

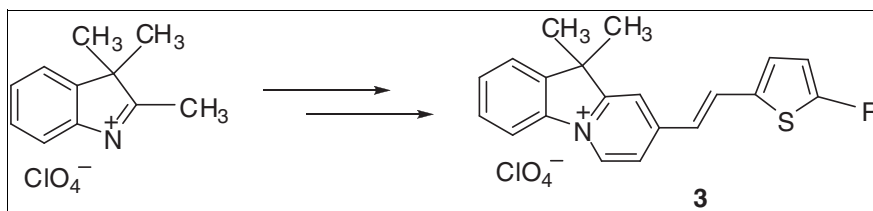
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Two novel compounds, 8-[2-(2-thienyl)vinyl]-10,10-dimethyl-10*H*-pyrido[1,2-*a*] indolium perchlorate (**3a**) and 8-[2-(5-phenyl-2-thienyl)vinyl]-10,10-dimethyl-10*H*-pyrido[1,2-*a*]indolium perchlorate (**3b**) were synthesized and characterized by IR, ¹H-NMR, elemental analyses, and X-ray diffraction. Crystal structural analysis suggested that either **3a** or **3b** exhibited good coplanarity and rings and vinyl in the target molecule could make up a large conjugated system. Ultraviolet–visible absorption analysis indicated both **3a** and **3b** possessed large maximum absorptions, and **3b** underwent a significant redshift (43.0 nm) in comparison with **3a**.

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INTRODUCTION

Substituted 10*H*-pyrido[1,2-*a*]indolium perchlorates can be used as photosensitive dyes, fluorescent whiteners, and organic light-guide sensitizers [1–3]. Since the first substituted 10*H*-pyrido[1,2-*a*]indolium perchlorate was prepared by Chapman in 1974 [4], many this kind of compounds such as methyl, phenyl, styryl, or furyl-substituted 10*H*-pyrido[1,2-*a*]indolium perchlorates have been synthesized [5–9]. On the basis of synthesis and spectral property study about a lot of this class of compounds, Liu *et al.* [10] found that the introduction of a conjugated substituent at the 8-position of 10*H*-pyrido[1,2-*a*]indolium ring can yield a significant redshift of the maximum absorption.

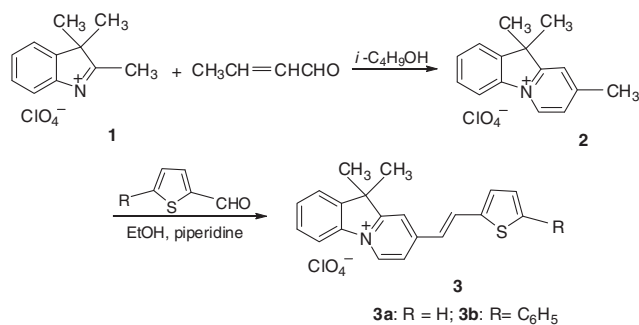
To further study the relationship between the structure and maximum absorption, the crystal structures of three compounds in this series were determined by single-crystal X-ray diffraction [11–13] and found that the dihedral angle between 10*H*-pyrido[1,2-*a*]indolium and substituted phenyl at 8-position was small, which meant the two groups were nearly planar. Therefore, the two groups were able to make up a conjugated system, and this was the reason for a significant redshift when a conjugated substituent was introduced at the 8-position. Considering thiophene possesses unique optical property and electronic transmission capability [14], herein, we introduced 2-thienyl vinyl or 5-phenyl-2-thienyl vinyl onto 8-position of 10*H*-pyrido[1,2-*a*]indolium and synthesized two target compounds, to obtain the compounds with large maximum

absorptions. Their structures were confirmed by IR, ¹H-NMR, elemental analyses, and X-ray diffraction. The synthetic route was shown in Scheme 1.

