



Synthesis, photochromic and fluorescence properties of new bithiazole-containing diarylethenes as cation sensors



Leyla Gundogdu^a, Mahmut Kose^a, Sakiko Takeuchi^b, Yasushi Yokoyama^b, Ersin Orhan^{c,*}

^a Department of Chemistry, Faculty of Arts and Science, Bülent Ecevit University, 67100 Zonguldak, Turkey

^b Department of Advanced Materials Chemistry, Graduate School of Engineering, Yokohama National University, Hodogaya, Yokohama 240-8501, Japan

^c Department of Chemistry, Faculty of Arts and Science, Düzce University, 81620 Düzce, Turkey

ARTICLE INFO

Keywords:

Photochromism
Diarylethene
2,2'-bithiazole
Fluorescence switch
Sensor

ABSTRACT

Two new bithiazole-containing diarylethenes, 1-[5-methyl-2-(5-methyl-2-thiazolyl)-4-thiazolyl]-2,5-dimethyl-3-thienyl-3,3,4,4,5,5-hexafluorocyclopentene and 1-[5-methyl-2-(5-methyl-2-thiazolyl)-4-thiazolyl]-2-methyl-3-benzothienyl-3,3,4,4,5,5-hexafluorocyclopentene were synthesized and their photochromic and fluorescent properties have been investigated. They exhibited thermally irreversible photochromism and fluorescent switching in toluene. The effects of complexation of these two compounds with various metal cations such as Na⁺, Ag⁺, Hg⁺, Co²⁺, Ni²⁺, Cu²⁺, Ba²⁺, Zn²⁺, Cr³⁺, Pb²⁺, Cd²⁺, Sn²⁺, Al³⁺, Fe³⁺ on photochromic and fluorescent properties were also studied. Metal cations caused small effects on the absorption bands of their ring closed forms. However, fluorescence intensities of both compounds were strongly suppressed by Ni²⁺, Cu²⁺ and Fe³⁺.

1. Introduction

Photochromism is the reversible conversion of a chemical species between two forms by the absorption of electromagnetic radiation, where the two forms have different absorption spectra [1]. Photochromic compounds can be divided into two classes. One is thermally reversible (T-type) which includes spiropyrans, spirooxazines, naphthopyrans, azobenzenes, and so on. The other is thermally irreversible (P-type) which includes fulgides and diarylethenes. Photochromic compounds are potential candidates for data storage, molecular switches, sunglasses, solar energy storage etc. Comprehensive reviews for fulgides and diarylethenes have been written by Yokoyama [2] and Irie [3]. Among them diarylethenes with heteroaromatic groups are the most promising candidates for the possible industrial applications because of their high fatigue resistivity, thermal stability as well as thermal irreversibility. The diarylethenes have two main parts. The ethene part of the molecule is usually perfluorocyclopentene. Recently, the ethene parts of the molecules have been manipulated by other suitable groups such as indenone [4], benz[f]indenone [5], coumarin [6], cyclopentenones [7], azulene [8], naphthoquinone [9], and pyridazinones [10], and so on. The aryl part of the molecule has been furnished by various kinds of five-membered heteroaromatic groups such as thiophene, benzothiophene, benzofuran, thiazole, indole and pyrrole.

In recent years, the design and synthesis of photo-switchable diarylethene-based ligands have received much attention. Photo-switchable ligands could be used to change photochromic and fluorescence properties of the molecule when they interact with the metal cations. As a result of this strategy, many works on fluorescent sensors to recognize certain metal cations, such as Zn²⁺ [11], Cu²⁺ [12], Al³⁺, Cr³⁺ [13] have been reported.

The bithiazole ring can act as a ligand so that the bithiazole incorporated in diarylethenes are expected to show high sensitivity and selectivity for metal cations, especially for transition metal ions. Although a diarylethene possessing two bithiazole rings as the side wings has been reported recently, it was used only to modulate the transmittance of the light to encode optical signals but not as the ligand for metal ions [14]. Thus, in this work, two new diarylethenes possessing a bithiazole group have been synthesized and their photochromic properties, including quantum efficiency and conversion ratio were determined. Metal-binding effects on the absorption and fluorescence spectra of these diarylethenes were also investigated with various metal ions in acetonitrile solutions.

