Absolute asymmetric photocyclization in chiral diarylethene co-crystals with octafluoronaphthalene†

Masakazu Morimoto,*[ab] Seiya Kobatake[bc] and Masahiro Irie*[a]

Received (in Cambridge, UK) 6th September 2007, Accepted 17th October 2007
First published as an Advance Article on the web 25th October 2007
DOI: 10.1039/b713694c

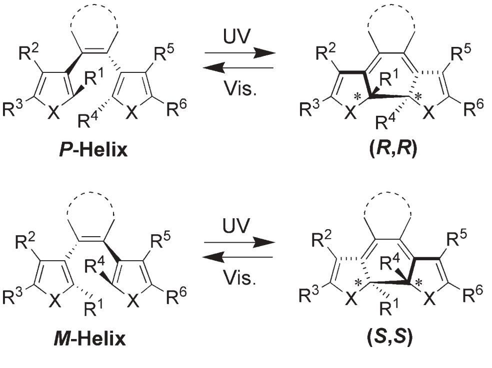
A photochromic diarylethene containing naphthyl groups formed a chiral crystal when co-crystallized with octafluoronaphthalene, although both molecules are achiral, and underwent highly enantioselective photocyclization owing to the conformational confinement in the crystal.

Absolute asymmetric reactions in chiral crystals spontaneously formed from achiral molecules in the absence of any external dissymmetric influence are of great interest in the field of solid-state photochemistry.[1] So far, considerable numbers of absolute asymmetric photochemical reactions have been reported.[2] Most of them are intra- and intermolecular reactions in one-component crystals. Absolute asymmetric photoreactions in chiral two-component co-crystals composed of different achiral molecules are scarcely observed[3] due to the low likelihood of fulfilling the following two conditions: the spontaneous chiral co-crystallization from the two achiral components and the adoption of a molecular conformation and arrangement suitable for the photoreactions. The successful examples include [2 + 2] photocycloaddition in a charge-transfer complex crystal,[3a] photodecarboxylating condensation in a crystal of a hydrogen-bonded pair of acridine and diphenylacetic acid[3b] and photocyclization of isopropylbenzoylbenzoic acid derivatives in salt crystals with amines.[3c]

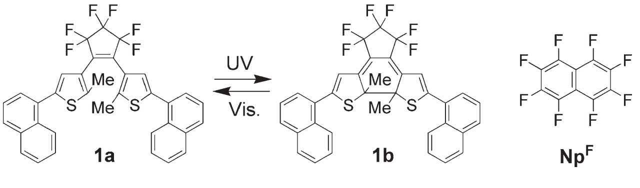
Photochromic diarylethene derivatives undergo reversible cyclization/cycloreversion reactions between open- and closed-ring isomers upon irradiation with ultraviolet (UV) and visible light.[4] The photochemical conrotatory cyclization of the open-ring isomer generates two enantiomers of the closed-ring isomer with (*R*,*R*) and (*S*,*S*) absolute configurations originating from two asymmetric carbon atoms at reacting positions (Scheme 1). The cyclization reactions from *P*-helical (right-handed) and *M*-helical (left-handed) conformers of the open-ring isomer yield the (*R*,*R*) and (*S*,*S*) enantiomers, respectively. In general, the photocyclization in solution results in the formation of equal amounts of the two enantiomers. Diastereoselective photocyclization reactions take place in chiral environments, such as in solution,[5] amorphous,[6] gel,[7] and crystalline phases[8] of diarylethenes with chiral substituents. An absolute asymmetric photocyclization in a chiral crystal of an achiral diarylethene derivative has been successfully demonstrated.[9] In this communication, we report on an absolute asymmetric photocyclization of an achiral diarylethene derivative containing two naphthyl groups (**1**)[10] in chiral co-crystals with octafluoronaphthalene (**Np^F**) formed by intermolecular aryl–perfluoroaryl (Ar–Ar^F) interactions (Scheme 2).[11]

Synthesis and characterization of **1** have been already reported in a previous paper.[10] **1** underwent a thermally irreversible photochromic reaction in solution. Upon alternate irradiation with UV and visible light, a hexane solution of **1** reversibly changed its colour from colourless to bluish purple due to the isomerization between the open- and closed-ring isomers, **1a** and **1b**. Absorption spectra of **1** in hexane are shown in the ESI.†

In a previous paper,[10] we have reported that **1a** formed stoichiometric co-crystals with perfluorinated aromatic molecules, hexafluorobenzene (**Bz^F**) and octafluoronaphthalene (**Np^F**), by intermolecular Ar–Ar^F interactions,[11] and **1a** showed photochromic reactivity in the co-crystals as well as in the one-component crystal of **1a**. All of the crystals have centrosymmetric crystal structures and contain both *P*- and *M*-helix conformers of **1a** in



Scheme 1 Photochromism of diarylethenes. Photocyclization reactions from *P*- and *M*-helical conformers of the open-ring isomer yield (*R*,*R*) and (*S*,*S*) enantiomers of the closed-ring isomer, respectively.



