Photoresponsive rolling and bending of thin crystals of chiral diarylethenes†

Kingo Uchida,*[ab] Shin-ichiro Sukata,[a] Yuji Matsuzawa,[a] Masako Akazawa,[a] Jaap J. D. de Jong,[b] Nathalie Katsonis,[b] Yuko Kojima,[c] Shinichiro Nakamura,[c] Jetsuda Areephong,[b] Auke Meetsma[b] and Ben L. Feringa*[b]

Received (in Cambridge, UK) 4th October 2007, Accepted 21st November 2007
First published as an Advance Article on the web 4th December 2007
DOI: 10.1039/b715251e

Dithienylhexafluorocyclopentene with (*R*)- or (*S*)-*N*-phenylethylamide substituents formed rod-like and 0.2–1.0 μm-thick plate-like crystals by sublimation; upon UV irradiation, the crystals bent concavely to the incident light and finally rolled crystals were obtained; the bent crystals were reconverted to flat crystals by visible light irradiation.

Photochromism is defined as the reversible transformation of a single molecule between two states having different absorption spectra. Hence photochromic molecules often hold considerable potential for application as molecular switches and as control elements in molecular devices.[1] Diarylethenes are among the most promising of photochromic compounds,[2] not only as memory materials but also as switching units for molecular devices and in supramolecular systems.[3] Recently changes in the surface morphology of a diarylethene crystal were reported,[4] as well as modification of crystal shape. In particular, Irie and co-workers[5] reported the reversible bending of a rod-like crystal of 1,2-bis(5-methyl-2-phenyl-4-thiazolyl)perfluorocyclopentene upon UV and visible light irradiation. The mechanism of bending was attributed to differences in molecular stacking for the open- and the closed-ring isomers, which resulted in macroscopic contraction of the crystals along an axis. We have previously demonstrated that dithienylperfluorocyclopentene derivatives like **1oRR** (Fig. 1), with chiral, (*R*)-*N*-phenylethylamide groups at both ends of the molecule, undergo diastereoselective cyclisation in the crystalline state under UV irradiation.[6] We also demonstrated that chiral *N*-phenylethylamide-based diarylethenes form organogels and that the properties of the fibres as well as the transmission of chiral information from the molecular to the supramolecular level can be controlled reversibly by light.[7] In the present communication we disclose the photoresponse of thin crystals of **1oRR**, and **2oRR**, and show for the first time that reversible light-induced bending of crystals in both a convex and a concave manner can be achieved. Furthermore, we discovered that plate-like crystals of **1oRR** can be rolled up upon UV irradiation.

Diarylethenes **1oRR**, **1oRS**, **1oSS** and **2oRR** have been synthesised using procedures adapted from previous reports.[6] Upon UV and visible light irradiation, crystalline diarylethenes **1oRR**, **1oRS**, **1oSS** and **2oRR** showed the same photochromic behaviour as **1oRR** in acetonitrile. The crystalline powders of **1oRR**, **1oSS**, **1oRS** and **2oRR** were inserted into a demountable optical cell having a thickness of 1 mm. This cell was placed horizontally, and a glass plate was placed on top of it.‡ The cell was subsequently heated at a temperature 10 °C below the compounds' melting points. Maintaining this temperature, thin crystal plates grew from the original crystalline powder of **1oRR** and **1oSS**.

Fig. 2a schematically shows a side view of the thin crystals growing on top of the crystal powder material of **1oRR** (shown at the bottom). The growing rate was around 0.1 mm min^{-1}. The thickness of the film was observed by SEM to be 0.2–1.0 μm as shown in Fig. 2b. Compound **1oSS** formed similar thin crystalline plates. As expected, these thin crystals of **1oRR** and **1oSS** had the same melting point of 269.9–271.2 °C. **1oRR** and **1oSS** also formed thin plate-like crystals from methanol, ethanol, 2-propanol, and acetonitrile with mp 273.0–274.0 °C. The molecular packing of **1oRR** in the crystal state has already been reported.[6]

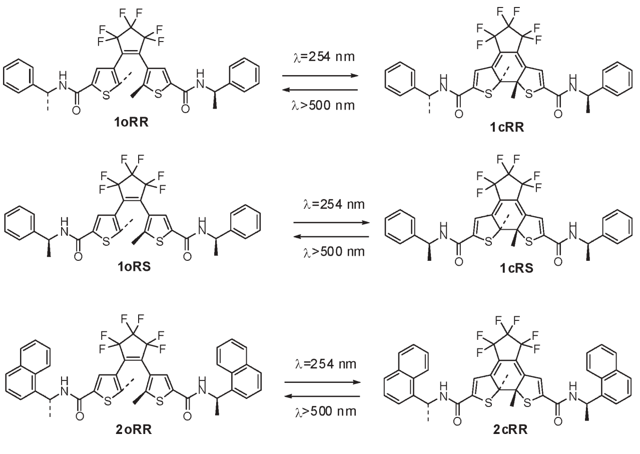

Fig. 1 Dithienylethene derivatives used in the study. o = open form, c = closed form.

