



# Effects of solvents on the growth of an asymmetrical photochromic diarylethene crystal



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## ABSTRACT

An asymmetrical photochromic diarylethene with one pyridine unit was synthesized, which could have two types of crystals controlled through the evaporation of either an ether solution or a hexane/chloroform ( $V = 1:1$ ) solution at room temperature, respectively. The obtained open-ring isomer and closed-ring isomer of the diarylethene could be interconverted in solution, in a solid film, and even in the crystalline phase via alternating irradiation with UV and visible light. The diarylethene exhibited proton-controlling fluorescence switching behavior through alternating the stimulation of trifluoroacetic acid and triethylamine. Its fluorescence intensity could also be modulated reversibly through alternating irradiation with UV and visible light. Thus, the diarylethene could be used as a multi-addressable fluorescence switch when triggered with light and acid/base. Cyclic voltammograms with an oxidation wave of the closed-ring isomer was clearly observed at 0.82 V.

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## 1. Introduction

Crystal growth in solution is dominated by not only solute but also solvent due to the solute-surface and solvent-surface interactions [1–4]. Therefore, many solvents have been used to tune the crystal morphology for special needs. For example, Wang et al. reported that long prismatic *a*-hydroxy-16 $\alpha$ ,17 $\alpha$ -epoxyprogesterone could be crystallized from pure acetone and *N,N*-dimethylformamide, while the corresponding blocky crystal was produced from pure chloroform [5]. The thin plate crystal of the drug phenytoin can be produced by a “watering-out” technique, while its needle shape crystal can be obtained from alcoholic solution and its rhombic shape can be obtained from acetone solution [3]. The needle-like crystals of dipyrindamole can be obtained from benzene and acetonitrile, while its rectangular crystal can be produced from methanol [4]. Hammond et al. reported a method to estimate solution binding on crystal surfaces through interfacial tension, which was used to calculate the solution-effected attachment energies to predict the solvent-mediated crystal morphology [6,7]. Recently, solvent effects on the morphology of organic crystal can be explored with a corrected attachment energy (AE) model, which is in reasonable agreement with the experimental result re-

crystallized from the acetone solution [8]. Furthermore, a new occupancy model to predict effects of solvent on crystal morphologies was proposed by Zhang [9].

Photoswitchable compounds have received much attention due to their potential applications in optical data storage [10–16], organic memory [17], fluorescence sensing of specific ions [18,19], full color display [20,21], and photoswitchable organocatalysis [22]. Up to present, various types of photochromic diarylethenes have already been reported [23–25]. Although many studies have been done on the use of diarylethene photoswitches in material science technologies and the topochemical reaction in crystals [26], the effects of solvents on the growth of isomeric crystals have been rarely reported [27]. Here, we reported that two different single crystals can be obtained from the evaporation of a solution of one diarylethene compound either in ether or hexane/chloroform ( $V = 1:1$ ) at room temperature, and this compound has excellent photochromism, photo- and proton-controlled fluorescent switching properties in solution.

## 2. Experimental

**General:** All solvents were purified through distillation before use. NMR spectra were recorded on a Bruker AV400 (400 MHz) spectrometer with  $\text{CDCl}_3$  as the solvent and tetramethylsilane as an internal standard. IR spectra were performed using a Bruker Vertex-70 spectrometer. The elemental analysis was measured

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with a PE CHN 2400 analyzer. Melting point was determined with a WRS-1B melting point determination apparatus. The crystal reflection absorption spectra were measured on a Hitachi spectrophotometer-U-3900/3900H spectrometer. The other absorption spectra were measured on an Agilent 8453 UV/VIS spectrometer. Photo-irradiation was carried out with an SHG-200 UV lamp, a CX-21 ultraviolet fluorescence analysis cabinet and a BMH-250 Visible lamp. Light of appropriate wavelengths was isolated through 297 nm and 313 nm light filters. Fluorescent spectra were measured on a Hitachi F-4600 spectrophotometer. The quantum yields were determined through comparison of the reaction yields of the diarylethene in hexane with the known yield of the compound