Scheme 2 Diarylethene **1** containing two naphthyl groups (**1a**: open-ring isomer, **1b**: closed-ring isomer) and octafluoronaphthalene (**Np^F**).

---

[a] *Department of Chemistry, Rikkyo University, Nishi-Ikebukuro 3-34-1, Toshima-ku, Tokyo 171-8501, Japan. E-mail: m-morimoto@rikkyo.ac.jp; iriem@rikkyo.ac.jp; Fax: +81-3-3985-2397; Tel: +81-3-3985-2397*
[b] *Precursory Research for Embryonic Science and Technology (PREST), Japan Science and Technology Agency (JST), Kawaguchi Center Building, Honcho 4-1-8, Kawaguchi-shi, Saitama 332-0012, Japan*
[c] *Department of Applied Chemistry, Graduate School of Engineering, Osaka City University, Sugimoto 3-3-138, Sumiyoshi-ku, Osaka 558-8585, Japan*

† Electronic supplementary information (ESI) available: Experimental section and supplementary data. See DOI: 10.1039/b713694c

the ratio of 1 : 1. We recently found that **1a** forms another polymorphic co-crystal with **Np^F** and the crystal has a chiral crystal structure, although both molecules are achiral and both of the one-component crystals are centrosymmetric.[10,12] By recrystallization of a mixture of **1a** and **Np^F** in the molar ratio of 1 : 2 from hexane, colourless plate-like crystals were obtained. The crystal structure was determined by X-ray crystallographic analysis.‡ The crystal has a monoclinic crystal system with a chiral space group C_2. Half a **1a** molecule and one **Np^F** molecule are crystallographically independent, and the crystal contains **1a** and **Np^F** in the molar ratio of 1 : 2. A **1a** molecule lies on a two-fold axis, and a symmetry operation of C_2 builds the entire structure of the molecule. The **1a** molecule also has two equivalent disordered structures on the hexafluorocyclopentene and thiophene rings in the 1 : 1 occupancy ratio (ESI).† Fig. 1 shows molecular packing structures in the chiral co-crystal. In the view from the *b*-axis (Fig. 1a), we can notice that a linear column structure, which is composed of **1a** and **Np^F** in the molar ratio of 1 : 2, runs along with the *c*-axis. In the column structure, intermolecular π–π stacking, between the naphthyl groups of **1a** molecules and **Np^F** molecules, due to Ar–Ar^F interactions[11] is observed. Each of the naphthyl groups of **1a** interacts with two **Np^F** molecules above and below. The planes of the naphthyl groups and the **Np^F** molecules are almost parallel to each other, and the shortest intermolecular distance between the carbon atoms is 3.35 Å, which is close to the sum of van der Waals radii of two sp^2 carbons. Interestingly, as can be seen from the *c*-axis view (Fig. 1b), all of the **1a** molecules set their hexafluorocyclopentene rings in the [010] direction. In addition, all of the **1a** molecules adopt a *P*-helical conformation in the central hexatriene part (this crystal is named (*P*)-**1a·Np^F**), and the distance between the reacting carbon atoms (3.49 Å) is short enough for the photocyclization to take place in the crystalline state.[13] Single crystals with the opposite chirality, (*M*)-**1a·Np^F**, in which **1a** is in an *M*-helical conformation, were also obtained from the same sample batch.‡