---

[a] *Department of Materials Chemistry, Faculty of Science and Technology, Ryukoku University, CREST-JST, Seta, Otsu, Shiga 520-2194, Japan. E-mail: uchida@chem.ryukoku.ac.jp; Fax: +81-77-543-7483; Tel: +81-77-543-7462*
[b] *Stratingh Institute for Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands. E-mail: b.l.feringa@rug.nl; Fax: +31-50-363-4296*
[c] *Mitsubishi Chemical Group Science and Technology Research Center, Inc. and CREST-JST, Japan Science and Technology Corporation, 1000 Kamoshida, Yokohama 227-8502, Japan*

† Electronic supplementary information (ESI) available: Absorption spectra of the diarylethenes, X-ray analysis of **1oRR**, description of **1oRR** and **2oRR** crystals and corresponding polar plots, IR spectra of **1oRR** and **1cRR**, ATR-IR spectra of the surface of the plate-like crystals before and after irradiation, synthesis of the diarylethenes, and supporting videos (growth of plate-like crystal of **1oRR**, reversible bending of plate-like crystal of **1oRR**, bending of a needle-shaped crystal of **1oRR**). See DOI: 10.1039/b715251e

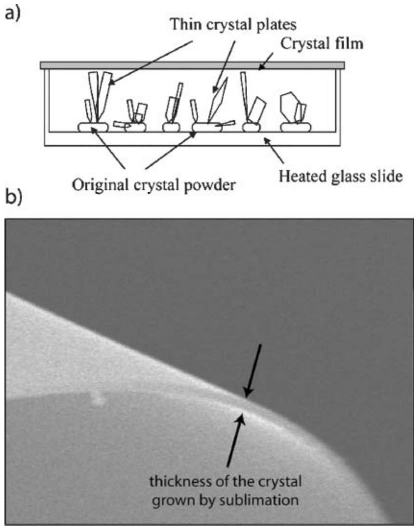

Fig. 2 a) Schematic representation of the set-up for crystal growth by sublimation. b) SEM image of the side view of the thin crystal grown by sublimation (magnification 15 000). The thickness of the plate-like crystal is 0.2–1.0 μm. See also the growth of the plate-like crystals in the supporting video (ESI).

By contrast, **1oRS** did not form thin film crystals upon sublimation – rather it melted in the cell, due to a change in stereochemistry in the vicinity of the amide moieties. This indicates that the intermolecular hydrogen-bonding plays an important role in crystal growth from the gas phase. Under these conditions the naphthyl derivative **2oRR** formed both rod-like and plate-like crystals. Both diarylethenes **1oRS** and **2oRR** formed needle-shaped crystals from methanol, ethanol, 2-propanol, and acetonitrile with melting points of 261.1–262.7 °C and 267.0–268.0 °C, respectively.

In single crystals of **1oRR**, two conformers form a ladder-like structure through multiple intermolecular hydrogen bonding (see ESI†), and each molecule participates in four hydrogen bonds that connect it to four (perpendicularly orientated) other molecules of different conformation. The amide moieties, linked by hydrogen bonds, form an infinite two-dimensional network along the base vectors [100] and [010], *i.e.* in the (001) plane.

The polar plot of the vapour grown crystals of **1oRR** is shown in Fig. 3. The plot shape was different from that of the crystals obtained from recrystallisation in solution,[6] which might be related to the fact that melting points are also different from that obtained from recrystallisation in solution. The order parameter $(A_{//} - A_{\perp})/(A_{//} + 2A_{\perp})$ obtained from the plot was 0.064, while the parameter of the crystals from solution was 0.028. Because the plate-like crystals are too thin, X-ray analysis of the thin crystal has so far been unsuccessful in revealing a possible difference in structure.

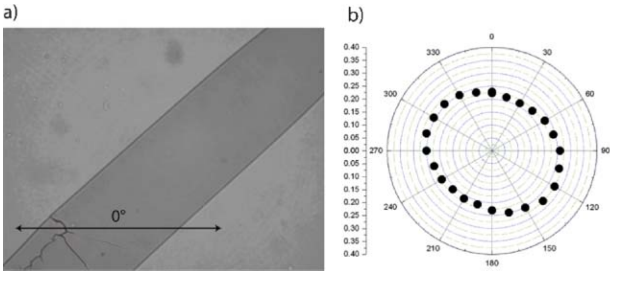

Fig. 3 a) Optical microscopy image of a plate-like crystal of **1oRR**. b) Polar plot of the thin film crystal of **1oRR** observed at λ = 598 nm which is the λ_{max} of the closed-ring isomer in the crystalline state.

