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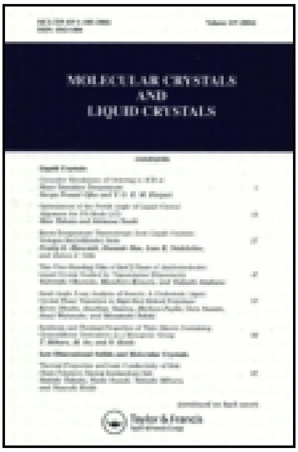

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Imidazole-Based Dithienylethenes: Synthesis, Photochromism, and Effects of Metal Ions

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Imidazole-Based Dithienylethenes: Synthesis, Photochromism, and Effects of Metal Ions

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A series of imidazole-bridging dithienylethenes was synthesized by the condensation of thiophene-based diketone and methoxyl-substituted benzaldehyde. Their UV–Vis absorption and fluorescent spectra were investigated before and after irradiation with UV light. It is worth mentioning that the metal ions such as Cd^{2+}, Cu^{2+}, and Fe^{3+} can obviously enhance the intensity of emission spectra.

Keywords Dithienylethene; effects of metal cations; imidazole unit; photochromism

Introduction

Dithienylethene is considered to be among the most promising systems for application in the field of optical memory materials and devices, because of their excellent switchable ability, thermal stability, fatigue resistance, and sensitivity [1]. Two isomers (ring-open and ring-closed isomers) of dithienylethene can reversibly be transformed upon irradiation with UV and visual light, as shown in Scheme 1. Cyclopentene has been extensively applied to dithienylethene and derivatives, as a connecting bridge between thiophenes. In order to explore the novel system of dithienylethene, some other bridge units such as ethane, maleic anhydride, maleimide, and thiophene have been used in the dithienylethenes [1]. Recently, chemists realized that the N-hetero imidazole can also be utilized as the connecting bridge in the dithienylethene system. For example, Huang and co-workers [2], Liu and Chen [3], Yam et al. [4] have reported imidazole-based dithienylethenes, and have confirmed that some dithienylethenes containing imidazole units possessed excellent photochromic properties.

In our previous works imidazole, as building block, was also introduced to the R sites (Scheme 1) of dithienylethene, and imidazole-based dithienylethenes revealed excellent photo switchable properties [5]. Furthermore, we also reported a series of imidazole-bridged dithienylethenes and investigated the effect of substituted groups on the imidazole ring [6]. Recently, we found that the open-ring and closed-ring isomers of imidazole-based dithienylethenes displayed high selectivity toward Fe^{3+}, and the addition of Fe^{3+} obviously suppressed their fluorescence intensity when imidazole unit as connecting bridge was introduced to the 2-site of thiophene [7]. In view of the obvious difference of this

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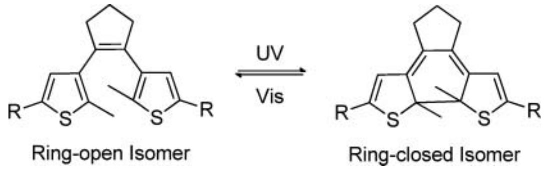


Scheme 1. Photochromic reactions of dithienylethene.

dithienylethene, herein, we further introduce the imidazole bridge to the 3-site of thiophene and synthesize a series of imidazole-based dithienylethenes, and investigate their UV–Vis absorption and fluorescence spectra before and after irradiation with UV light. Most interestingly, the metal ions such as Cd^{2+}, Cu^{2+}, Fe^{3+} can obviously enhance the intensity of emission spectra.

Experimental

General

All experiments were carried out under an argon atmosphere by using standard Schlenk techniques, unless otherwise stated. DMF was dried with magnesium sulfate was then distilled under vacuum. Tetrahydrofuran (THF) was dried with sodium wire and refluxed with benzophenone as indicator, then distilled until the solution turned blue. The 1,2-bis(5-cholro-2-methylthiophen-3-yl)ethane-1,2-dione **(1)** was prepared by literature methods [8]. All other starting materials were obtained commercially as analytical grade and used without further purification. ^1H and ^{13}C NMR spectra were collected on American Varian Mercury Plus 400 spectrometer (400 MHz) or 600 MHz. ^1H and ^{13}C NMR chemical shifts are relative to tetramethylsilane (TMS). Elemental analysis was performed on an Elementar Vario MICRO instrument. UV–Vis spectra were obtained on U-3310 UV Spectrophotometer. Fluorescence spectra were taken on a Fluoromax-P luminescence spectrometer (Horiba Jobin Yvon, Inc.).