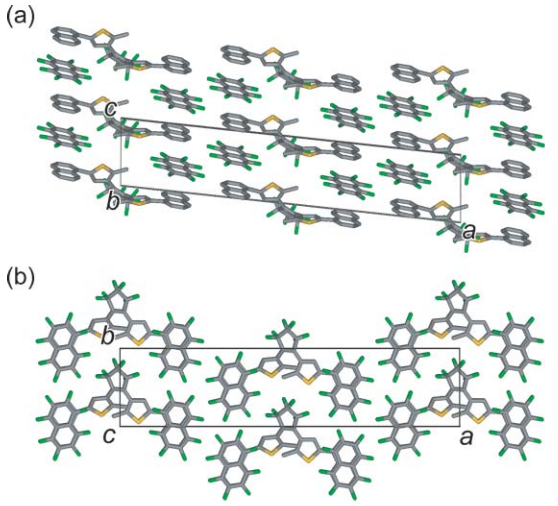


Fig. 1 Crystal structure of crystal (*P*)-**1a·Np^F** viewed from the *b*-axis (a) and *c*-axis (b). Only one of two equivalent disordered structures on hexafluorocyclopentene and thiophene rings is shown for clarity. Hydrogen atoms are omitted.

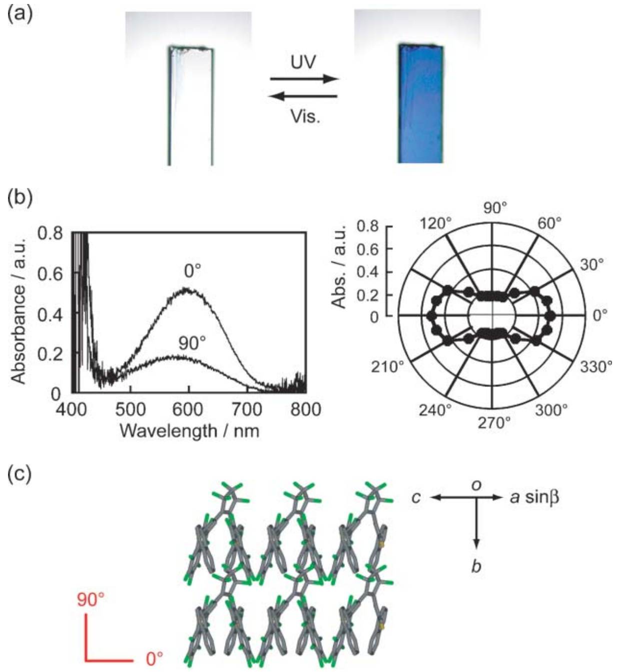


Fig. 2 (a) Photochromism of crystal (*M*)-**1a·Np^F**. (b) Polarized absorption spectra of coloured crystal (*M*)-**1a·Np^F** measured on the (−100) face and polar plots of absorbance at 600 nm *versus* angle of incident polarized light. (c) Molecular packing diagram of crystal (*M*)-**1a·Np^F** projected to the (−100) face. Red lines indicate the direction of incident polarized light in the measurement of the polarized absorption spectra.

The chiral co-crystals underwent photochromism. Fig. 2a shows photographs of the chiral co-crystal (*M*)-**1a·Np^F**. Upon irradiation with 365 nm light, the colourless crystal turned blue. Fig. 2b shows polarized absorption spectra of the coloured crystal measured on the (−100) face and the polar plots of the absorbance *versus* the angle of the incident polarized light. The absorption spectrum at 0° has a maximum at 600 nm. Upon rotation of the direction of the incident polarized light by as much as 90°, the absorption intensity decreases. The anisotropy of the absorption spectra reflects the regular orientation of the photogenerated closed-ring isomers and indicates that the photochromic reaction occurred in the single-crystalline phase.[14] The blue colour disappeared by irradiation with visible light ($\lambda > 480$ nm).

Enantioselectivity in the photocyclization in the chiral co-crystals was examined by HPLC analysis of the photoproduct with a chiral column, and was compared with that in the hexane solution as well as in the achiral one-component crystal of **1a**.[10] The HPLC chromatograms are shown in Fig. 3. As can be seen from Fig. 3a and 3b, the closed-ring isomers generated in hexane solution and in the achiral crystal of **1a** by irradiation with 365 nm light are racemic mixtures of the two enantiomers, (*R*,*R*)-**1b** and (*S*,*S*)-**1b**, in equal amounts.§ In the chiral co-crystals (*P*)-**1a·Np^F** and (*M*)-**1a·Np^F**, on the other hand, highly enantioselective reactions took place, as shown in Fig. 3c and 3d. One of the enantiomers was selectively produced, but the other was not detected. On the basis of the conformation of the open-ring isomer in the co-crystals, the photoproducts are considered to be (*R*,*R*)-**1b** for (*P*)-**1a·Np^F** and (*S*,*S*)-**1b** for (*M*)-**1a·Np^F**. The reaction conversion was 6% for (*P*)-**1a·Np^F** and 11% for (*M*)-**1a·Np^F**, and the enantiomeric excess was $>99\%$ for both. The reversible photochromism with such a high enantioselectivity observed in the crystals was attributed to the long and rigid stacking of the

