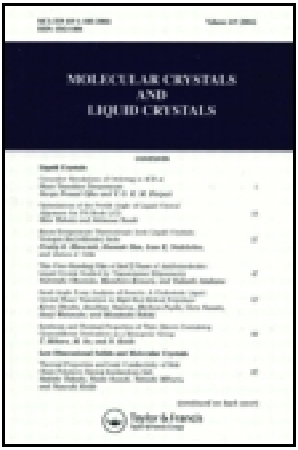

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# Crystal Engineering of Photochromic Diarylethene Derivatives by Aryl-perfluoroaryl Interaction

Masakazu Morimoto [a], Seiya Kobatake [a] & Masahiro Irie [a]

[a] Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Hakozaki, Higashi-ku, Fukuoka, Japan

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# Crystal Engineering of Photochromic Diarylethene Derivatives by Aryl-perfluoroaryl Interaction

**Masakazu Morimoto**
**Seiya Kobatake**
**Masahiro Irie**
Department of Chemistry and Biochemistry, Graduate School of
Engineering, Kyushu University, Hakozaki, Higashi-ku,
Fukuoka, Japan

*Aryl-perfluoroaryl interaction was used for the crystal engineering of photochromic diarylethene derivatives. A diarylethene derivative having pentafluorophenyl groups, 1,2-bis(2-methyl-5-pentafluorophenyl-3-thienyl)perfluorocyclopentene (***1a***), formed 1:1 stoichiometric cocrystals with different diarylethenes, 1,2-bis(2-ethyl-5-phenyl-3-thienyl)perfluorocyclopentene (***2a***) and 1,2-bis[2-methyl-5-(1-naphthyl)-3-thienyl]perfluorocyclopentene (***3a***). In the cocrystals* **1a**· **2a** *and* **1a**· **3a***, highly selective photocyclization reactions of* **2a** *or* **3a** *were observed. Unique nanostructures in which the colorless and colored molecules were periodically arranged were constructed in the photoirradiated cocrystals.*

**Keywords:** aryl-perfluoroaryl interaction; crystal engineering; diarylethene; photochromism

## INTRODUCTION

Diarylethene derivatives exhibit thermally stable and fatigue-resistant photochromic performance not only in solution but also in the single-crystalline phase [1–7]. Diarylethene crystals have potential applications to optoelectronic devices, such as optical memory media and optical switches. For such applications, the crystal structure and

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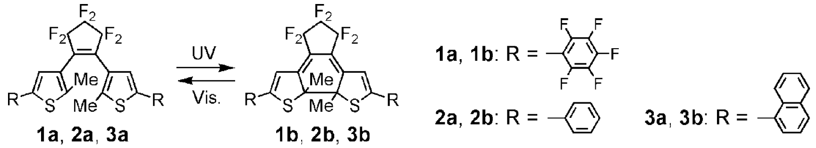
Address correspondence to Masahiro Irie, Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Hakozaki 6-10-1, Higashi-ku, Fukuoka 812-8581, Japan. E-mail: irie@cstf.kyushu-u.ac.jp

the photochromic reactivity need to be controlled precisely by modifying the individual molecular structures as well as utilizing intermolecular interactions in the crystals.

Here, we report on the crystal engineering of photochromic diarylethenes derivatives by utilizing intermolecular aryl-perfluoroaryl interaction. The aryl-perfluoroaryl interaction is a special class of aromatic interactions via which complementary stackings between aromatic and perfluoroaromatic groups are formed [8,9]. A diarylethene derivative having two pentafluorophenyl groups, **1a**, and ones having phenyl and naphthyl groups, **2a** and **3a**, can be used as building units for the crystal engineering. We prepared cocrystals composed of different diarylethenes, **1a· 2a** and **1a· 3a**, and examined their crystal structures and photochromic performance.



