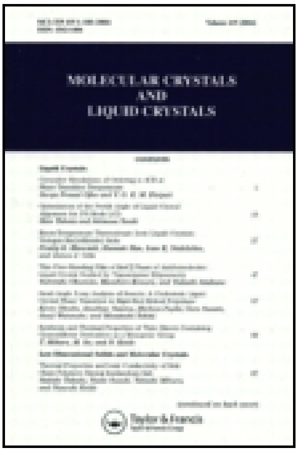

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Synthesis and Properties of Photochromic Diarylethene Containing *N*-Salicylideneaniline Units

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A symmetrical diarylethene containing N-salicylideneaniline (Schiff base) units was synthesized. The structure was well confirmed by NMR spectroscopy, mass spectrometry, and elemental analysis. Its photochromism was investigated by UV/Vis absorption spectra and NMR. The result displayed that diarylethene can well perform photoisomerization, but no obvious intramolecular proton transfer was observed. Furthermore, we checked the effects of metal cations for the properties of N-salicylideneaniline-based diarylethene, which indicated that Cu^{2+} *and* Fe^{3+} *cations can significantly affect the UV/Vis absorption spectra of diarylethene ring-open and ring-closed isomers.*

Keywords Diarylethene; effects of metal cations; *N*-salicylideneaniline photochromism

Introduction

Photochromism is a reversible transformation between two isomers with different absorption spectra caused by alternating irradiation with UV and visible light. The design and synthesis of novel photochromic molecules is the subject of intense research because of the potential application in photonic devices such as memory media and optical switching [1]. Photochromic compounds, such as spiropyrans [2], azobenzenes [3], fulgides [4], and diarylethenes [5], have been extensively investigated. Among various types of these photochromic compounds, diarylethenes with heterocyclic aryl groups, especially those bearing two thiophene or benzothiophene rings, are the most promising candidates for technological applications by virtue of their excellent thermally irreversible property, remarkable fatigue resistance, and high sensitivity (Scheme 1) [6–21]. *N*-Salicylideneaniline (Schiff base) as the photochromic system has been investigated for various applications such as molecular memories and switches [22–25]. Most studies on the photochromic system mainly focus on the intramolecular proton transfer from the *o*-hydroxy group to the imine, where the proton transfer will cause a change of molecular structure and lead to some changes of properties under the condition of light irradiation as shown in Scheme 1.

In order to investigate the properties of the multi-photochromic system, herein, we designed and synthesized the *N*-salicylideneaniline-based diarylethene. Moreover, we

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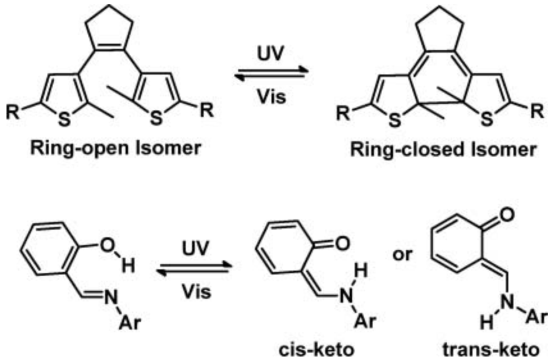


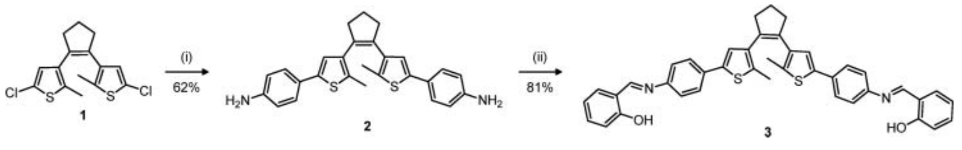
Scheme 1. Photochromic reactions of diarylethene and *N*-salicylideneaniline.

describe the photoisomerization reaction of diarylethene through the investigation of the effects of metal cations on the photochromic properties in the solution. The results indicate that (1) the *N*-salicylideneaniline-based diarylethene showed good photoisomerization, and (2) Cu^{2+} and Fe^{3+} cations affect the UV/Vis absorption spectra upon irradiation with UV light.