RESULTS AND DISCUSSION

The target compounds **3a** and **3b** were prepared from 8,10,10-trimethyl-10*H*-pyrido[1,2-*a*]indolium perchlorate and 2-thiophene carboxaldehyde or 5-phenyl-2-thiophene-carboxaldehyde by aldol reaction. In this type reaction, the *cis*- and *trans*-configuration products may be afforded. In our experiment, however, only *trans*-isomer was obtained due to the large steric hindrances of 10*H*-pyrido[1,2-*a*]indolium and thiophene rings, which was seen from their crystal structures (Figs. 1 and 2) and was also confirmed by a coupling constant of 16 Hz for the hydrogen atoms attached to the C C double bond in ¹H-NMR spectrum. In the crystal of **3a**, the single bond lengths of C11 C14 and C15 C16 were 1.484(10) and 1.409(9) Å, respectively, both shorter than the normal C C bond (1.540 Å), which meant both the two single bonds possessed a partial double bond character and the electron density was delocalized among C11, C14, C15, and C16 atoms. The torsion angles of the atoms from the rings and vinyl moiety were 0.0° or 180.0°, suggesting that 10*H*-pyrido[1,2-*a*]indolium ring, vinyl moiety, and thiophene ring were well coplanar. As a result, the three groups could make up a large conjugated system. Additionally, there were two weak intramolecular

Scheme 1. Synthetic route of the title compounds.



hydrogen bonds in the molecule, C12 H12...O1 [H12...O1, 3.559(11) Å, 157.5°] and C17 H17...O2 [H17...O2, 3.294(15) Å, 154.3°], making the molecule more stable.

Similarly, in the crystal of **3b**, the single bond lengths of C12 C15 and C16 C17 bonds were 1.492(7) and 1.487(7) Å, respectively, also both shorter than the normal C C bond, suggesting that both the two single bonds were of a partial double bond character. Furthermore, the torsion angles of C11 C12 C15 C16, C12 C15 C16 C17, C15 C16 C17 S1, and S1 C20 C21 C26 were 2.1(8)°, -178.7(4)°, 4.3(7)°, and -3.7(6)°, respectively, slightly deviating from 0.0° or -180°, which meant 10*H*-pyrido[1,2-*a*]indolium, vinyl, thiophene, and benzene rings were nearly coplanar. The dihedral angles between 10*H*-pyrido[1,2-*a*]indolium ring and vinyl, thiophene ring and vinyl, thiophene, and benzene rings were 7.59°, 4.67°, and 5.19°, respectively. Therefore, it was deduced that the four moieties in **3b** formed a larger conjugated system.

As shown in Figure 3, there were three absorption bands in compound **3a**, of which λ , λ , and λ were 267.8, 291.0, and 401.6 nm, respectively. According to the method of ref. 15, it was deduced λ was attributed to the $\pi \rightarrow \pi^*$

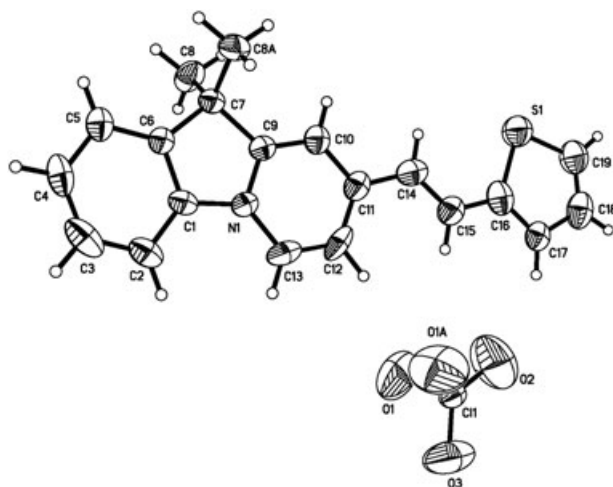


Figure 1. Molecular structure of **3a**; ellipsoids are drawn at the 50% probability level.