* Corresponding author.

E-mail address: ersinorhan@duzce.edu.tr (E. Orhan).

<https://doi.org/10.1016/j.jlumin.2018.06.014>

Received 20 February 2018; Received in revised form 8 May 2018; Accepted 5 June 2018

Available online 06 June 2018

0022-2313/ © 2018 Elsevier B.V. All rights reserved.

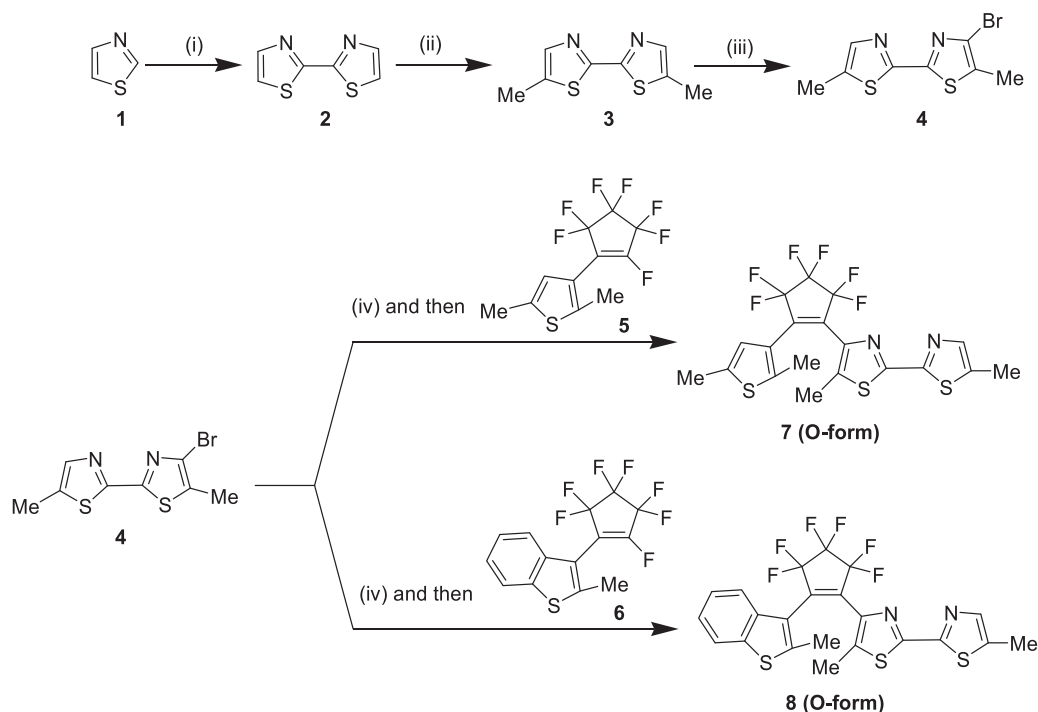


Fig. 1. Synthesis of diarylethenes **7** and **8**. Reagents and conditions: (i) 5 mol% CoCl₂, O₂; (ii) n-BuLi/2Me-I; (iii) Br₂, propylene oxide / THF, r.t; (iv) n-BuLi / THF (-63 °C).

2. Experimental

2.1. Material and methods

2.1.1. Reagents

2-(Thiazol-2-yl)thiazole (**2**) [15], 2,5-dimethyl-3-(perfluorocyclopent-1-enyl)thiophene (**5**) [16] and 2-methyl-3-(perfluorocyclopent-1-enyl)benzo[*b*]thiophene (**6**) [17] were prepared according to the procedures in the literature.