SCHEME

## RESULTS AND DISCUSSION

First, the combination of **1a** and **2a** was examined. By recrystallization of a 1:1 (molar ratio) mixture of **1a** and **2a** from hexane, colorless single crystals were obtained. X-ray crystallographic analysis of the crystal was carried out. The crystal had a unit cell of triclinic $P\,\bar{1}$ and contained both **1a** and **2a** in the molar ratio of 1:1. Figure 1a shows a molecular packing diagram in the cocrystal **1a· 2a**. The crystal

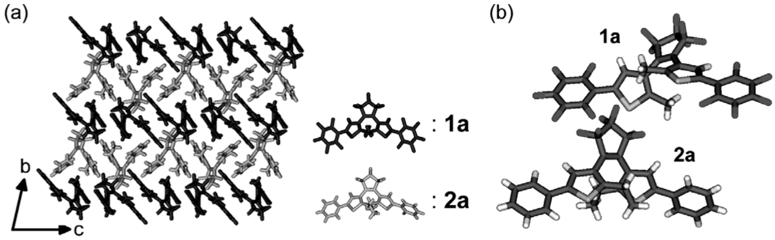


**FIGURE 1** Molecular packing diagram (a) and typical molecular structures (b) of **1a** and **2a** in cocrystal **1a· 2a**.

has a layered structure in which uni-molecular layers of **1a** and **2a** are alternately stacked. However, no stackings between the phenyl and pentafluorophenyl groups are observed in the cocrystal. Figure 1b shows molecular structures of **1a** and **2a** in the cocrystal. Both **1a** and **2a** are fixed in photoreactive anti-parallel conformations, and the distances between reacting carbon atoms are short enough for photochromic reactions to take place in the single-crystalline phase (3.56 Å for **1a** and 3.71 Å for **2a**) [5].

Recrystallization of a mixed hexane solution of **1a** and **3a** gave colorless single crystals. The crystal had a unit cell of monoclinic *C*2/*c* and contained both **1a** and **3a** in the molar ratio of 1:1. The molecular packing structure in the cocrystal **1a· 3a** was quite different from that in the cocrystal **1a· 2a**, as shown in Figure 2a. The pentafluorophenyl groups of **1a** and the naphthyl groups of **3a** are stacked well by intermolecular aryl-perfluoroaryl interaction. As can be seen from the diagram viewed from the *b*-axis in Figure 2a, **1a** and **3a** molecules are alternately aligned via the aryl-perfluoroaryl interaction to form linear chain structures along the *a*-axis. Furthermore, the diagrams viewed from the *a*-, *b*-, and *c*-axes indicate that **1a** and **3a** molecules are packed in a three-dimensional alternating arrangement in the co-crystal. Molecular structures of **1a** and **3a** in the cocrystal are shown in Figure 2b. Both molecules have anti-parallel conformations, and the distances between reacting carbons are 3.65 Å and 3.63 Å for **1a** and **3a**, respectively [5].

The cocrystals **1a· 2a** and **1a· 3a** showed photochromism. Upon irradiation with ultraviolet (UV) light, the colorless crystals **1a· 2a**

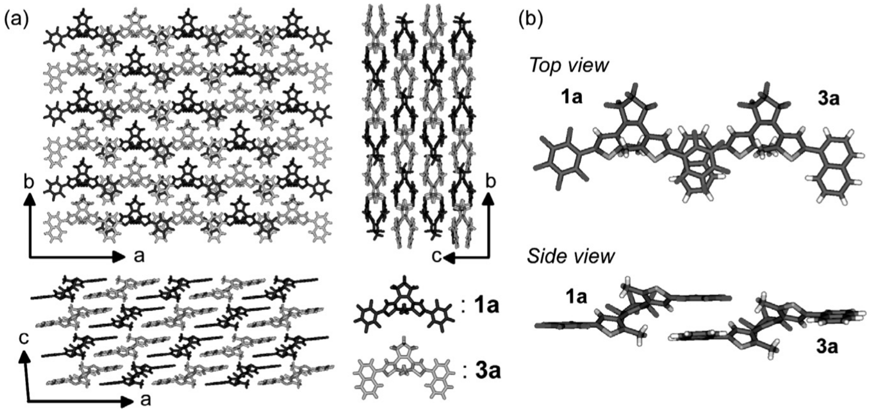


**FIGURE 2** Molecular packing diagrams (a) and typical molecular structures (b) of **1a** and **3a** in cocrystal **1a· 3a**.