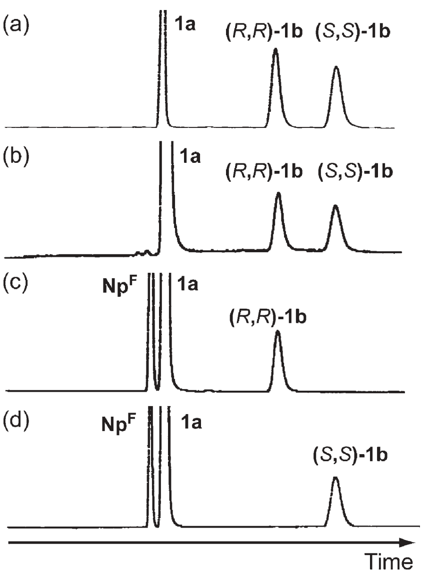


Fig. 3 HPLC chromatograms of **1** after photocyclization by 365 nm light irradiation in hexane solution (a), in the achiral one-component crystal of **1a** (b) and in chiral co-crystals (*P*)-**1a**·**Np**$^{\mathbf{F}}$ (c) and (*M*)-**1a**·**Np**$^{\mathbf{F}}$ (d). The detection wavelength is 329 nm. The retention times for **Np**$^{\mathbf{F}}$, **1a**, (*R*,*R*)-**1b**, and (*S*,*S*)-**1b** are 16, 18, 31 and 37 min, respectively.

naphthalene–octafluoronaphthalene piles which should not waver largely during photochemical transformations.

In conclusion, achiral diarylethene **1a** formed chiral crystal structures, in which only one of the two enantiomeric conformers exists, when co-crystallized with **Np**$^{\mathbf{F}}$ by intermolecular Ar–Ar^F interactions. In the chiral co-crystals, highly enantioselective photocyclization took place owing to the conformational confinement, although a racemic mixture of the closed-ring isomer was obtained in the achiral one-component crystal of **1a**. This is the first example of reversible absolute asymmetric photocyclization in chiral co-crystals of achiral components. Photochromic crystals with asymmetric structures have the potential for application to photoswitchable nonlinear optic devices and photoresponsive ferroelectrics.

The authors thank Dr A. Tsuda at the University of Tokyo for the measurement of CD spectra. This work was partly supported by Grants-in-Aid for Scientific Research (S) (No. 15105006) and Young Scientists (B) (No. 19750023) from the Ministry of Education, Culture, Sports, Science and Technology of Japan, and PREST, JST.

Notes and references

‡ Crystal data for (*P*)-**1a**·**Np**$^{\mathbf{F}}$: $C_{55}H_{22}F_{22}S_2$, $M = 1164.85$, $T = 123(2)$ K, monoclinic C_2, $a = 37.128(5)$, $b = 8.4977(11)$, $c = 7.3472(9)$ Å, $\beta = 96.026(2)^\circ$, $V = 2305.2(5)$ Å^3, $Z = 2$, R ($I > 2\sigma$) = 0.0528, wR_2 (all data) = 0.1448, Flack parameter = −0.05(12). Crystal data for (*M*)-**1a**·**Np**$^{\mathbf{F}}$: $C_{55}H_{22}F_{22}S_2$, $M = 1164.85$, $T = 123(2)$ K, monoclinic C_2, $a = 37.136(3)$, $b = 8.5070(8)$, $c = 7.3452(6)$ Å, $\beta = 96.0270(10)^\circ$, $V = 2307.7(3)$ Å^3, $Z = 2$, R ($I > 2\sigma$) = 0.0572, wR_2 (all data) = 0.1541, Flack parameter = −0.03(14). The details are described in the ESI.† CCDC 658341 and 658342. For crystallographic data in CIF format see DOI: 10.1039/b713694c

§ CD spectra of the two enantiomers are mirror images with opposite signs in the Cotton effect. See the ESI.†

1 (*a*) K. Penzien and G. M. J. Schmidt, *Angew. Chem., Int. Ed. Engl.*, 1969, **8**, 608; (*b*) G. M. J. Schmidt, *Pure Appl. Chem.*, 1971, **27**, 647; (*c*) B. S. Green, M. Lahav and D. Rabinovich, *Acc. Chem. Res.*, 1979, **12**, 191.