2.1.2. General

The ¹H NMR spectra were recorded on Bruker 400 MHz spectrometers for samples in CDCl₃. The signals are expressed as parts per million down fields from tetramethylsilane, used as an internal standard (δ-value). Mass spectra were taken with an AB Sciex 4000 QTRAP LC-MS/MS. Fluorescence spectra were recorded on an Agilent Cary Eclipse Fluorescence Spectrophotometer. UV–Vis spectra were recorded on a Varian Cary 100 Bio UV–VIS spectrophotometer. Photoirradiation with 366 nm light was carried out using a 500-W high-pressure mercury lamp, separated by filters. Photoirradiation with 578 nm light was carried out with a 500 W xenon lamp, separated by filters. Quantum yields of photochromic reactions were determined from the change in the concentration of isomers detected by HPLC (JASCO X-LC 3000 equipped with a column, Agilent ZORBAX Rx-Sil RRHT) during the photoirradiation according to the procedures reported previously [18]. Chemical reactions were carried out under a dry nitrogen atmosphere. Tetrahydrofuran (THF) was refluxed over sodium wire for several hours, and then distilled under argon atmosphere immediately before use. Solvents were dried over anhydrous sodium sulfate. Flash column chromatographic separation was carried out on Merck Kieselgel 60 (70–230 mesh) with a particle size of 0.063–0.200 mm using ethyl acetate and hexane as the eluent. A preparative thin layer chromatography (PTLC) was carried out on silica gel 60 from Merck with a particle size of 5–40 μm. An analytical thin-layer chromatography was performed on Merck pre-coated silica gel 60 GF-254 with 0.25-mm thick TLC plates.

2.2. Synthesis

2.2.1. 5,5'-dimethyl-2,2'-bithiazole (**3**)

A hexane solution of 2 M n-butyl lithium (6 mL, 12 mmol) was added to a stirring solution of 2,2'-bithiazole (**2**) (5.9 mmol, 1 g) in dry THF (30 mL) at -63 °C under a nitrogen atmosphere. After 40 min stirring, MeI (0.89 mL, 14.26 mmol) was added and the mixture was allowed to warm up slowly to room temperature. After overnight stirring, the reaction mixture was quenched by water and extracted with ethyl acetate. The organic layer was washed with sat. aq. NaCl, dried with anhydrous Na₂SO₄, and the drying agent was filtered off. After removing the solvent in a rotary evaporator, the residue was purified by column chromatography on silica gel using ethyl acetate/hexane as the eluent to give **3** as a yellow solid. Yield 0.47 g (40%). mp: 286–288 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 2.54 (6H, s), 7.52 (2H, s). ¹³C NMR (150 MHz, CDCl₃, ppm): δ 12.09, 135.69, 141.49, 160.19.

2.2.2. 4-bromo-5,5'-dimethyl-2,2'-bithiazole (**4**)

Propylene oxide (0.5 mL, 7.15 mmol) and Br₂ (0.37 mL, 7.15 mmol) was added to a stirring solution of 5,5'-dimethyl-2,2'-bithiazole (**3**) (0.47 g, 2.38 mmol) in dry THF (15 mL) under a nitrogen atmosphere at 0 °C. After overnight stirring, the reaction was quenched by the successive addition of the aqueous solutions of 10% Na₂S₂O₃ and 10% NaHCO₃, and the reaction mixture was extracted with ethyl acetate. The organic layer was washed with sat. aq. NaCl, dried with anhydrous Na₂SO₄, and the drying agent filtered off. After removing the solvent in a rotary evaporator, the residue was purified by column chromatography on silica gel using hexane as the eluent to give (**4**) as a white solid. Yield 0.4 g (61%). mp: 109–111 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 2.38 (3H, s), 2.46 (3H, s), 7.44 (1H, s). ¹³C NMR (150 MHz, CDCl₃, ppm): δ 12.15, 13.13, 125.22, 130.80, 136.71, 141.68, 158.80, 159.11.

2.2.3. 4-(2-(2,5-dimethylthiophen-3-yl)-3,3,4,4,5,5-hexafluorocyclopent-1-en-1-yl)-5,5'-dimethyl-2,2'-bithiazole (**7**)

A hexane solution of 2 M n-butyllithium (1 mL, 2 mmol) was added to a stirring solution of 4-bromo-5,5'-dimethyl-2,2'-bithiazole (**4**)

Download English Version:

<https://daneshyari.com/en/article/7839785>

Download Persian Version:

<https://daneshyari.com/article/7839785>

[Daneshyari.com](https://daneshyari.com)