1o** crystal shows that two conformers exist in the unit cell. The distances between the reacting carbon atoms in the thiophene rings of two (green- and blue-colored) conformers are 3.462 and 3.477 Å, respectively, which are short enough for a photocyclization reaction to occur in the crystalline

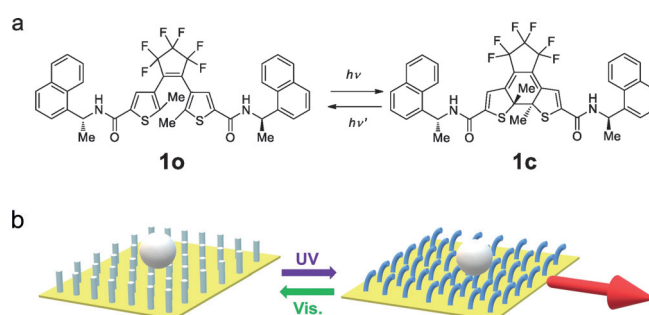


Figure 1. a) Molecular structure of the open- (left) and closed-ring (right) isomers of diarylethene derivative and b) the concept of the photoreactive object transportation system.

state (Figure 2). Moreover, molecules of **1o** were packed so as to bend away from the incident UV light, when the crystal was irradiated from any side face of the crystal, regardless of which face was irradiated. When the crystal of **1o** was irradiated with UV light, the *a* and *b* axis of the unit cell expanded by 0.21 and 0.96 %, respectively. On the other hand, the *c* axis of the unit cell contracted by 0.55 % (Table S1). The irradiation of the crystal of **1o** with UV light induced the elongation of the long axis of the unit cell, because the height of the molecule increased. Therefore, the crystal of **1o** bends away from the incident UV light. Based on the above findings, the bending motion of crystalline **1o** was suitable for our strategy to transport an object in the desired direction. Thus, we designed the photoactuated object transportation surface consisting of many vertically aligned **1o** crystals.

The (source) microcrystalline surface of **1o** was prepared by coating a solution onto a glass substrate. A THF solution of **1o** (600 mg mL⁻¹) was coated onto the glass substrate, the solvent evaporated at room temperature, and an amorphous film of **1o** remained. When the amorphous film was heated at

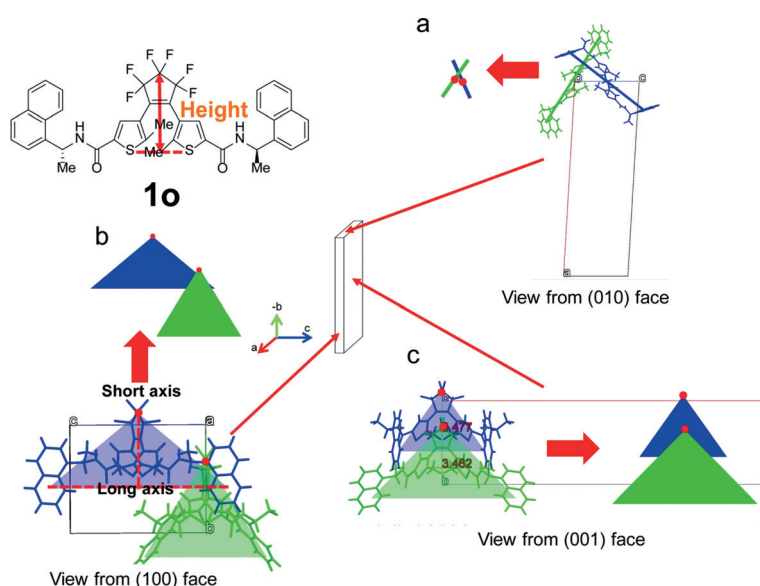


Figure 2. a) X-ray crystallographic analysis and schematic illustration of the molecular packing of two conformers of **1o** in the unit cell view from the (010) face, b) in the unit cell view from (100) face, c) in the unit cell view from (001) face.