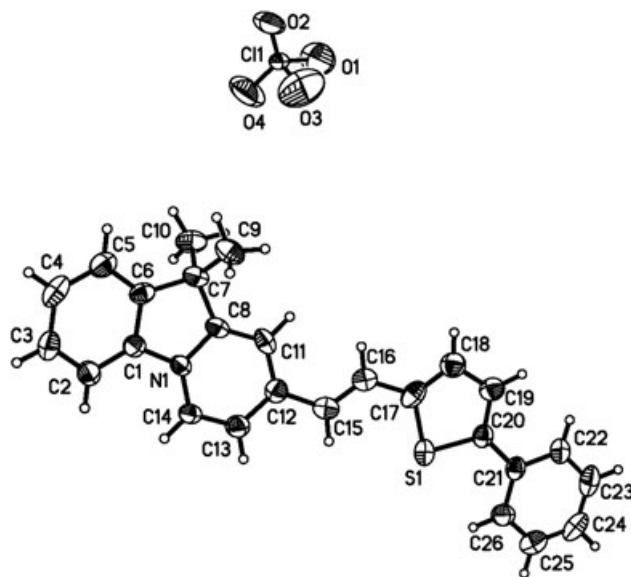


Figure 2. Molecular structure of **3b**; ellipsoids are drawn at the 50% probability level.

transition of the whole conjugated system in the molecule, while λ may be resulted from the $\pi \rightarrow \pi^*$ transition of the partial conjugated system related to 10*H*-pyrido[1,2-*a*]indolium moiety, due to a maximum absorption of 280 nm in 8-methyl-10*H*-pyrido[1,2-*a*]indolium perchlorate [10]. In addition, as the maximum absorption of thiophene is 231.0 nm, and an enhancement is 30 nm when adding a vinyl moiety in a conjugated system so that λ was the $\pi \rightarrow \pi^*$ transition of the partial conjugated system related to thiophene and vinyl moieties. Moreover, it can be seen from Figure 3 that there were two absorption bands in compound **3b**, of which λ and λ were 300.6 and 444.6 nm, respectively. In the same way, it was deduced that λ in **3b** was attributed to the $\pi \rightarrow \pi^*$ transition of the whole molecule, whereas λ was assigned to the $\pi \rightarrow \pi^*$ transition

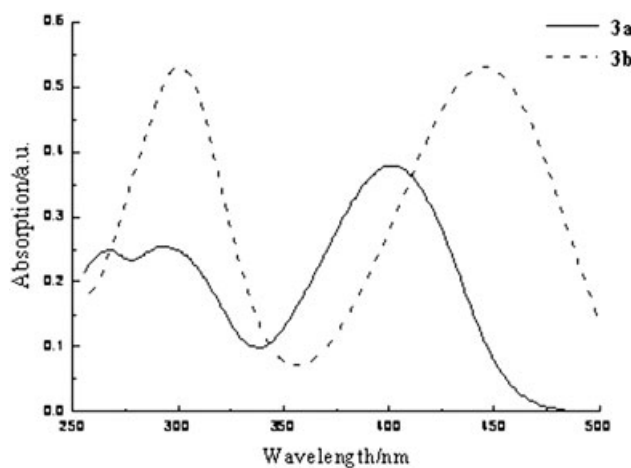


Figure 3. The absorption spectrum of the target compounds in CH₃OH.

Table 1
Selected bond lengths (Å) and bond angles (°) for **3a** and **3b**.

3a					
N1–C1	1.415(7)	C11–C12	1.414(10)	C15–C16	1.409(9)
N1–C9	1.349(6)	C11–C14	1.484(10)	C16–C17	1.333(10)
N1–C13	1.371(7)	C14–C15	1.303(10)	S1–C16	1.742(8)
C9–N1–C1	110.6(4)	C12–C11–C14	126.6(5)	C15–C16–S1	124.5(6)
C9–N1–C13	119.5(5)	C15–C14–C11	124.4(6)	C17–C16–S1	111.5(5)
C10–C11–C12	114.6(6)	C14–C15–C16	124.7(7)	C18–C19–S1	112.2(6)
3b					
N1–C1	1.422(5)	C12–C15	1.492(7)	S1–C17	1.755(6)
N1–C8	1.374(5)	C15–C16	1.293(7)	C19–C20	1.365(7)
N1–C14	1.350(6)	C16–C17	1.487(7)	C20–C21	1.473(7)
C12–C13	1.386(7)	C17–C18	1.336(8)	S1–C20	1.713(5)
C8–N1–C1	111.0(4)	C16–C15–C12	123.6(5)	C19–C20–S1	109.6(4)
C14–N1–C8	121.6(4)	C15–C16–C17	125.9(5)	C19–C20–C21	127.8(5)
C13–C12–C11	116.8(4)	C16–C17–S1	123.3(5)	C22–C21–C20	119.7(5)
C11–C12–C15	125.1(4)	C18–C17–S1	112.4(4)	C26–C21–C22	117.4(5)

