



A multi-responsive molecular switch based on a diarylethene derivative containing dinitrobenzenesulfonic amide groups



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ABSTRACT

Diarylethene derivatives-based multi-responsive molecular switches are indispensable for application to sensors for biological and materials sciences. The constructing of molecular switches that can respond to sulfur compounds remains a challenge. In this work, we report the design and syntheses of a new DAES-based molecular switch **3** using two strongly electron-withdrawing 2,4-dinitrobenzenesulfonyl groups as functional groups and bisthiénylene perfluordiarylethene **2** as the photoswitching trigger. The new molecular switch **3** exhibits prominent photochromism in solution. More importantly, among various sulfur compounds, molecular switch **3** shows specific responses toward benzenethiol and hydrosulfide ions.

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1. Introduction

In recent years, molecular switches have attracted intensive interest because of their potential application in life science, molecular device and information storage at the molecular level [1–3]. Photochromic molecules act as photoswitches and have been extensively investigated for controlling various chemical and physical properties [4–7]. Compared with other photochromic molecules such as azobenzenes [8], fulgides [9] and spiropyrans [10], diarylethene derivatives (DAEs) are one of the most promising photoresponsive families for applications in molecular switches due to their excellent photoreactivity, thermal stability, and fatigue resistance [11–15]. The functionalization of DAEs backbones with specific functional groups [16,17] can enable DAEs to respond not only to light but also to other external stimuli such as acid/base [18–20], metal cations [21–23], anions [24,25], and biomolecules [26]. Recently, a few research groups have developed a series of DAES-based multi-responsive molecular switches and extended their applications to biological and materials sciences [27–30]. For

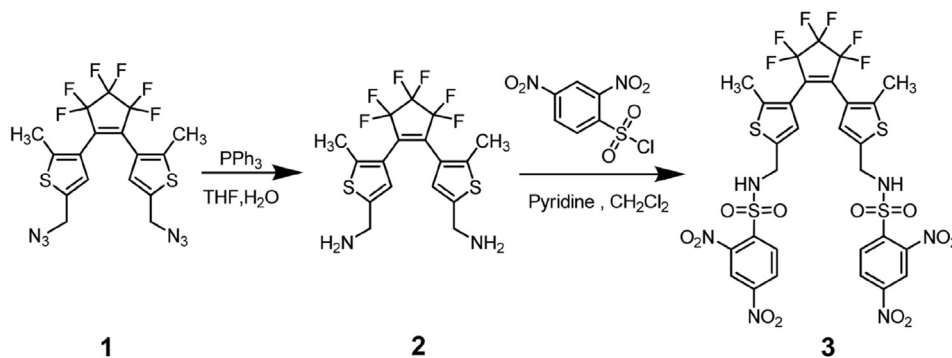
instance, Zhu and co-workers reported a photochromic diarylethene containing a benzo[*b*]thiophene-1,1-dioxide unit as an ethene bridge which allows access to multiple states triggered by metal cations, protons and light [31]. Later on, they also constructed a DAES-based multi-responsive molecular switch that can specifically respond to mercury(II) ions [32]. Recently, Yi and co-workers developed a thiazole orange-modified diarylethene molecular switch of which photochromic properties can respond to macromolecule DNA [26] and cucurbit [8] uril [33]. DAES-based multi-responsive molecular switch are indispensable for application to sensors for biological and materials sciences [34]. On the other hand, sulfur compounds are a class of useful chemicals which are widely used in preparation of agrochemicals, pharmaceuticals, and various industrial products [35]. However, DAES-based multi-responsive molecular switches that can respond to sulfur compounds have rarely been developed.

Herein, we report the design and syntheses of a new DAES-based molecular switch **3** (Scheme 1) using two strongly electron-withdrawing 2,4-dinitrobenzenesulfonyl (DNBS) groups as functional groups [36] and bisthiénylene perfluordiarylethene **2** as the photoswitching trigger. Compound **3** shows prominent photochromism in solution, as well as good thermal stability and fatigue resistance. We realize multi-addressable switchings of **3** triggered by sulfur compounds and

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Scheme 1. Synthetic route to the target compound **3**.

light. More importantly, among various sulfur compounds, molecular switch **3** shows specific responses toward benzenethiol and hydrosulfide ions.

2. Experimental

2.1. Materials

All the commercial reagents unless otherwise annotated were purchased from Sigma Aldrich, Alfa Aesar and were used without further purification. 3,3'-(perfluorocyclopent-1-ene-1,2-diyl)bis(5-(azidomethyl)-2-methylthiophene) (**1**) was prepared according to a literature procedure [37].