Synthesis of Dithienylethenes 3a–c

Aldehyde **2** (1.0 mmol) was added to a solution of ammonium acetate (0.8 mmol), refluxing glacial acetic acid (15 mL), under an argon atmosphere at 120°C, and it was refluxed for 2 h. The 1,2-bis(5-cholro-2-methylthiophen-3-yl)ethane-1,2-dione **(1)** (1.0 mmol) was added to the reaction solution above, which continued to react further overnight. The reaction mixture was allowed to cool down to room temperature, and then transferred to ice water (50 mL), which was carefully neutralized with 10% sodium carbonate solution to a pH of 6.5–7.0. The formed precipitate was collected and the crude product was washed with water; the dried solid was dissolved in dichloromethene (DCM). Then dried with sodium sulfate, upon removal of solvent under reduced pressure, the solution was purified on a silica gel column using petroleum ether/ethyl acetate (4:1) as the eluent to obtain the target compounds as white powder in yields of 69%–80%.

*Compound **3b**.* ^1H NMR (400 MHz, DMSO): $\delta = 2.02$ (s, 3H, CH_3), 2.23 (s, 3H, CH_3), 3.82 (s, 3H, OCH_3), 6.83, 7.12 (s, 1H, thiophene-H), 6.94 (m, 1H, Ar-H), 7.38 (t, $J = 8.0$ Hz, 1H, Ar-H), 7.61 (t, $J = 8.0$ Hz, 1H, Ar-H), 7.61 (s, 1H, Ar-H), 12.72 (s, 1H, -NH). ^{13}C NMR

(100 MHz, DMSO): δ 13.53 (s, CH_3), 13.88 (s, CH_3), 55.15 (s, O-CH_3), 111.14, 114.30, 117.48, 122.83, 123.49, 124.33, 127.55, 128.35, 129.85, 131.44, 131.83, 133.53, 134.13, 135.74, 145.49, 159.55 (s, thiophene, ethene, Ar). Anal. Calcd. for $C_{20}H_{16}Cl_2N_2OS_2$: C, 55.17; H, 3.70; N, 6.43. Found: C, 55.27; H, 3.61; N, 6.46.

Synthesis of Dithienylethenes 4a–c

Methyl iodide was added (1.8 mmol) to a solution of **3** (0.9 mmol), in *N*,*N*-dimethylformamide (10 mL), in the presence of potassium carbonate (1.8 mmol) under dark conditions for 12 h at room temperature. The reaction mixture was allowed to cool, and transferred to about 50 mL of water. The formed precipitate was collected and the crude product was washed with water; the dried solid was redissolved in DCM. Then dried with sodium sulfate, upon removal of solvent under reduced pressure, the solution was purified on a silica gel column using petroleum ether/ethyl acetate (5:1) as the eluent to obtain the target compound as a white solid in yields of 36%–41%.

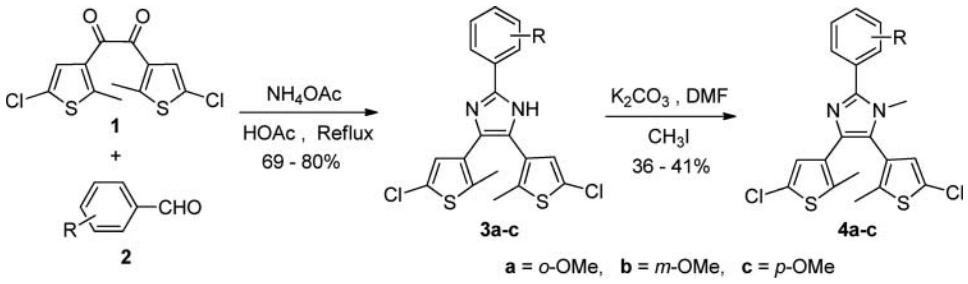
*Compound **4a**.* ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.05$ (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 3.32 (s, 3H, N-CH_3), 3.85 (s, 3H, OCH_3), 6.70, 6.80 (s, 1H, thiophene-H), 6.99 (d, $J = 8.4$ Hz, 1H, Ar-H), 7.07 (t, $J = 7.2$ Hz, 1H, Ar-H), 7.43 (t, $J = 7.2$ Hz, 1H, Ar-H), 7.57 (d, $J = 8.4$ Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.82 (s, CH_3), 14.25(s, CH_3), 32.14 (s, N-CH_3), 55.53 (s, O-CH_3), 110.97, 119.93, 120.94, 123.85, 124.59, 126.51, 126.72, 127.39, 130.93, 131.14, 132.40, 133.81, 135.09, 138.07, 146.03, 157.27 (s, thiophene, ethene, Ar). MS (*m/z*): 448 $[M]^+$. Anal. Calcd. for $C_{21}H_{18}Cl_2N_2OS_2$: C, 56.12; H, 4.04; N, 6.23. Found: C, 56.29; H, 3.89; N, 6.25.