Experimental

General. All manipulations were carried out under an argon atmosphere by using standard Schlenk techniques, unless otherwise stated. THF was distilled under nitrogen from sodium-benzophenone. EtOH was distilled under drying pipe from magnesium-iodine. 1,2-bis(5-chloro-2-methylthiophen-3-yl)cyclopent-1-ene **(1)** was prepared by literature methods [26]. All other starting materials were obtained commercially as analytical-grade and used without further purification. ^{1}H and ^{13}C NMR spectra were collected on American Varian Mercury Plus 400 spectrometer (400 MHz). ^{1}H and ^{13}C NMR chemical shifts are relative to TMS. UV/Vis spectra were obtained on U-3310 UV Spectrophotometer. Elemental analysis was performed on an Elementar Vario MICRO instrument.

Synthesis of compounds 2 and 3. Intermediate **2** was prepared according to the synthetic route presented in Scheme 2 by a modified procedure of reported method [26]. Compound **2**: Yield, 62%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.95 (s, 6H, CH_3), 1.97–2.07 (m, 2H, CH_2), 2.82 (t, $J = 7.2$ Hz, 4H, CH_2), 3.73 (s, 4H, NH_2), 6.65 (d, $J = 8.8$ Hz, 4H, Ar), 6.88 (s, 2H, thiophene-H), 7.30 (d, $J = 8.4$ Hz, 4H, Ar). Synthesis of **3**: To a solution of salicylic aldehyde (2.0 mmol) in anhydrous EtOH (80 mL) was added **2** (1.0 mmol) with anhydrous magnesium sulfate acting as drying agent under an argon atmosphere. After



Scheme 2. Regents and conditions: (i) *n*-BuLi, $B(OBu)_3$, THF; $Pd(PPh_3)_4$, 4-iodoaniline, Na_2CO_3, THF, ethylene glycol, H_2O; (ii) 2-hydroxybenzaldehyde, EtOH, anhydrous $MgSO_4$, reflux.

the mixture was refluxed for 24 h, a great deal of precipitate was obtained. The formed precipitate was collected and the crude product was washed with EtOH to give a dark yellow solid in a yield of 81% ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.03 (s, 6H, CH_3), 2.08–2.17 (m, 2H, CH_2), 2.86 (t, $J = 6.8$ Hz, 4H, CH_2), 6.92 (t, $J = 7.2$ Hz, 2H, Ar), 7.01 (d, $J = 8.8$ Hz, 2H, Ar), 7.05 (s, 2H, thiophene-H), 7.25 (d, $J = 8.8$ Hz, 4H, Ar), 7.31–7.38 (m, 4H, Ar), 7.53 (d, $J = 8.4$ Hz, 4H, Ar), 8.62 (s, 2H, CH=N), 13.26 (s, 2H, OH), ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.48 (s, CH_3), 23.00 (s, CH_2), 38.42 (s, CH_2), 117.20, 119.06, 119.21, 121.65, 124.17, 126.13, 132.21, 133.10, 133.29, 134.66, 134.87, 136.82, 138.86, 146.89, 161.10, 161.77 (s, Ar, ethene, CH=N, thiophene). Anal. Calcd for $C_{41}H_{34}N_2O_2S_2$: C, 75.66; H, 5.27; N, 4.30. Found: C, 75.47; H, 5.43; N, 4.21.

Results and Discussion

Synthesis and Characterization

The target diarylethene incorporating *N*-salicylideneaniline units **3** was obtained by the condensation reaction of 2-hydroxybenzaldehyde and 4,4′-(4, 4′-(cyclopent-1-ene-1,2-diyl)bis(5-methylthiophene-4,2-diyl))dianiline **2** in the presence of excess anhydrous magnesium sulfate acting as drying agent in a good yield of 81%, in which the compound **2** was synthesized by the Suzuki coupling reaction. The target compound **3** was characterized by ^{1}H NMR, ^{13}C NMR, and elemental analysis.

