

## Phenanthrene-bridged diarylethenes: Synthesis, photochromism and non-destructive readout



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### ABSTRACT

Here we report on the synthesis and photochromism of a group of newly designed phenanthrene-bridged diarylethenes. The structure of one diarylethene derivative was determined by single crystal X-ray diffraction analysis. The photochromic dyes cyclize smoothly in polar organic solvents and water upon UV light irradiation while undergo fading under visible light. These photochromic materials have non-destructive readout capability through fluorescent modulation. Fluorescent read-out lights of them are 390 and 385 nm respectively. The non-destructive read out capability of them was studied with density functional theory and the results indicated that the cyclization probably took place at the second rather than the first excited states.

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### 1. Introduction

Photochromic materials (PMs) have received much attention in the past decades, because of their potential applications in optical information storage media, biological probe and live cell imaging [1–12]. The molecular structures, physical properties and cytotoxicity of these materials are switchable under irradiation with different wavelength light [13]. Several recent pioneering works have also revealed that water-soluble PMs are particularly attractive as they can offer invaluable chemical tools for biomedical research [4,13–19]. Diarylethene is one kind of the most promising PMs for the applications because of their excellent fatigue resistance and its thermal irreversibility [1,20,21]. In order to prepare water-soluble PMs, Sulfonyl, N-methylpyridinium, and poly (ethylene glycol) were introduced respectively to thiophene rings of traditional diarylethenes bridged by perfluorocyclopentene [14,15,22–24]. For practical applications, non-destructive readout capability is another important factor. Fluorescent modulation associated with isomerization of diarylethenes is regarded as a promising means to achieve non-destructive readout.

However, photostimulation excitation occurs in the absorption range of either open or closed form of the diarylethenes, resulting in undesirable competition between the ring closure or opening, respectively, and fluorescence [25].

Phenanthrene-bridge was once used in photochromic diarylethenes [26]. Here, we report a group of new phenanthrene-bridged diarylethene derivatives, of which the photochromic properties in various solvents were investigated. Two compounds containing methyl esters (1) and carboxyl groups (2) (Scheme 1) were designed to improve their solubility in polar solvents. Our PMs have non-destructive readout capability through fluorescent modulation and our theoretical calculations indicated that the mechanism probably was the avoidable competition between photoreaction and photoluminescence.

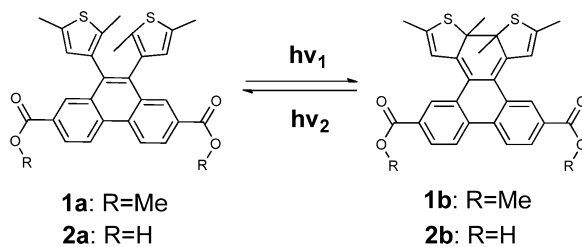
### 2. Experimental

#### 2.1. General

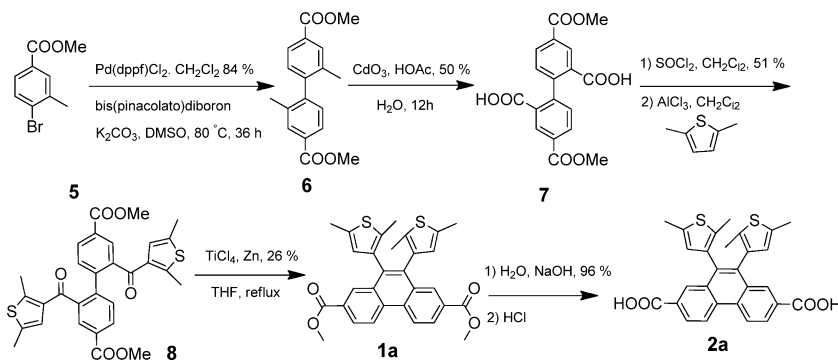
Solvents used in photochemical measurements were spectroscopic grade and purified by distillation before use. <sup>1</sup>H NMR spectra were recorded on a NMR spectrometer (Bruker-AVANCE-400, 400 MHz). Samples were dissolved in CDCl<sub>3</sub> with tetramethylsilane as an internal standard. Mass spectra were measured with a mass spectrometer (Esquire HCT PLUS). Absorption and

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Scheme 1.



Scheme 2.

fluorescence spectra were measured with a Hitachi U-3010 absorption spectrophotometer and a Hitachi F-4500 fluorescence spectrophotometer, respectively. The fluorescence quantum yields were obtained by comparing with 7-amino-4-methylcoumarin. Photoirradiation was carried out using an USHIO 1kW high-pressure mercury lamp as the light source. Monochromatic light was obtained by passing the light through a band-pass filter ( $\Delta\lambda_{1/2} = 15$  nm).