*Compound **4b**.* ^{1}H NMR (600 MHz, $CDCl_3$)–$\delta = 2.04$ (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 3.56 (s, 3H, N-CH_3), 3.89 (s, 3H, OCH_3), 6.69, 6.79 (s, 1H, thiophene-H), 6.99 (d, $J = 8.4$ Hz, 1H, Ar-H), 7.28 (d, $J = 12.6$ Hz, 2H, Ar-H), 7.40 (t, $J = 7.8$ Hz, 1H, Ar-H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 13.83 (s, CH_3), 14.21(s, CH_3), 33.09 (s, N-CH_3), 55.32 (s, O-CH_3), 114.25, 114.73, 120.95, 124.76, 124.84, 126.26, 126.78, 127.14, 127.26, 129.49, 130.69, 131.56, 134.21, 135.10, 138.43, 147.78, 159.62 (s, thiophene, ethene, Ar). MS (*m/z*): 448 $[M]^+$. Anal. Calcd. for $C_{21}H_{18}Cl_2N_2OS_2$: C, 56.12; H, 4.04; N, 6.23. Found: C, 56.22; H, 3.88; N, 6.35.

*Compound **4c**.* ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.03$ (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 3.55 (s, 3H, N-CH_3), 3.87 (s, 3H, OCH_3), 6.71, 6.79 (s, 1H, thiophene-H), 7.03 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.69 (d, $J = 8.4$ Hz, 2H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.86 (s, CH_3), 14.24(s, CH_3), 33.06 (s, N-CH_3), 55.30 (s, O-CH_3), 113.98, 122.75, 124.36, 124.84, 126.40, 126.74, 127.20, 127.29, 130.15, 130.76, 134.15, 134.84, 138.33, 147.94, 160.09 (s, thiophene, ethene, Ar). MS (*m/z*): 448 $[M]^+$. Anal. Calcd. for $C_{21}H_{18}Cl_2N_2OS_2$: C, 56.12; H, 4.04; N, 6.23. Found: C, 56.25; H, 3.91; N, 6.24.

Results and Discussion

Imidazole-based dithienylethenes were synthesized according to the following synthetic route. As outlined in Scheme 2, compounds **3a–c** were obtained in 69%–80% of yields by the condensation of thiophene-based diketone **1** and substituted benzaldehyde **2** in the presence of ammonium acetate in acetic acid under nitrogen atmosphere. In this case, it was worth mentioning that dithienylethenes **3a** and **3c** have been reported by Liu and



Scheme 2. Synthetic route of imidazole-based dithienylethenes.

Chen [3]. Subsequently, N-methylation of imidazole was performed with CH_3I in the presence of K_2CO_3 in DMF under nitrogen atmosphere to afford compounds **4a–c**. All of the imidazole-based dithienylethenes were characterized by standard analytical techniques such as ^1H NMR, ^{13}C NMR, and elemental analysis.