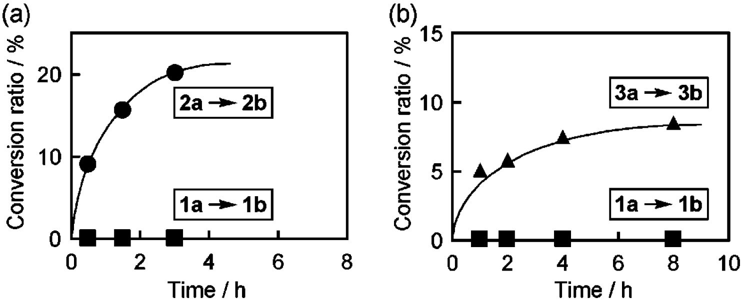


**FIGURE 3** Time dependence of conversion ratios from open-ring isomers to closed-ring isomers in cocrystals **1a**˙ **2a** (a) and **1a**˙ **3a** (b) upen irradiation with 405-nm light. Squares, circles, and triangles indicate the conversion from **1a** to **1b**, from **2a** to **2b**, and from **3a** to **3b**, respectively.

and **1a**˙ **3a** turned blue and green, respectively. These colors were thermally stable in the dark, and were completely bleached upon irradiation with visible light ($\lambda > 450$ nm). In order to examine details of the photochromic behavior of the cocrystals, the composition ratio of the colored cocrystals was monitored by HPLC. Figure 3 shows the time dependence of conversion ratios from the open-ring isomers to the closed-ring ones in the cocrystals **1a**˙**2a** and **1a**˙**3a** upon irradiation with 405-nm light. The 405-nm light induces efficient photocyclization reactions of the homocrystals **1a**, **2a**, and **3a** [4]. In the cocrystal **1a**˙ **2a**, **2a** photoreacted selectively to produce the closed isomer **2b** up to the conversion ratio of 20% after 3-hours irradiation, while formation of **1b** was not discerned. The cocrystal **1a**˙ **3a** also showed similar photochromic behavior. **3a** reacted to produce **3b**, while conversion from **1a** to **1b** was strongly suppressed.

Such dramatic difference in the photoreactivity between homocrystals and cocrystals can be explained as follows. Absorption edges of **2a** and **3a** in hexane are located at longer wavelength than that of **1a**. This means that excited $S_1$ energy levels of **2a** and **3a** are lower than that of **1a**. In the cocrystals, two different diarylethene molecules are closely packed, and the intermolecular distance between them is less than 1 nm. Although photocyclization reactions of diarylethene derivatives in the single-crystalline phase usually proceed very fast (in less than 10 ps) [10], the close intermolecular contact in the cocrystals allows the excited energy transfer from **1a** to **2a** or **3a**. The excited energy absorbed by **1a** is considered to be efficiently transferred to **2a** or **3a** and to cause the highly selective photocyclization reactions of **2a** or **3a** in the cocrystals.

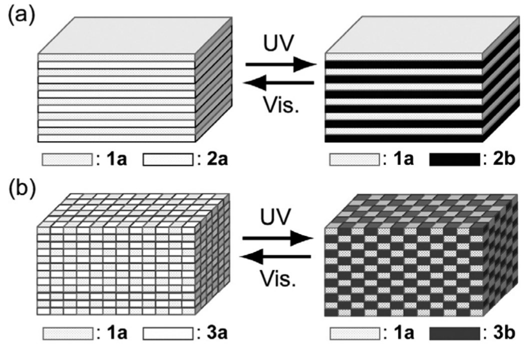


**FIGURE 4** Schematic illustrations of photochromic reaction in cocrystals **1a**· **2a** and **1a**· **3a** (b).

Figure 4 shows schematic illustrations of photochromic reactions in the cocrystals **1a**· **2a** and **1a**· **3a** having well-controlled nano-structures. In the UV-irradiated crystals, the colored and colorless molecules, which have different refractive indices, are arranged periodically in the molecular revel. Such photoreversible periodic refractive index changes in the crystalline nano-structures have potential for the application to a variety of photonic nano-devices.

## CONCLUSIONS

Here, recent developments in the crystal engineering of photochromic diarylethenes by aryl-perfluoroaryl interaction have been described. The diarylethene **1a** formed 1:1 stoichiometric cocrystals with the different diarylethenes **2a** and **3a**, and the crystals showed photochromism. UV irradiation prepared unique nano-structures in which the colorless and colored molecules were periodically arranged.

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