200 °C for 20 min, it crystallized (Figures S2 and S3). This crystallization is essential, as it was observed that the subsequent sublimation process at elevated temperatures does not proceed because of decomposition of **1o**. In the current study we tried to fabricate the photoactuated surface by sublimating a crystalline film of **1o** onto the glass substrate. To prepare the object transportation surface, we sublimated the microcrystalline film of **1o** at 260 °C for 1.5 h under ambient atmosphere onto the clean and flat target glass substrate (Figure S4). However, standing platelet crystals of **1o** were not obtained on the glass substrate. Instead of the rough surface covered with standing platelet crystals, we obtained an amorphous film of **1o** with a nearly flat surface. This result suggested that the nucleus of the crystal growth was not generated on the amorphous surface. Noting the importance of surface rough structures for crystallization, we followed the strategy taken by Lin and co-workers. They reported the vertical growth of ZnO nanowires (NWs), where the surface roughness assisted the nucleation of ZnO.^[10] The Zn atoms from the gas phase have enough thermal energy to move freely on a smooth surface. On the other hand, the Zn atoms are stuck once they migrate into pits or craters, due to higher energy barriers for migration. Consequently, the rough surface provides nucleation sites for crystal growth. In the next attempt to prepare the crystalline film of **1o** by sublimation, we made dot-shaped microstructures consisting of **1o** generated densely on the glass substrate upon sublimation at 250 °C for 20 min under ambient atmosphere (Figure 3b). We intended to use the dotted structured rough surface, which was amorphous (Figure 3d), as the precursor in the nucleation process. The average diameter and height of a dotted structure were 0.30 and 0.43 μm, respectively. When the temperature was elevated by only 10 °C, the dotted structures were not obtained within the same heating period (Figure S5a).

By using the dotted structured target surface (Figure 4a–c), we sublimated **1o** from the crystalline film of **1o** as the source. Still, no standing bending crystals were grown on the glass substrate; furthermore, the dotted structures were covered with newly sublimed **1o** and each grew to become a grain (Figure 4d,e), according to the scanning electron microscopy (SEM) observation. Since the dotted structures do not serve as seeds for the crystallization of bending needle-like or thin platelet crystals, we attempted to change the continuous growth mode of the **1o** dots during sublimation by magnetron sputtering the dotted surface with Au-Pd alloy (Figure 4f). Use of this dotted surface with the Au-Pd alloy as a target substrate resulted in the accelerated growth of thin platelet crystals of **1o** on each of the dots on the glass substrate (Figure 4g,h, Figure S6). The average length and width of the platelet crystals of the **1o** on the glass substrate was 384.5 and 10.5 μm, respectively (Figure S7). To confirm the effect of the dotted structures, we sublimated the crystalline film of **1o** onto both the areas with dotted structures and without dotted

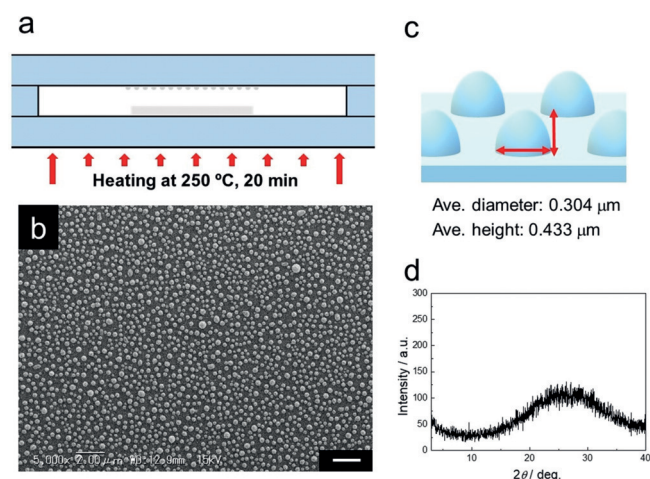


Figure 3. a) Schematic illustration of the generation of amorphous dotted microstructures. b) SEM image of the dotted microstructures on the glass substrate. Scale bar: 2.0 μm; magnification: 5000×. c) Schematic illustration of dotted microstructures. The average diameter and height of the dotted microstructures were 0.30 and 0.43 μm, respectively. d) XRD diffraction of the surface of the dotted substrate. This XRD measurement indicates that the dotted structures were amorphous.

structures (Figure S8). On the surface with dotted structures, platelet crystals of **1o** were observed, while on the flat surface, no crystals were generated. Additionally, the sublimation of **1o** onto a surface with gentle irregularities that had been a magnetron sputtered with Au-Pd alloy (Figure S5a) did not generate thin platelet crystals (Figure S5b). These results indicated that the dotted structures assist the nucleation by limiting the migration of the molecules on the substrate.