1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene in hexane ( $\Phi_{o-c} = 0.59$ ,  $\Phi_{c-o} = 0.013$ ) [28]. Suitable crystals of **1o** were obtained through the slow evaporation of different solutions. Crystal data (Table 1) of diarylethene **1o** were collected on a Bruker SMART APEX II CCD diffractometer by using a MULTI scan technique at 294(2) K and Mo K $\alpha$  radiation. Crystal structures were solved through direct methods and refined through full-matrix least-squares procedures on  $F^2$  in SHELXTL-97 program. All nonhydrogen atoms were refined anisotropically. Electrochemical examinations were performed in a one-compartment cell by using a Model 263 potentiostat-galvanostat (EG&G Princeton Applied Research) under computer control at room temperature. Platinum-electrodes (0.5 mm in diameter) served as working electrode and counter electrode. Platinum wire served as quasireference electrode. A formal potential  $E_{1/2} = +0.35$  V versus platinum wire was calibrated by using the ferrocene (Fc/Fc<sup>+</sup>) redox couple. The typical electrolyte was acetonitrile (5 mL) with 0.1 mol L<sup>-1</sup> of tetrabutylammonium tetrafluoroborate ((TBA)BF<sub>4</sub>) and 4.0 × 10<sup>-3</sup> L<sup>-1</sup> of dithienylethene. All solutions were deaerated with a dry argon stream and maintained under argon during electrochemical experiments.

## 2.1. Synthesis of diarylethene

The synthesis route for diarylethene **1o** is shown in Fig. 1. Suzuki coupling of pyridine with thiophene boronic acid [29] gave pyridylthiophene derivatives. They were lithiated and then coupled with (2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene [30] to

give the unsymmetrical diarylethene derivative **1o** (Fig. 1). The structure of **1o** was confirmed by NMR, IR and elemental analysis.

### 2.1.1. {[1-(2-Methyl-5-phenyl)-2-(2-methyl-5-(3-pyridyl))thiophen-3-yl] perfluorocyclopentene(**1o**)}

Compound **1o** was synthesized by a similar reported method [31]. To a stirred anhydrous THF solution containing 3-bromo-2-methyl-5-(3-pyridyl)thiophene [32] (1.70 g, 6.70 mmol) add dropwise a 2.50 mol L<sup>-1</sup> *n*-BuLi in hexane solution (2.68 mL, 6.70 mmol), the mixture was continuously stirred for 30 min at 195 K under argon atmosphere. Then, (2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (2.45 g, 6.70 mmol) [30] was slowly added to the reaction mixture at 195 K, and the mixture was stirred for 2.0 h at this low temperature (Fig. 1). The reaction was quenched by water and extracted with ether. The organic layer was dried over MgSO<sub>4</sub>, filtrated and evaporated after it was washed with 1 M aqueous NaCl and then water followed by drying over MgSO<sub>4</sub>. Evaporation of the solvent gave the crude product which was purified by column on silica gel using hexane as the eluent to obtain 0.91 g of **1o** in 26% yield. M.p. 403–404 K for **1o-1** and 398–399 K for **1o-2**; IR ( $\nu$ , KBr, cm<sup>-1</sup>) 761, 804, 892, 988, 1059, 1117, 1192, 1273, 1342, 1387, 1417, 1593, 1635; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  1.97 (s, 3H, -CH<sub>3</sub>), 1.99 (s, 3H, -CH<sub>3</sub>), 7.28 (s, 1H, thiophene-H), 7.32 (s, 1H, thiophene-H), 7.33 (t, 2H, *J* = 8.0 Hz, benzene-H), 7.39 (t, 2H, *J* = 8.0 Hz, benzene-H, pyridyl-H), 7.55 (d, 2H, *J* = 8.0 Hz, benzene-H), 7.82 (d, 1H, *J* = 8.0 Hz, pyridyl-H), 8.54 (d, 1H, *J* = 4.0 Hz, pyridyl-H), 8.81 (s, 1H, pyridyl-H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  13.5, 122.3, 123.7, 125.6, 126.2, 128.0, 129.0, 129.4, 132.7, 133.2, 138.4, 141.3, 142.4, 142.5, 146.7, 148.9; Anal. Calcd for C<sub>26</sub>H<sub>17</sub>F<sub>6</sub>NS<sub>2</sub> (%): Calcd C, 59.88; H, 3.29. Found C, 59.91; H, 3.27.