2 (*a*) A. Elgavi, B. S. Green and G. M. J. Schmidt, *J. Am. Chem. Soc.*, 1973, **95**, 2058; (*b*) S. V. Evans, M. Garcia-Garibay, N. Omkaram, J. R. Scheffer, J. Trotter and F. Wireko, *J. Am. Chem. Soc.*, 1986, **108**, 5648; (*c*) A. Sekine, K. Hori, Y. Ohashi, M. Yagi and F. Toda, *J. Am. Chem. Soc.*, 1989, **111**, 697; (*d*) V. Ramamurthy and K. Venkatesan, *Chem. Rev.*, 1987, **87**, 433; (*e*) J. R. Scheffer and M. Garcia-Garibay, in *Photochemistry on Solid Surfaces*, ed. M. Anpo and T. Matsuura, Elsevier, Amsterdam, 1989, pp. 501–525; (*f*) B. L. Feringa and R. A. van Delden, *Angew. Chem., Int. Ed.*, 1999, **38**, 3418; (*g*) M. Sakamoto, *J. Photochem. Photobiol., C*, 2006, **7**, 183.

3 (*a*) T. Suzuki, T. Fukushima, Y. Yamashita and T. Miyashi, *J. Am. Chem. Soc.*, 1994, **116**, 2793; (*b*) H. Koshima, K. Ding, Y. Chisaka and T. Matsuura, *J. Am. Chem. Soc.*, 1996, **118**, 12059; (*c*) H. Koshima, H. Kawanishi, M. Nagano, H. Yu, M. Shiro, T. Hosoya, H. Uekusa and Y. Ohashi, *J. Org. Chem.*, 2005, **70**, 4490.

4 M. Irie, *Chem. Rev.*, 2000, **100**, 1685.

5 (*a*) T. Yamaguchi, K. Uchida and M. Irie, *J. Am. Chem. Soc.*, 1997, **119**, 6066; (*b*) E. Murguly, T. B. Norsten and N. R. Branda, *Angew. Chem., Int. Ed.*, 2001, **40**, 1752; (*c*) Y. Yokoyama, H. Shiraishi, Y. Tani, Y. Yokoyama and Y. Yamaguchi, *J. Am. Chem. Soc.*, 2003, **125**, 7194; (*d*) M. Kose, M. Shinoura, Y. Yokoyama and Y. Yokoyama, *J. Org. Chem.*, 2004, **69**, 8403; (*e*) T. Okuyama, Y. Tani, K. Miyake and Y. Yokoyama, *J. Org. Chem.*, 2007, **72**, 1634; (*f*) Y. Tani, T. Ubukata, Y. Yokoyama and Y. Yokoyama, *J. Org. Chem.*, 2007, **72**, 1639.

6 T. Yamaguchi, K. Nomiyama, M. Isayama and M. Irie, *Adv. Mater.*, 2004, **16**, 643.

7 J. J. D. de Jong, L. N. Lucas, R. M. Kellogg, J. H. van Esch and B. L. Feringa, *Science*, 2004, **304**, 278.

8 (*a*) T. Kodani, K. Matsuda, T. Yamada, S. Kobatake and M. Irie, *J. Am. Chem. Soc.*, 2000, **122**, 9631; (*b*) S. Yamamoto, K. Matsuda and M. Irie, *Org. Lett.*, 2003, **5**, 1769; (*c*) 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.

9 S. Yamamoto, K. Matsuda and M. Irie, *Angew. Chem., Int. Ed.*, 2003, **42**, 1636.

10 M. Morimoto, S. Kobatake and M. Irie, *Chem. Rec.*, 2004, **4**, 23.

11 (*a*) C. R. Patrick and G. S. Prosser, *Nature*, 1960, **187**, 1021; (*b*) E. A. Meyer, R. K. Castellano and F. Diederich, *Angew. Chem., Int. Ed.*, 2003, **42**, 1210.

12 A. Del Pra, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1972, **B28**, 3438.

13 S. Kobatake, K. Uchida, E. Tsuchida and M. Irie, *Chem. Commun.*, 2002, 2804.

14 (*a*) S. Kobatake, T. Yamada, K. Uchida, N. Kato and M. Irie, *J. Am. Chem. Soc.*, 1999, **121**, 2380; (*b*) S. Kobatake, M. Yamada, T. Yamada and M. Irie, *J. Am. Chem. Soc.*, 1999, **121**, 8450.