of the partial conjugated system related to substituted pyrido[1,2-*a*]indolium moiety.

Comparing the maximum absorption attributed to the $\pi \rightarrow \pi^*$ transition of the whole molecule, it was found that λ in **3b** showed an obvious redshift (43.0 nm) in comparison with λ in **3a**. Moreover, **3b** underwent a remarkable redshift (83.6 nm) in comparison with 8–styryl analog [10]. Additionally, as shown in Figure 3, **3b** exhibited a larger absorption intensity ($\lg \epsilon = 4.42$) than **3a** ($\lg \epsilon = 4.28$). The reason was that there was a larger conjugated system in **3b**, reducing the energy of the $\pi \rightarrow \pi^*$ transition.

CONCLUSIONS

Two novel compounds, 8–substituted–10,10–dimethyl–10*H*–pyrido[1,2-*a*]indolium perchlorates containing thienyl moiety (**3a** and **3b**) were synthesized by the condensation of 8,10,10–trimethyl–10*H*–pyrido[1,2-*a*]indolium perchlorate and 2–thiophene carboxaldehyde or 5–phenyl–2–thiophene carboxaldehyde. Their structures were characterized by IR, ¹H–NMR, elemental analysis, and X–ray diffraction. Crystal structural analysis suggested that either **3a** or **3b** exhibited good coplanarity, so the rings and vinyl moiety in **3a** or **3b** could make up a large conjugated system.

Ultraviolet–visible (UV–vis) absorption analysis indicated both **3a** and **3b** possessed large maximum absorptions, and **3b** underwent a significant redshift (43.0 nm) in comparison with **3a**.

EXPERIMENTAL

Melting points were measured on an X–5 microscopic melting–point apparatus and are uncorrected. IR spectra were recorded in KBr pellet on a Nicolet–380 infrared spectrophotometer. ¹H–NMR spectra were carried out on a Varian Mercury Plus 400 spectrometer using tetramethylsilane as an internal standard. Elemental analyses were performed with a Vario EL III Elemental Analyzer. UV–vis spectrum was measured on Shimadzu 2450 PC UV–vis spectrophotometer using methanol as a solvent. X–ray data were collected on a Bruker Smart APEX CCD diffractometer.

2,3,3–Trimethyl–3*H*–indolium perchlorate(**1**) and 8,10,10–trimethyl–10*H*–pyrido [1,2-*a*]indolium perchlorate(**2**) were prepared according to the refs. 16 and 6, respectively. 5–Phenyl–2–thiophenecarboxaldehyde was prepared by the application of Vilsmeier formylation to 5–phenylthiophene[17, 18]. The other chemicals were of analytical grade and were distilled before use.

8–[2–(2–Thienyl)vinyl]–10,10–dimethyl–10*H*–pyrido[1,2-*a*]indolium perchlorate (3a**)**. A mixture of 8,10,10–trimethyl–10*H*–pyrido[1,2-*a*]indolium perchlorate (1.5 g, 4.8 mmol) and

Table 2
Selected torsion angles (°) for **3a** and **3b**.