Photochromic Behavior

The photochromic behavior of diarylethene **3** induced by photoirradiation in acetonitrile was measured at room temperature. The diarylethene underwent photoisomerization between **3o** (ring-open isomer) and **3c** (ring-closed isomer) upon alternating irradiation with UV light ($\lambda = 302$ nm) and visible light ($\lambda > 402$ nm; Fig. 1 (inset)). As shown in Fig. 1, the absorption maximum of compound **3** in acetonitrile was observed at 278 nm ($\varepsilon = 2.34 \times 10^4$ L mol^{-1} cm^{-1}) and 368 nm ($\varepsilon = 3.39 \times 10^4$ L mol^{-1} cm^{-1}) as a result of a π-π^* transition [27]. This colorless solution changed to purple and a new absorption band at 560 nm ($\varepsilon = 3.60 \times 10^5$ L mol^{-1} cm^{-1}) was observed when it was irradiated with 302 nm UV light in the acetonitrile as a result of the formation of ring-closed isomer **3c**. Upon irradiation with visible light ($\lambda > 402$ nm), the colored **3c** underwent a cycloreversion reaction and formed the initial colorless ring-opened isomer **3o**. The photochromic behavior in this system indicated that such isomerization only involved the diarylethene section, and no obvious intramolecular proton transfer in the *N*-salicylideneaniline scetions was observed from the *o*-hydroxy group to the imine. At the same time, the photochromic behavior of the diarylethene **3** was examined by means of ^{1}H NMR spectroscopy. The ratios between the closed and open isomers at the photostationary state were measured from the ^{1}H NMR spectra. The photocyclization yield of diarylethene **3** was 47% according to the^{1}H NMR data. As shown in Fig. 2, the proton signal of the methyl groups attached to the thiophene rings were observed at $\delta = 2.03$ ppm for ring-open isomer while the ring-closed isomer showed an obvious down-field shift ($\delta = 2.17$ ppm). The other signals of protons such as hydroxyl and imine groups showed little change, which indicated that there was no intramolecular proton transfer from the *o*-hydroxy group to the imine in this system.

Subsequently, in order to further demonstrate that no obvious intramolecular proton transfer occurred in the system, we checked the IR spectra of diarylethene **3** ring-open and ring-closed isomers. According to the IR spectra, no obvious changes were found, which

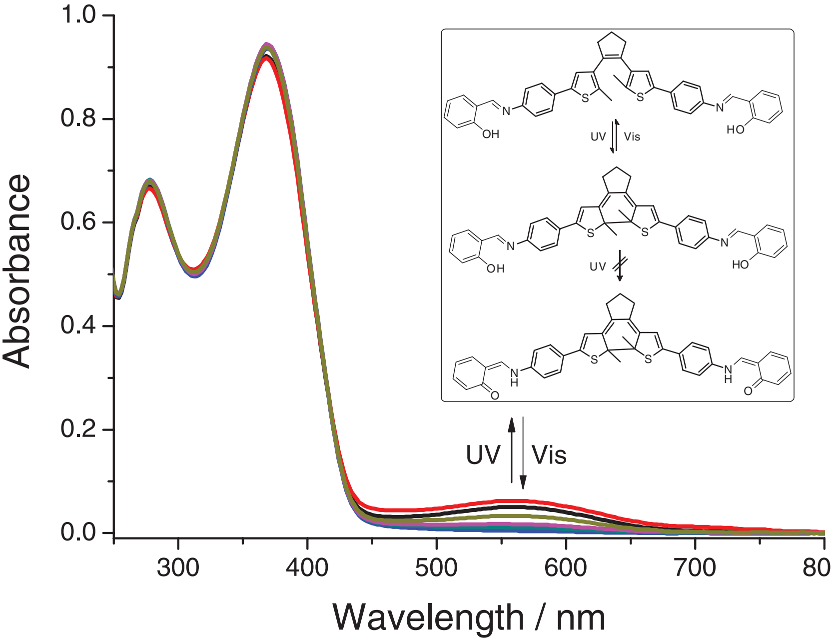


Figure 1. Absorption spectral changes of diarylethene **3** by photoirradiation in acetonitrile (2.0 × 10^{-5} mol L^{-1}) at room temperature. (Inset) Photochromic reaction of diarylethene **3**.

further confirmed that there was no intramolecular proton transfer from the *o*-hydroxy group to the imine, and the result was in agreement with the results of photochromic properties and NMR experiments.