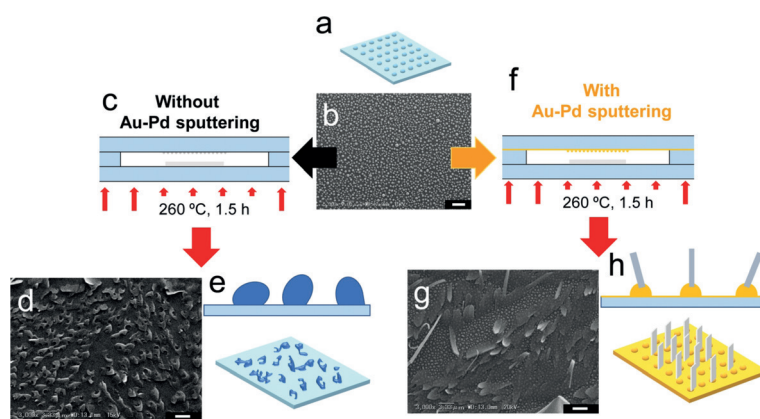


Figure 4. The effect of the dotted structures with Au-Pd sputtering. a) Schematic illustration of the dotted substrate. b) SEM image of the dotted microstructures. Scale bar: 2.0 μm; magnification: 5000×. c) Schematic illustration of the sublimation onto the dotted substrate without Au-Pd sputtering. d) The SEM image of the dotted substrate after sublimation of crystalline film of **1o** onto the dotted substrate without Au-Pd sputtering. Scale bar: 3.33 μm; magnification: 3000×. e) Schematic illustration of the structures on surface without sputtering after the first sublimation. f) Schematic illustration of the sublimation onto the dotted substrate with Au-Pd sputtering. g) The SEM image of the dotted substrate after sublimation of the crystalline film of **1o** onto the dotted substrate with Au-Pd sputtering. Scale bar: 3.33 μm; magnification: 3000×. h) Schematic illustration of the surface structures on the sputtered surface after sublimation.

Next the object transportation system controlled only by photoirradiation was designed. To clarify the bending behavior of the crystals grown on the glass substrate, we irradiated the photoactuated surface with UV light from various directions. The bending behavior was observed by using a digital microscope (KEYENCE, 28 fps, Figure S9, Supporting Information movie 3). At first, the object transportation surface was irradiated with UV light ($\lambda = 254$ nm) from the right side, and the whole crystals bent away from the light. Subsequently, the surface was irradiated with visible light applied from the top, and the crystals reverted to the original position (observation light of the digital microscope: white light). Furthermore, upon UV light irradiation from the left side, crystals bent away from the photoirradiation, and crystals also reverted to the original position upon visible-light irradiation. The Young's modulus of the crystals was determined to be as large as 5.5 GPa. The measurement was carried out by means of a manual beam-bending test (Figure S10).^[9b,c] This value is much larger than those of typical polymer materials (ca. 1 GPa).^[11] These results suggest that the assembled surface of photobendable crystals can be applied for light-induced actuation to establish an object transportation system.

We demonstrated the transportation by using a polystyrene bead (PB) (average diameter 1 mm) as a target and by applying UV- and visible-light irradiation from various directions. When the PB was placed on the nanostructured surface, the motion of the PB was observed upon UV- and visible-light irradiation (Figure 5, Supporting Information movie 4). First UV light ($\lambda = 254$ nm) was applied from the bottom of the screen and the PB moved upward, accompanied by the cooperative bending of the crystals. Continuing irradiation with UV light ($\lambda = 254$ nm) from the right side induced the PB to move to the left side, such that the transportation direction corresponded to the direction of UV incidence. Upon irradiation with visible light orthogonal to the surface, the PB returned to the lower right, which was the original position. As shown in the Supporting Information movie 3, continuous irradiation with UV or visible light

caused the PB to move in the direction of the bending direction of the crystals. Consequently, we succeeded in transporting the PB object exclusively by photoirradiation in any desired direction by changing the direction of the incident light.

In conclusion, we have designed an object transportation system actuated only by light irradiation using a crystalline film of **1o**. In order to prepare the photoactuated smart surface, a glass substrate was covered with microstructured dots of **1a** and then sputtered with Au-Pd alloy; this surface preparation plays a key role for the generation of the nuclei for crystal growth of **1o** on the target substrate. The bending behavior of the platelet crystal of **1o** was suitable to design a responsive surface, and the surface covered with **1o** crystals showed reversible cooperative crystal bending upon irradiation with UV and visible light. Finally, this photo-actuated surface can transport a PB in a controlled manner in a desired direction depending on the direction of incident light. For longer transportation of an object, we will realize local photoinduced bending on assembly by using laser light in the future. This smart surface will be applicable for remote-controlled object transportation in various environments and holds potential for the development of soft robots.