The thin rod-like crystals of diarylethene **1oRR** or **1oSS** (0.49 mm × 0.07 mm) bent concave to the incident light upon irradiation with UV light at 254 nm (Fig. 4a). More remarkably, the plate-like crystals rolled up into a curled film crystal with 0.08 mm diameter as shown in Fig. 4b. Depending on the direction of the incident light and the nature of the thin film crystals, concave bending along the main axis of the plate-like crystals was also observed (Fig. 4c). The bending of the rod-like crystals (Fig. 4a) and concave bending along the main axis (Fig. 4c) are fully reversible upon photochemical ring-opening of **1cRR** to **1oRR**.

Upon irradiation with UV light at 254 nm (254 nm Hg lamp @12W), the bending of a plate-like crystal of **1oRR** occurred within 3 s (see video in ESI†). This plate-like crystal was 0.6 mm in length and 0.2 mm in width. Its recovery from the rolling under visible light irradiation took about 2 s (Xe lamp @500W). Both response times depend on the light intensity which is used.

We assume that the bending mechanism which takes place in our systems is similar to that reported by Irie and co-workers.[5] The shrinkage would occur on the surface of the crystal in response to the formation of the closed-ring isomer at the crystal surface. The formation of the closed-ring isomer was ascertained by IR spectral changes as observed in attenuated total reflection infrared (ATR-IR) spectra of the crystal surface (see ESI†).

Thin crystals of **2oRR** also rolled up under UV light. The degree of bending was dependent on the thickness of the crystal. Interestingly, both plate-like and rod-like crystals of the naphthyl derivative **2oRR** formed by sublimation, bent in a convex way to

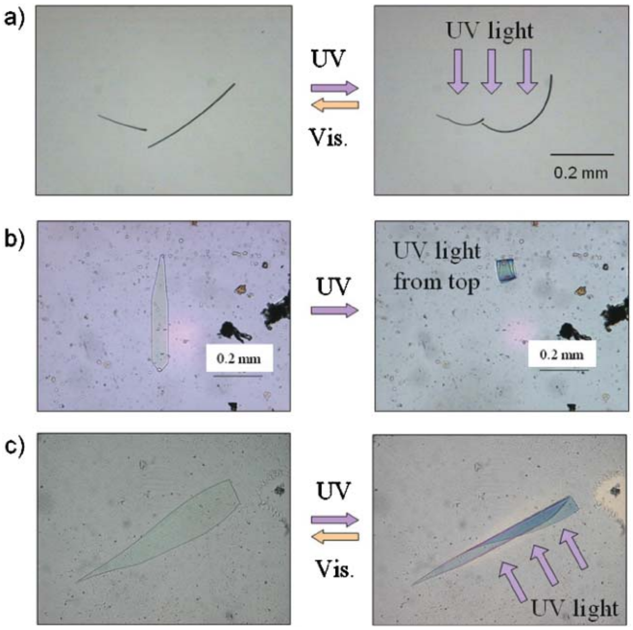

Fig. 4 Rod-like and plate-like crystals of **1oRR** before and after UV irradiation at λ = 254 nm. a) Bending of the needle-shaped crystal of **1oRR** occurs concavely upon UV light irradiation (see also supporting video in the ESI†). b) Rolling of the plate-like crystal occurs concavely to the incident UV light irradiation. c) Length-wise rolling of a plate-like crystal is possible by using side irradiation. Length-wise rolling is reversible.

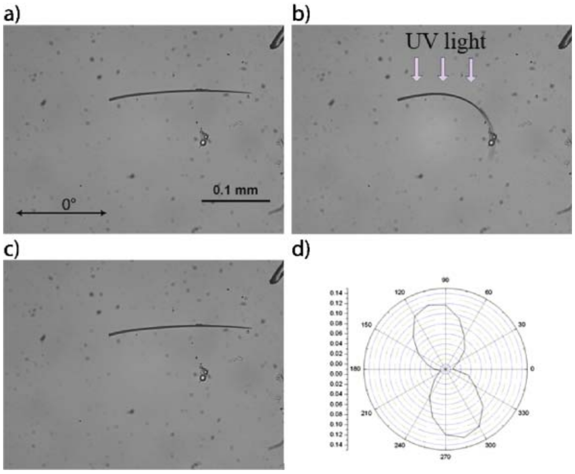

Fig. 5 (a) A needle-shaped crystal of **2oRR** before UV irradiation (0.2 mm × 0.007 mm). (b) After UV (λ = 254 nm) irradiation, the needle crystal bent convex to incident UV light. (c) After visible (λ > 500 nm) light irradiation, the bent crystal recovered its original shape. (d) The polar plot at λ = 671 nm after UV irradiation of the crystal.