Further details on the crystal structure have been deposited at the Cambridge Crystallographic Data Centre as supplemental publication CCDC 761617, 761618 for **1o-1** and **1o-2**, respectively. Copies of the data could be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +544 0 1223 336 033 or e-mail: deposit@ccdc.cam.ac.uk).

## 3. Results and discussion

### 3.1. Effects of solvent on crystal structure of diarylethene

The diarylethene **1** can be crystallized to two single crystals in different solutions. Single crystal **1o-1** was obtained from ether solution at room temperature and single crystal **1o-2** was from hexane/chloroform (*V* = 1:1). In order to investigate the relationship between the conformations and the photochromic behavior of diarylethene **1o**, final structural conformations of these compounds were obtained according to the X-ray crystallographic data in Table 1. As shown in Fig. 2, the molecule **1o-1** was a photoactive *anti*-parallel conformation which could undergo photocyclization reaction. In single crystal **1o-2**, there are two asymmetrical and independent molecules (molecule **1o-2-I** and molecule **1o-2-II**) (Fig. 2). The data in Table 1 showed that the crystal system and space group of single crystal **1o-1** were monoclinic and P2(1)/c, respectively; while, the crystal system and space group of **1o-2** were triclinic and P-1, respectively. The unit cell dimension data of **1o-1** and **1o-2** were different (Table 1), indicating that their crystal densities were different, which were 1.482 g cm<sup>-3</sup> for crystal **1o-1** and 1.446 g cm<sup>-3</sup> for crystal **1o-2**, respectively.

As shown in Fig. 2, diagrams of **1o-1** and **1o-2** were packed in a photoactive *anti*-parallel conformation. Neighboring molecules were *anti*-parallel and crisscrossing each other in the cell. The molecules were connected to each other through intermolecular hydrogen bonds (C–H...S) to form crystal **1o-1** (Table 2 and

**Table 1**  
Crystal data of diarylethene **1o-1** and **1o-2**.

	1o-1	1o-2
Formule	C <sub>26</sub> H <sub>17</sub> F <sub>6</sub> NS <sub>2</sub>	C <sub>52</sub> H <sub>34</sub> F <sub>12</sub> N <sub>2</sub> S <sub>4</sub>
Formular weight	521.53	1043.05
Temperature	291(2)	291(2)
Crystal system	Monoclinic	Triclinic
Space group	P2(1)/c	P-1
Unit cell dimension		
<i>a</i> (Å)	11.5467(1)	11.7667(1)
<i>b</i> (Å)	14.101(2)	13.6135(18)
<i>c</i> (Å)	14.404(2)	15.352(2)
$\alpha$ (°)	90.00	81.152(2)
$\beta$ (°)	94.466(2)	82.911(2)
$\gamma$ (°)	90.00	82.661(2)
Volume (Å <sup>3</sup> )	2338.1(6)	2396.4(6)
<i>Z</i>	4	2
Density (calcd.) (g/cm <sup>3</sup> )	1.482	1.446
Goodness-of-fit on $F^2$	1.051	1.029
Final <i>R</i> indices [ $I/2\sigma(I)$ ]		
<i>R</i> 1	0.0535	0.0582
<i>wR</i> 2 <sup>a</sup>	0.1342	0.1508
<i>R</i> indices (all data)		
<i>R</i> 1	0.0746	0.0871
<i>wR</i> 2	0.1485	0.1742

<sup>a</sup> **1o-1**,  $w = 1/[\sigma^2(F_o^2) + (0.0627P)^2 + 1.7938P]$  where  $P = (F_o^2 + 2F_c^2)/3$ . **1o-2**,  $w = 1/[\sigma^2(F_o^2) + (0.0795P)^2 + 1.418P]$  where  $P = (F_o^2 + 2F_c^2)/3$ .

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