## 2.2. Synthesis

The synthetic route for diarylethenes is shown in Scheme 2. McMurry coupling reaction has been applied to prepare phenanthrene-bridged diarylethenes in the past cases [26]. This strategy is also used in the synthesis of our compounds, however the yield is relatively low. In order to introduce the methyl esters and carboxyl groups at the specific positions of phenanthrene, compound **5** was chosen as the key starting material. Friedel-Craft reaction was applied to prepare ketone **8**. The acyl chloride and 2,5-dimethylthiophene were stirred in dichloromethane under catalysis of excess  $\text{AlCl}_3$  to give **6** in yield of 51%. The structures of all compounds were confirmed by elemental analysis, NMR, and IR spectroscopy. Single crystal of **1a** was obtained and X-ray crystallographic analyses were carried out to confirm its structure.

### 2.2.1. Synthesis of dimethyl 2,2'-dimethylbiphenyl-4,4'-dicarboxylate (**6**)

This compound was synthesized according to reference [27]. Dry DMSO (120 ml) was added by syringe to 4-bromo-3-methylbenzoic acid methyl ester (15.57 g, 68 mmol), bis(pinacolato)diboron (8.64 g, 34 mmol),  $\text{PdCl}_2(\text{dppf})$  (1.97 g, 4 mol%) and  $\text{K}_2\text{CO}_3$  (28.15 g, 204 mmol) under an atmosphere of argon and the mixture was stirred and heated at 80 °C for 36 h. The cooled reaction mixture was poured into water and extracted with ethyl acetate (3 ml  $\times$  150 ml). The combined extracts were washed with water (300 ml), brine (300 ml) and dried over  $\text{Na}_2\text{SO}_4$ . The solution was concentrated by rotary evaporation and loaded onto a column of silica gel and the product was obtained by eluting with cyclohexane ethyl acetate (96:4) and removal of the solvent. Yield 8.44 g (84%). Mp

186–188 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.97 (s, 2H), 7.91 (d,  $J$  = 7.9 Hz, 2H), 7.16 (d,  $J$  = 7.9 Hz, 2H), 3.94 (s, 6H), 2.08 (s, 6H).

### 2.2.2. 4,4'-dimethoxycarbonylbiphenyl-2,2'-dicarboxylic acid (**7**)

A solution of chromium trioxide (600 mg, 6 mmol) in water (0.2 ml) and acetic acid (1 ml) was slowly added to a stirred solution of **6** (298 mg, 1.0 mmol) in acetic acid (3 ml) at room temperature. Then the mixture was stirred at 45 °C for 12 h and cooled to room temperature then poured into water (50 ml). The solution was extracted with ethyl acetate (5 ml  $\times$  50 ml) and the combined organic extracts were dried over  $\text{Na}_2\text{SO}_4$ . The solution was concentrated by rotary evaporation and loaded onto a column of silica gel. The product was obtained by eluting with cyclohexane, ethyl acetate, ethanol and acetic acid (60:20:20:0.05). Yield 176 mg (50%). Mp 273–275 °C;  $^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  = 8.43 (s, 2H), 8.10 (d,  $J$  = 7.8 Hz, 2H), 7.33 (d,  $J$  = 7.9 Hz, 2H), 3.91 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz, DMSO)  $\delta$  = 167.0, 165.4, 146.5, 131.3, 130.5, 130.0, 128.8, 52.4; ESI-MS:  $[\text{M}-1]^-$  = 356.8; Anal. Calcd. for  $\text{C}_{18}\text{H}_{14}\text{O}_8$ : C, 60.34; H, 3.94; Found: C, 60.28; H, 3.90.

### 2.2.3. Dimethyl 2,2'-bis(2,5-dimethylthiophene-3-carbonyl)biphenyl-4,4'-dicarboxylate (**8**)

Diphenic acid **7** (458.9 mg, 1.28 mmol) and  $\text{SOCl}_2$  (2 ml) were suspended in  $\text{CH}_2\text{Cl}_2$  (15 ml) and heated to reflux for 4 h. The unreacted  $\text{SOCl}_2$  was evaporated and 2,5-dimethylthiophene (0.22 ml, 215 mg, 1.92 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (20 ml) was added. The mixture was cooled in an ice-bath to 0 °C and  $\text{AlCl}_3$  (1.02 g, 7.68 mmol) was added in several portions. After 30 min stirring at 0 °C the temperature was allowed to rise to r.t. and stirring continued for 16 h. Ice-cold water was then slowly added to destroy the  $\text{AlCl}_3$ , the organic layer was separated and the water layer extracted with ethyl acetate (3  $\times$  20 ml). The combined organic extracts were then dried over  $\text{Na}_2\text{SO}_4$  and the solvents evaporated. Purification by chromatography (silica gel, Hexane:Ethylacetate/24:1) yielded 356.6 g (51%) of product **8** as a white powder. Mp 177–179 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.09 (d,  $J$  = 8.0 Hz, 2H), 8.09 (d,  $J$  = 8.0 Hz, 2H), 7.97 (s, 2H), 7.97 (s, 2H), 7.42 (d,  $J$  = 8.0 Hz, 2H), 7.42 (d,  $J$  = 8.0 Hz, 2H), 6.44 (s, 2H), 3.84 (s, 6H), 2.39 (s, 6H), 2.16 (s, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 190.6, 166.2, 149.7, 144.2, 140.2,

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