the incident UV light as shown in Fig. 5a–c. This opposite behaviour as compared to the behaviour of plate-like crystals of **1oRR** could be due to different crystal packings. Indeed, in crystals of **2oRR**, intermolecular hydrogen bonding expands along the long axis of the crystal and the long axis of the diarylethene molecule is perpendicular to the long axis of the crystal. The polar plot of the crystalline rod of **2oRR**, showing a dumbbell shape (Fig. 5d), is consistent with this observation. The plot was perpendicular to the long axis of the crystal, indicating a different alignment of the molecules compared to the crystal of **1oRR**. Although the structure of the crystal formed by the closed isomer under UV irradiation is still unclear, the differences in the molecular packing are likely to affect the bending directions.

The bending of the rod-like crystal of **2oRR** is fully reversible upon irradiation with visible light (λ > 500 nm) as seen in Fig. 5c. The original shape of the rod-like crystal is recovered. Again we attribute the reversible light-induced bending to a change in packing (shrinkage or expansion) in the surface layer exposed to the incident UV light beam. The photochemical ring closure results in contraction of the crystal phase and bending of the rod-like crystal. Ring-opening of **2cRR** with visible light reverses this effect. The response times of the thin crystals of **2oRR** and **2cRR** are similar to those reported for **1oRR** and **1cRR** and similarly depend on the light intensity which is used.

To fully understand why concave or convex changes in shape occur, a detailed mechanistic study on the change in crystal morphology upon UV and visible irradiation will be necessary. The ability to tune bending (and curving) of crystals in a concave or convex manner by rather small variations in molecular structure offers fascinating opportunities to develop light-actuated mechanical systems.

The present work was supported by Grant-in-Aid for Science Research in a Priority Area "New Frontiers in Photochromism (No. 471) and (B) (18350101) from the Ministry of Education, Culture, Sports, Science, and Technology (MEXT), Japan. Financial support from the Netherlands Organisation for Scientific Research (NWO-CW) and the Zernike Institute for Advanced Materials is gratefully acknowledged. We thank Zeon Corp. Ltd. for supplying the octafluorocyclopentene.

Notes and references

‡ A quartz cell AB20-UV-1.0 621016131 (GL Science Inc., Japan) and a cover glass (Matsunami Neo Micro Cover Glass, 24 × 45 mm, thickness 0.12–0.17 mm) were used for making the thin plate crystals.

1 (*a*) *Photochromism: Molecules and Systems*, ed. H. Dürr and H. Bouas-Laurent, Elsevier, Amsterdam, 1990; (*b*) *Molecular Switches*, ed. B. L. Feringa, Wiley-VCH, Weinheim, 2001.
2 (*a*) M. Irie, *Chem. Rev.*, 2000, **100**, 1685; (*b*) M. Irie and M. Mohri, *J. Org. Chem.*, 1988, **53**, 803; (*c*) M. Irie and K. Uchida, *Bull. Chem. Soc. Jpn.*, 1998, **73**, 985; (*d*) S. H. Kawai, S. L. Gilat and J.-M. Lehn, *Chem.–Eur. J.*, 1995, **1**, 285; (*e*) G. M. Tsivgoulis and J.-M. Lehn, *Chem.–Eur. J.*, 1996, **2**, 1399.
3 (*a*) B. L. Feringa, N. P. M. Huck and A. M. van Schoevaars, *Adv. Mater.*, 1996, **8**, 681; (*b*) B. L. Feringa, N. P. M. Huck and H. A. van Doren, *J. Am. Chem. Soc.*, 1995, **117**, 9929.
4 (*a*) M. Irie, S. Kobatake and M. Horichi, *Science*, 2001, **291**, 1769; (*b*) K. Uchida, N. Izumi, S. Sukata, Y. Kojima, S. Nakamura and M. Irie, *Angew. Chem., Int. Ed.*, 2006, **45**, 6470.
5 S. Kobatake, S. Takami, H. Muto, T. Ishikawa and M. Irie, *Nature*, 2007, **446**, 778.
6 K. Uchida, M. Walko, J. J. D. de Jong, S. Sukata, S. Kobatake, A. Meetsma, J. van Esch and B. L. Feringa, *Org. Biomol. Chem.*, 2006, **4**, 1002.
7 J. J. D. de Jong, L. N. Lucas, R. M. Kellogg, J. H. van Esch and B. L. Feringa, *Science*, 2004, 278.