Effects of Metal Cations

The photochromic properties of diarylethene **3** induced by addition of various metal ions (K^+, Ag^+, Ca^{2+}, Mn^{2+}, Zn^{2+}, Cu^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, and Cd^{2+}) in acetonitrile was investigated at room temperature. In Fig. 3, the absorption maxima of the diarylethene **3** ring-open isomer was red-shifted (35 nm) when Cu^{2+} (10.0 eq.) was added before UV light irradiation, which may be attributed to the metal to ligand charge transfer (MLCT).

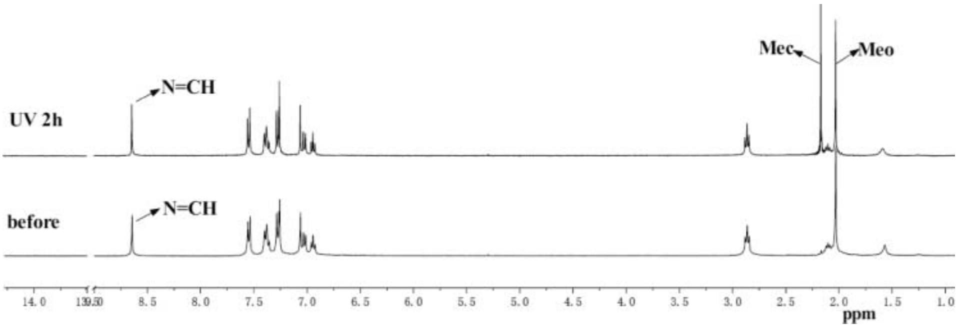


Figure 2. ^{1}H NMR (400 MHz, $CDCl_3$) spectral changes upon 302 nm light irradiation.

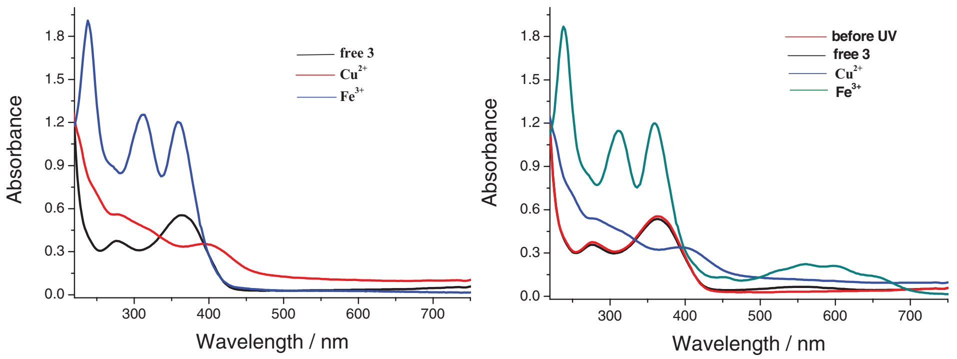


Figure 3. UV/Vis absorption spectra of compound **3** (2×10^{-5} M) in acetonitrile upon the addition of various metal ions (10 eq): (left) ring-open isomer; (right) ring-closed isomer.

After irradiation with UV light, the introduction of Cu^{2+} also induced a similar MLCT. Subsequently, we found that Fe^{3+} also affected the UV/Vis absorption. As shown in Fig. 3, three obvious absorption bands were observed at 238 nm, 312 nm, and 358 nm when Fe^{3+} was added to the acetonitrile solution of diarylethene **3**. At the same time, a similar phenomenon was also observed in the ring-closed isomer of diarylethene **3**, possibly because of the coordination of Fe^{3+} with the Schiff-base and hydroxyl groups of diarylethene **3**. However, other metal ions such as K^+, Ag^+, Ca^{2+}, Mn^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, and Cd^{2+} did not exhibit such effects.

Conclusions

A novel diarylethene bearing *N*-salicylideneaniline unit has been synthesized. We described the photoisomerization reaction of diarylethene by UV/Vis absorption spectra and NMR. The result displayed that diarylethene can well perform the photoisomerization, but no obvious intramolecular proton transfer was found. Furthermore, we checked the effects of metal cations for the properties of *N*-salicylideneaniline-based diarylethene, which indicated that Cu^{2+} and Fe^{3+} cations can significantly affect the UV/Vis absorption spectra of diarylethene ring-open and ring-closed isomers.

Acknowledgments

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