These dithienylethenes displayed excellent solubility in the common solvents. Subsequently, the UV–Vis absorption spectra and fluorescent spectra of the dithienylethenes were measured at room temperature in acetonitrile. As described in Fig. 1(A), a new absorption band in the region of visual light was observed, which indicated that compound

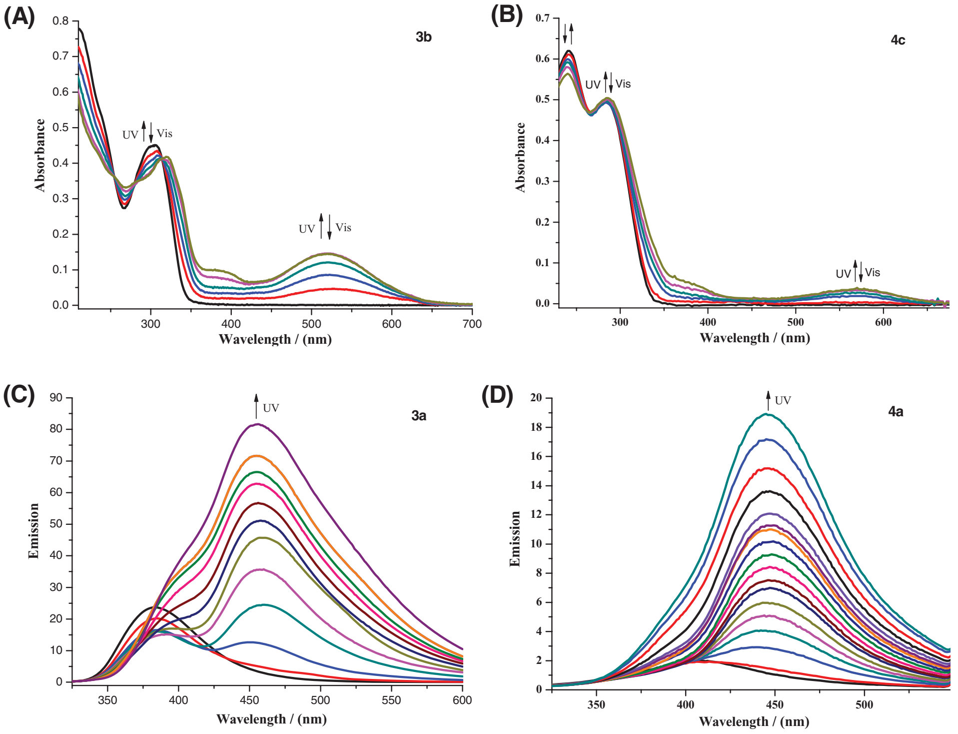


Figure 1. Absorption spectral changes of dithienylethenes by photoirradiation in acetonitrile (2.0×10^{-5} mol·L^{-1}) at room temperature. (A) **3b** and (B) **4c**. Emission intensity changes of partial dithienylethenes in acetonitrile (2.0×10^{-5} mol·L^{-1}) with UV-light irradiation. (C) **3a** and (D) **4a**.

Table 1. Absorption and fluorescence data of dithienylethenes **2–3** and **8–10** in acetonitrile (2.0×10^{-5} mol·L^{-1})

Compounds	λ_{max}^{Abs} (nm) Open isomer	λ_{max}^{Abs} (nm) Closed isomer	λ_{max}^{em} (nm) Open isomer	λ_{max}^{em} (nm) Closed isomer
3a	310	506	384	456
3b	298	520	385	451
3c	296	533	389	480
4a	288	564	407	445
4b	290	566	389	470
4c	287	570	414	473

3b underwent a photoisomerization upon irradiation with UV light ($\lambda = 302$ nm). Meanwhile, a reversible open-ring reaction was also found upon irradiation with visible light ($\lambda > 402$ nm). Similar properties also existed in compounds **3a** and **3b**. It has been noted that compound **3a** showed a 12- to 14-nm red-shift compared to compounds **3b** and **3c** before irradiation with UV light, as shown in Table 1. It was possibly attributed to the existence of intramolecular N–H$\cdots$ O hydrogen bond (imidazole ring and methoxyl group). Although the methoxyl groups of compounds **3b** and **3c** are in 3- and 4-sites of benzene ring, they displayed similar absorption. According to the data in Table 1, closed-ring isomers of the dithienylethenes revealed a 14-nm red-shift from **3a** to **3c**, respectively. The results suggested that the difference in position of substituted group can affect the photoisomerization.