Acknowledgements

We thank Prof. Nathalie Katsonis (Laboratory for Biomolecular Nanotechnology, University of Twente) for useful scientific discussions. This work was supported by the Ministry of Education, Culture, Sports, Science and Technology, Japan (MEXT) as a Supported Program for the Strategic Research Foundation at Private Universities and by JSPS KAKENHI Grant Number JP26107012 in Scientific Research on Innovative Areas "Photosynergetics", the CREST program (JPMJCR17N2) of the Japan Science and Technology Agency, and JSPS KAKENHI Grant Number JP18J20078 in JSPS Research Fellow. B.L.F. acknowledges the Ministry of Education, Culture and Science of the Netherlands (Gravitation program no. 024.001.035). K.U.'s collaborative work with University of Groningen, the Netherlands, was supported by the visiting scientists' program of Ryukoku University. The synchrotron radiation experiments were performed using the BL02B1 and BL40XU beamlines of SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal Nos. 2014B1213, 2015A1240, 2015B1215, 2016A1080, 2016B1125, 2017A1084, 2017A1120, 2017B1134, 2017B1159, 2018A1104, 2018A1208, 2018B1091, 2018B1092, 2018B1674, 2019A1110, 2019A1670, and 2019A1741).

Conflict of interest

The authors declare no conflict of interest.

Keywords: crystal growth · diarylethenes · object transportation system · photoactuators · photochromism

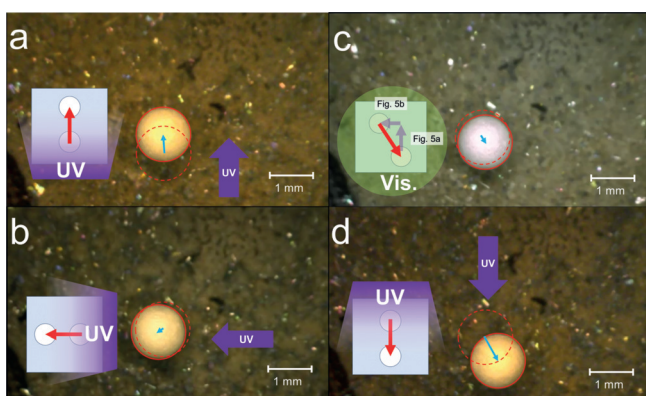


Figure 5. Photographs showing the transportation of the PB upon UV- and visible-light irradiation. a) After UV-light irradiation from the bottom of the screen, b) after UV-light irradiation from the right side of the screen, c) after visible-light irradiation orthogonal to the surface, d) after UV-light irradiation from the top of the screen. Scale bars: 1 mm.

How to cite: *Angew. Chem. Int. Ed.* **2019**, *58*, 13308–13312
Angew. Chem. **2019**, *131*, 13442–13446

