



# Dithienylethenes containing aromatic carbons: Synthesis, photochromism and anion recognition



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## ABSTRACT

A series of novel dithienylethenes with different aromatic carbons were efficiently synthesized using a four-component Ugi reaction and their structures confirmed by NMR spectroscopy, mass spectroscopy (MS) and elemental analysis. Their photochromic properties and fluorescence behaviors have been measured upon irradiation with UV light in solution. Investigations on their photochromic properties indicated that the dithienylethene derivatives had good reversibility upon irradiation with UV or visible light. In addition, they displayed excellent fluorescence switchable behavior. It was found that the degree of conjugation in the aromatic ring had a great effect on their photochromism and fluorescence properties. Moreover, the anthracene-based dithienylethene derivatives displayed high selectivity towards iodide and the pyrene-based dithienylethenes derivatives could act as a colorimetric fluoride sensor.

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## 1. Introduction

Photochromism is a reversible transformation between two isomers with different absorption spectra caused by alternating irradiation with UV and visible light. During the past few decades, photochromic materials have received a lot of attention because of their potential applications as photoswitchable molecular devices and optical memory storage media [1]. Photochromic compounds such as spiroopyrans [2], azobenzene [3], fulgides [4], and diarylethenes [5] have been extensively investigated. Among the various types of photochromic compounds, dithienylethene derivatives (DTE) are the most promising candidates for technological applications by virtue of their excellent thermally irreversible properties, high photoisomerization quantum yields and remarkable fatigue resistance [6]. For practical applications, several attempts to modulate the photochromic properties of diarylethenes have recently been reported. Tian and co-workers [7–12] found that photochromism could be enhanced through coordination to various metal cations. Irie et al. [13–15] modulated the photochromic properties of dithienylethene using intramolecular hydrogen bonds. Huang's group [16,17] gated the spectral properties of dithienylethene by means of Lewis acid–base interactions.

A key current area regarding the photochromic properties of dithienylethenes is the development of novel structures with unique properties. In 1959, Ugi et al. reported that isocyanides underwent a four-component reaction (4-CR) in the presence of an amine, aldehyde or ketone and a nucleophile to provide a single condensation product [18–20]. In addition, this transformation is referred to as the four-component Ugi reaction (U-4CR). Therefore, it is an attractive synthetic challenge to utilize a dithienylethene-functionalized carboxylic acid as the nucleophile in the one pot Ugi reaction with an amine, aldehyde and isocyanide. Herein, we have designed and synthesized a series of novel dithienylethene derivatives **I** and **II** with different aromatic carbons using a four-component Ugi reaction (Fig. 1 and Scheme 1). In addition, their photochromism and anion recognition properties were investigated.

## 2. Materials and methods

### 2.1. Experimental

All manipulations were carried out under an argon atmosphere by using standard Schlenk techniques, unless otherwise stated. DMF was dried with magnesium sulfate then distilled under vacuum. THF was dried with sodium/benzophenone. 4, 4'-(cyclopent-1-ene-1,2-diyl)bis (5-methylthiophene-2-carboxylic acid) (**1**) [21], 5-methyl-4-(2-(2-methyl-5-phenylthiophen-3-yl) cyclopent-1-en-1-yl)thiophene-2-carboxylic acid (**2**) [22] and isocyanides (**3**) [23]

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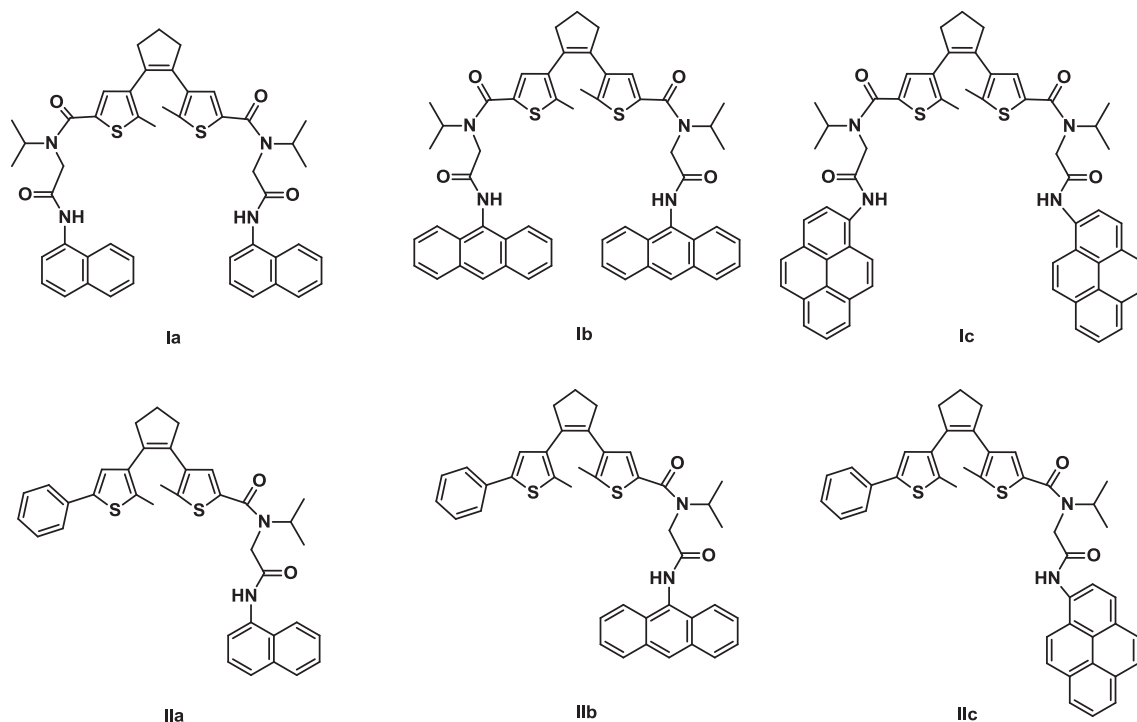