After N-methylation of NH on the imidazole ring, compounds **4a–c** showed similar UV–Vis absorbance. Interestingly, a weak blue shift could be observed in Table 1, possibly owing to the decrease of the conjugated degree after N-methylation on the imidazole rings, which was well in agreement with our previous report [5a, 7]. Upon irradiation with UV light, a new absorbance band at 570 nm was observed for compound **4c** in Fig. 1(B). A similar phenomenon was also found in the solution of compounds **4a** and **4b** as shown in Table 1, and these compounds also displayed very good reversibility. It is worth mentioning that compounds **4a–c** revealed very obvious red shifts in comparison to compounds **3a–c**. Subsequently, we investigated fluorescence spectra of the dithienylethenes in acetonitrile (2.0×10^{-5} mol·L^{-1}). As can be observed in Fig. 1(C) and (D), obvious "turn-on" fluorescent changes could be found in the solution of compounds **3a** and **4a** when they underwent a UV-light irradiation. Other compounds also possessed similar properties in Table 1.

Further investigation based on metal ions binding was performed because of the coordinative function of imidazole unit, in which different metal ions (such as Cd^{2+}, K^+, Cu^{2+}, Zn^{2+}, Co^{2+}, Ca^{2+}, Fe^{3+}, Hg^{2+}, Ni^{2+}, and Cu^+) were added to the acetonitrile solution of dithienylethenes **3** and **4**. According to Fig. 2(A), the obvious fluorescent enhancement of compound **3c** in acetonitrile (2×10^{-5} M) was observed when the metal ions Cu^{2+}, Fe^{3+}, and Cd^{2+} were added, respectively, while other metal ions displayed little changes. Furthermore, the introduction of Cu^{2+} showed the largest enhancement of fluorescent intensity, while the effect of Cd^{2+} was the weakest. Similar experiments were carried out in the acetonitrile solution of compounds **3a** and **3b**, and the same results were easily achieved. Subsequently, N-methylated compounds **4a–c** were subjected to perform the same reaction. According to Fig. 2(B), it is suggested that compound **4a** possessed completely the same binding properties toward Cu^{2+}, Fe^{3+}, and Cd^{2+}. Uniformly, the binding properties

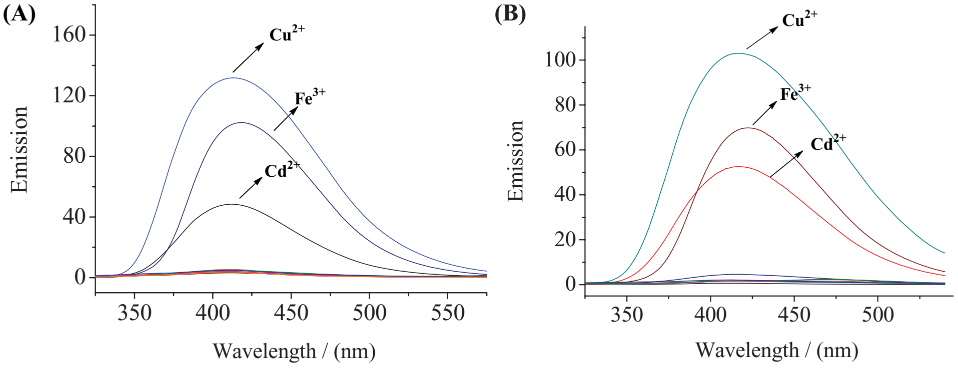


Figure 2. Fluorescence responses of partial dithienylethenes (2×10^{-5} M) in acetonitrile upon the addition of Cd^{2+}, K^+, Cu^{2+}, Zn^{2+}, Co^{2+}, Ca^{2+}, Fe^{3+}, Hg^{2+}, Ni^{2+}, and Cu^+ (10 eq.). (A) **3c** and (B) **4a**.

of compounds **4b** and **4c** were well in agreement with compound **4a**. From these data, we found that metal ions Cu^{2+}, Fe^{3+}, and Cd^{2+} can affect their fluorescence spectra.

Conclusion

In summary, a series of imidazole-bridged dithienylethenes was synthesized in good yields. UV–Vis absorption and fluorescence spectra of the dithienylethenes were investigated before and after irradiation with UV light. The results indicated that these compounds revealed very good reversibility upon irradiation with UV and visual light, and possessed the “turn-on” fluorescent properties. Meanwhile, we found that metal ions can affect fluorescence spectra of the dithienylethenes. It is worth mentioning that the metal ions such as Cd^{2+}, Cu^{2+}, Fe^{3+} can obviously enhance the intensity of emission spectra. Further research will focus on the selective binding toward metal ions.

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