- [1] a) T. Kudernac, N. Ruangsupapichat, M. Parschau, B. Maciá, N. Katsonis, S. R. Harutyunyan, K.-H. Ernst, B. L. Feringa, *Nature* **2011**, *479*, 208–211; b) J. Chen, F. K.-C. Leung, M. C. A. Stuart, T. Kajitani, T. Fukushima, E. van der Giessen, B. L. Feringa, *Nat. Chem.* **2018**, *10*, 132–138; c) C. O. Dietrich-Buchecker, J.-P. Sauvage, *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 189–192; *Angew. Chem.* **1989**, *101*, 192–194; d) M. C. Jiménez, C. O. Dietrich-Buchecker, J.-P. Sauvage, *Angew. Chem. Int. Ed.* **2000**, *39*, 3284–3287; *Angew. Chem.* **2000**, *112*, 3422–3425; e) R. A. Bissell, E. Córdova, A. E. Kaifer, J. F. Stoddart, *Nature* **1994**, *369*, 133–137; f) J. M. Spruell, A. Coskun, D. C. Friedman, R. S. Forgan, A. A. Sarjeant, A. Trabolsi, A. C. Fahrenbach, G. Barin, W. F. Paxton, S. K. Dey, M. A. Olson, D. Benítez, E. Tkatchouk, M. T. Colvin, R. Carmielli, S. T. Caldwell, G. M. Rosair, S. G. Hewage, F. Duclairoir, J. L. Seymour, A. M. Z. Slawin, W. A. Goddard, M. R. Wasielewski, G. Cooke, J. F. Stoddart, *Nat. Chem.* **2010**, *2*, 870–879.
- [2] F. Xia, L. Jiang, *Adv. Mater.* **2008**, *20*, 2842–2858.
- [3] a) P. B. Clapham, M. C. Hutley, *Nature* **1973**, *244*, 281–282; b) K. Choi, S. H. Park, Y. M. Song, Y. T. Lee, C. K. Hwangbo, H. Yang, H. S. Lee, *Adv. Mater.* **2010**, *22*, 3713–3718; c) N. Nishikawa, S. Sakiyama, S. Yamazoe, Y. Kojima, E. Nishihara, T. Tsujioka, H. Mayama, S. Yokojima, S. Nakamura, K. Uchida, *Langmuir* **2013**, *29*, 8164–8169.
- [4] a) K. Autumn, Y. A. Liang, S. T. Hsieh, W. Zesch, W. P. Chan, T. W. Kenny, R. Fearing, R. J. Full, *Nature* **2000**, *405*, 681–685; b) K. Liu, J. Du, J. Wu, L. Jiang, *Nanoscale* **2012**, *4*, 768–772.
- [5] a) O. Tabata, H. Hirose, S. Aoki, R. Yoshida, E. Kokufuta, *Sens. Actuators A* **2002**, *95*, 234–238; b) R. Yoshida, *Adv. Mater.* **2010**, *22*, 3463–3483; c) O. Kuksenok, P. Dayal, A. Bhattacharya, V. V. Yashin, D. Deb, I. C. Chen, K. J. Van Vliete, A. C. Balazs, *Chem. Soc. Rev.* **2013**, *42*, 7257–7277; d) S. Ben, J. Tai, H. Ma, Y. Peng, Y. Zhang, D. Tian, K. Liu, L. Jiang, *Adv. Funct. Mater.* **2018**, *28*, 1706666; e) Y. Lin, Z. Hu, M. Zhang, T. Xu, S. Feng, L. Jiang, Y. Zheng, *Adv. Funct. Mater.* **2018**, *28*, 1800163; f) C. L. van Oosten, C. M. Bastiaansen, D. J. Broer, *Nat. Mater.* **2009**, *8*, 677–682; g) A. H. Gelebart, M. Mc Bride, A. P. H. J. Schenning, C. N. Bowman, D. J. Broer, *Adv. Funct. Mater.* **2016**, *26*, 5322–5327.
- [6] A Video showing the movement of the cilia of *Paramecium aurelia*, <https://www.youtube.com/watch?v=HXcEACQv5-8>.
- [7] a) Y. Naitoh, *Science* **1966**, *154*, 660–662; b) M. Noguchi, Y. Nakamura, K. Okamoto, *Cell Motil. Cytoskeleton* **1991**, *20*, 38–46; c) O. Kutomi, M. Seki, S. Nakamura, H. Kamachi, M. Noguchi, *Protoplasma* **2013**, *250*, 1219–1227.
- [8] M. Irie, T. Fukaminato, K. Matsuda, S. Kobatake, *Chem. Rev.* **2014**, *114*, 12174–12277.
- [9] a) S. Kobatake, S. Takami, H. Muto, T. Ishikawa, M. Irie, *Nature* **2007**, *446*, 778–781; b) M. Morimoto, M. Irie, *J. Am. Chem. Soc.* **2010**, *132*, 14172–14178; c) F. Terao, M. Morimoto, M. Irie, *Angew. Chem. Int. Ed.* **2012**, *51*, 901–904; *Angew. Chem.* **2012**, *124*, 925–928; d) K. Uchida, S. Sukata, Y. Matsuzawa, M. Akazawa, J. J. D. de Jong, N. Katsonis, Y. Kojima, S. Nakamura, J. Areephong, A. Meetsma, B. L. Feringa, *Chem. Commun.* **2008**, 326–328; e) D. Kitagawa, H. Nishi, S. Kobatake, *Angew. Chem. Int. Ed.* **2013**, *52*, 9320–9322; *Angew. Chem.* **2013**, *125*, 9490–9492.
- [10] a) S.-T. Ho, K.-C. Chen, H.-A. Chen, H.-Y. Lin, C.-Y. Cheng, H.-N. Lin, *Chem. Mater.* **2007**, *19*, 4083–4086; b) S.-T. Ho, C.-Y. Wang, H.-L. Liu, H.-N. Lin, *Chem. Phys. Lett.* **2008**, *463*, 141–144.
- [11] C. L. van Oosten, K. D. Harris, C. W. M. Bastiaansen, D. J. Broer, *Eur. Phys. J. E* **2007**, *23*, 329–336.

Manuscript received: June 18, 2019

Accepted manuscript online: July 15, 2019

Version of record online: August 5, 2019