2.2. Spectroscopic measurements

^1H NMR spectra were recorded on a Bruker AV500 spectrometer at 25 °C. Chemical shifts (δ) were measured in parts per million (ppm). The optical switch experiments were carried out using a photochemical reaction apparatus with a 500 W medium-pressure mercury lamp (CEL-M500) at room temperature. UV/Vis spectra of photochromic studies were recorded using a HITACHI U-3900 spectrophotometer.

2.3. Synthetic procedure

2.3.1. Preparation of compound **2**

Compound **1** (260 mg, 0.54 mmol) was added into a mixed solution of THF (15 mL) and H_2O (1 mL), Triphenylphosphine (570 mg, 2.17 mmol) was added to the solution. The solution was stirred at room temperature for 12 h. The solvent was removed in vacuo, and then water (100 mL) was added. The residue was extracted with CH_2Cl_2 (3×30 mL), and the combined organic phases were dried with MgSO_4 , filtered and the solvents evaporated in vacuo. The crude product was purified by chromatography over silica gel. Elution with a 1:9 ethylacetate/hexane mixture afforded **2** as grey solid (140 mg, 0.33 mmol), yield: 55%. ^1H NMR (500 MHz, CDCl_3) δ 6.88 (s, 2H), 4.00 (s, 4H), 2.87 (s, 4H), 1.90 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 145.5, 140.6, 124.5, 123.1, 77.3, 77.0, 76.8, 41.4, 14.5. HRMS m/z $[\text{M}+2\text{H}]^{2+}$ calcd for $\text{C}_{17}\text{H}_{18}\text{F}_6\text{N}_2\text{S}_2^{2+}$ 214.04025, found 214.04027.

2.3.2. Preparation of compound **3**

Compound **2** (100 mg, 0.23 mmol) was dissolved in dry pyridine (15 mL). The mixture was then cooled to 0 °C, and a solution of 2,4-dinitrobenzenesulfonylchloride (122 mg, 0.46 mmol) in dry CH_2Cl_2 (5 mL) was slowly added. After being stirred at 0 °C for 30 min, the mixture was then stirred at room temperature overnight. After the

completion of the reaction, removing the solvent under reduced pressure, the residue was purified by flash column chromatography to give the title compound as a yellow solid compound **3** (153 mg, yield 42%). ^1H NMR (500 MHz, CD_3CN) δ 8.63 (d, $J = 2.2$ Hz, 2H), 8.42 (dd, $J = 8.7, 2.2$ Hz, 2H), 8.15 (d, $J = 8.7$ Hz, 2H), 6.91 (s, 2H), 6.73 (s, 2H), 4.46 (s, 4H), 1.75 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 149.8, 147.9142.7, 139.3, 137.0, 132.3, 127.1, 126.9, 124.3, 120.7, 42.4, 14.9. HRMS m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{31}\text{H}_{28}\text{F}_6\text{N}_6\text{NaO}_6\text{S}_4^{+}$ 781.1314, found 781.1305.

3. Results and discussion

3.1. Synthesis

The syntheses of target compound **3** are shown in Scheme 1 (experimental details are described in the supporting information). First, compound **2** (4,4'-(perfluorocyclopent-1-ene-1,2-diyl)bis(5-methylthiophene-4,2-diyl)dimethanamine was synthesized by the reduction reaction of 3,3'-(perfluorocyclopent-1-ene-1,2-diyl)bis(5-(azidomethyl)-2-methylthiophene) **1** with triphenylphosphine in the mixed solution of water and tetrahydrofuran in 43% yield. Then the target photochromic molecule **3** was prepared by protecting the amino group of compound **2** using the strongly electron-withdrawing DNBS group in dry pyridine in 42% yield. Their structures were fully characterized by ^1H NMR, ^{13}C NMR, and HRMS, and shown in the experimental section (Figs. S1–S6).

3.2. Photochromic properties

Compound **3** exhibited reversible and bistable photochromism. It can be reversibly photoswitched between a colorless open form (OF) and a colored closed form (CF). As shown in Fig. 1, OF-**3** has no absorption band in the visible range. Upon irradiation at UV light (254 nm), the colorless solution turns red along with an increase in the new peak located at 528 nm in the visible region, which can be ascribed to the photocyclization of OF-**3**. Moreover, upon irradiation at visible light ($\lambda > 450$ nm), the red solution of **3** gradually turned colourless, resulting from the photocyclo-reversion of **3**. The fatigue resistance of the dinitrobenzenesulfonyl groups-based diarylethene **3** was examined after 5-cycle irradiation of UV (254 nm, for 3.0 min) and visible light ($\lambda > 450$ nm, for 3.0 min). As shown in Fig. S15, **3** exhibit excellent fatigue resistance.

3.3. Multi-stimulus response behavior

Interestingly, when added thiophenol (PhSH), OF-**3** shows no photochromic activity in solution upon irradiation with 254 nm UV light (Fig. 2b). This means that the photochromism of OF-**3** can be

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