3a					
C2–C1–C6–C7	180.0(2)	C10–C11–C14–C15	180.0(2)	C14–C15–C16–S1	0.0(2)
C13–N1–C1–C2	0.0(3)	C11–C14–C15–C16	180.0(2)	C19–S1–C16–C15	180.0(0)
C7–C9–C10–C11	180.0(2)	C14–C15–C16–C17	180.0(1)	C15–C16–C17–C18	180.0(1)
3b					
C1–N1–C8–C11	175.6(4)	C12–C15–C16–C17	–178.7(4)	C15–C16–C17–S1	4.3(7)
C2–C1–C6–C7	179.8(4)	C13–C12–C15–C16	–176.5(5)	C19–C20–C21–C22	–4.7(7)
C7–C8–C11–C12	177.7(5)	C14–N1–C1–C2	0.7(7)	S1–C20–C21–C22	173.7(4)
C11–C12–C15–C16	2.1(8)	C15–C16–C17–C18	–176.3(5)	S1–C20–C21–C26	–3.7(6)

2-thiophene carboxaldehyde (0.54 g, 4.8 mmol) in anhydrous ethanol (12 mL) was added five drops of piperidine. After refluxing for 5 h with stirring, the resulting mixture was cooled to room temperature, and solid was filtered under reduced pressure and recrystallized from EtOH-CH₃CN (V:V = 5:2), affording compound **3a** as a yellow needle.

Yield 71.0%, mp 291.7–292.8°C. IR (KBr), ν (cm⁻¹): 1639.3 (C N⁺), 1362.8 [C(CH₃)₂], 1083.7, 620.8 (ClO), 958.7 [H C C H (E)]. ¹H-NMR (400 MHz, DMSO-*d*₆), δ (ppm): 1.72 [s, 6H, C(CH₃)₂], 7.24–8.35 (m, 7H, indole-H + thiophene-H), 7.28 [d, *J* = 16 Hz, 1H, CH CH (E)], 8.34 (d, *J* = 6.8 Hz, 1H, pyridinium-7-H), 8.36 [d, *J* = 16 Hz, 1H, CH CH (E)], 8.70 (s, 1H, pyridinium-9-H), 9.67 (d, *J* = 6.8 Hz, 1H, pyridinium-6-H). Anal. Calcd. for C₂₀H₁₈ClNO₄S: C, 59.48; H, 4.49; N, 3.47. Found: C, 59.16; H, 4.32; N, 3.51.

8-[2-(5-Phenyl-2-thienyl)vinyl]-10,10-dimethyl-10H-pyrido[1,2-*a*]indolium perchlorate (3b). **3b** was also prepared *via* the same procedure as described in **3a**. Red needle, yield 73.4%, mp 279.1–281.0°C. IR (KBr), ν (cm⁻¹): 1639.9 (C N⁺), 1362.1 [C(CH₃)₂], 1094.8, 621.5 (ClO), 955.8 [H C C H (E)]. ¹H-NMR (400 MHz, DMSO-*d*₆), δ (ppm): 1.77 [s, 6H, C(CH₃)₂], 7.33 [d, *J* = 16 Hz, 1H, CH CH (E)], 7.44–7.78 (m, 7H, Ph-H + thiophene-H), 7.80–8.40 (m, 4H, indole-H), 8.33 (d, *J* = 6.8 Hz, 1H, pyridinium-7-H), 8.39 [d, *J* = 16 Hz, 1H, CH CH (E)], 8.76 (s, 1H, pyridinium-9-H), 9.72 (d, *J* = 6.8 Hz, 1H, pyridinium-6-H). Anal. Calcd. for C₂₆H₂₂ClNO₄S: C, 65.06; H, 4.62; N, 2.92. Found: C, 64.93; H, 4.68; N, 3.07.

Single crystals of compound **3a** and **3b** suitable for data collection were selected and data were collected at 298(2) K on a Bruker Smart APEX CCD diffractometer equipped with a graphite-monochromated Mo K α radiation (λ = 0.71073 Å) by using φ and ω scan modes. The structures were each solved by direct methods *via* SHELXS-97 program [19], and refined by full-matrix least-squares techniques on *F*². All the nonhydrogen atoms were refined anisotropically, while the hydrogen atoms were located geometrically and refined isotropically. The supplementary crystal data of compound **3a** and **3b** are deposited with CCDC Nos. 799241 and 806375, respectively, and these data can

be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. The selected bond lengths and bond angles are summarized in Table 1 and the selected torsion angles for nonhydrogen atoms are given in Table 2.

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