Fig. 1. The dithienylethenes **Ia**, **Ib**, **Ic**, **IIa**, **IIb**, and **IIc**.

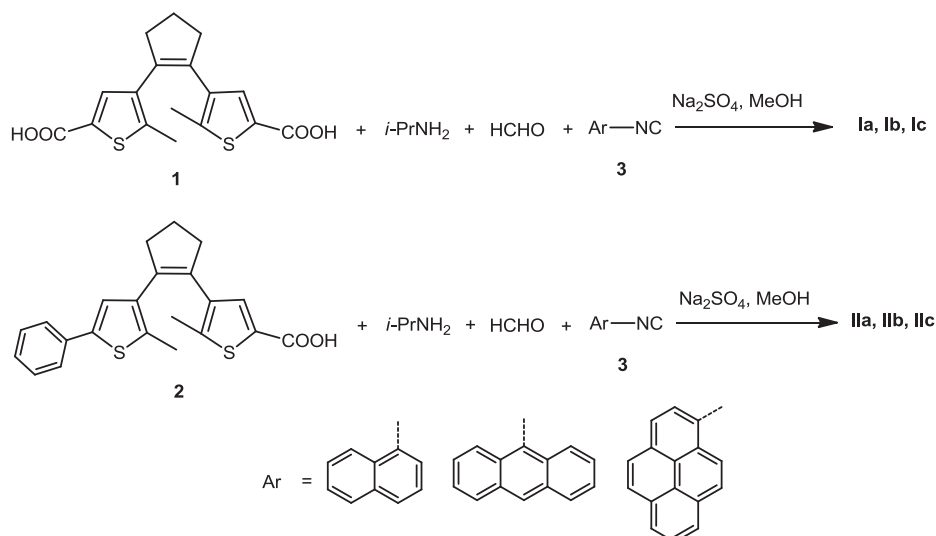
were prepared by literature methods. All other starting materials were obtained commercially as analytical-grade and used without further purification.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were collected on American Varian Mercury Plus 400 spectrometer (400 MHz) or 600 MHz.  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts are relative to TMS. UV–Vis spectra were obtained on U-3310 UV Spectrophotometer. Fluorescence spectra were taken on a Fluoromax-P luminescence spectrometer.

## 2.2. Synthesis

### 2.2.1. Synthesis of dithienylethenes I with different aromatic ring

Target compounds **I** were prepared according to the synthetic route presented in Scheme 1.

**Synthesis of Ia:** To a solution of  $\text{Na}_2\text{SO}_4$  (0.50 g) in methanol (40 mL) was added isopropamide (0.118 g, 2 mmol) and para-formaldehyde (0.06 g, 2 mmol) at ambient temperature. After stirring for 2 h, the solution of compound **1** (0.35 g, 1 mmol) in methanol (60 mL) was added to the mixture and stirred for another 0.5 h. A solution of **3** (2 mmol) in methanol (10 mL) was added slowly in 2 h and the reaction mixture was stirred for 2 days at ambient temperature. The mixture was filtrated in vacuum, and the filtrate was concentrated for column chromatography (eluent: petroleum ether/ethyl acetate, 1: 1) to give an ivory-white solid (0.28 g) in a yield of 35%.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 9.96 (s, 2H, N–H), 7.48–8.12 (m, 14H, Ar–H), 7.06 (s, 2H, thiophene-H), 4.48 (s, 2H, CH), 4.25 (s, 4H,  $\text{CH}_2$ ), 2.82 (s, 4H,  $\text{CH}_2$ ), 2.12 (s, 8H,  $\text{CH}_2$ ), 1.27 (d,  $J$  = 6.5 Hz, 12H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 169.21 (s, CO),



Scheme 1. Synthesis of the dithienylethenes **I** and **II**.

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