A Novel Bisthienylethene as Acidichromic and Photochromic Yellow Dye

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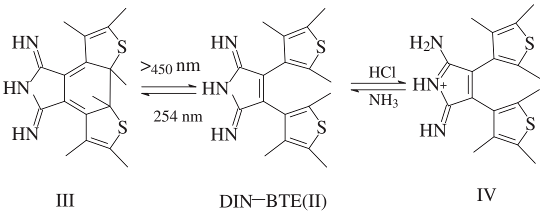
A novel bisthienylethene as yellow colour photochromic and acidichromic dye has been prepared by a simple and low cost route, and its PC film shows a fast response reversible colour change between colourless and yellow colour by exposure to gaseous acid and ammonia.

In recent years, a great number of photochromic compounds have been studied for use as optical switches and photon-mode rewritable memory devices.[1–4] In particular, 1,2-bisthienylethene derivatives (BTEs) is one of the most interesting kind compounds owing to their excellent thermal stability, fatigue resistance, and good quantum yields.[5–10] However, the most of BTE compounds coloured in magenta or cyan have been well studied, i.e. the photo-induced closed-ring forms reversibly absorb light in the region of longer wavelengths.[5,10–12] Yellow colour photochromic 1,2-bisthienylethene derivatives are more less than them,[5,13] while yellow as one of the three primary colours is urgently needed in order to realize a photon-mode rewritable full colour print. Although yellow fulgides or oxazolyfulgides and chromene derivatives have been synthesized,[14] the yellow BTE derivatives still need to be developed to realize photon-mode full colour tuning based on the same chemical analogy with the same stability and compatibility. In this letter we report a new diarylethene derivative (DIN-BTE) with yellow colour photochromism upon irradiation with UV light shown in Scheme 1.



Scheme 1. The photochromic and acidichromic switch of compound II.

Moreover, we also found an interesting acidichromism besides the photochromism of this compound. It shows a reversible colour change upon alternating exposure to HCl (g) and NH_3. Acidichromism is used to describe the reversible colour changes depending on the pH in the solution or upon alternating exposure to HCl and NH_3 in films.[15,16] The acidichromism has potential applications in pH sensors, photo- and chemical-switching systems and gas controlled reversible colour-change devices. To the best of our knowledge, the acidichromism of bisthienylethene derivatives is reported at the first time in this work.

DIN-BTE (**II**) as illustrated in Scheme 1 was synthesized by the addition reaction of 1,2-dicyano-1,2-bis(2,4,5-trimethyl-3-thienyl)ethene (**I**)[17,18] with ammonia. A gaseous stream of ammonia was bubbled through a solution of compound **I** in MeOH containing a catalytic amount of $NaOCH_3$ at room temperature for 2 h, then refluxing the solution for further 5 h. After cooling, the solvent was evaporated and the compound purified by column chromatography on silica gel (first petroleum ether/ether = 5:1, then CH_2Cl_2). The compound was obtained in 62% yield. DIN-BTE (II): ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.25 (s, 6H), 2.09 (s, 3H), 2.08 (s, 3H), 1.79 (s, 3H), 1.77 (s, 3H); ^{13}C NMR (250 MHz, $CDCl_3$): δ 166.37, 135.80, 134.88, 131.82, 130.94, 127.84, 14.18, 13.17, 12.99; IR (cm^{-1}): 3274.9, 3107.3, 2916.8, 2856.2, 2739.2, 1644.4, 1625.5, 1536.5, 1427.8, 1103.7, 833. MS (m/z): 343 (M$^+$). Anal. Calcd for $C_{18}H_{21}N_3S_2$: C, 62.97; H, 6.12; N, 12.24%. Found: C, 62.68; H, 6.09; N, 12.19%. Compound **III**, ^{1}H NMR (500 MHz, $CDCl_3$ gotten by the subtraction at the photo-stationary state): δ 2.21 (s, 6H), 2.01 (s, 6H), 1.80 (s, 6H). MS (m/z): 343 (M$^+$). Compound **IV**, ^{1}H NMR (500 MHz, DMSO-d_6): δ 2.23 (s, 3H), 2.15 (s, 3H), 1.99 (s, 3H), 1.93 (s, 3H), 1.83 (s, 3H), 1.67 (s, 3H); MS (m/z): 344 (M$^+$-Cl); IR $\nu_{\max}$ (cm^{-1}): 3400.6, 1628.5.

The absorption changes of DIN-BTE (**II**) in CH_2Cl_2 are shown in Figure 1, in which the absorption at 288 nm ($\varepsilon = 2.1 \times 10^4$ dm^3 mol^{-1} cm^{-1}) decreases upon irradiation with 254-nm light and two new absorption peaks appear at 395 and 458 nm ($\varepsilon = 1.2 \times 10^4$ dm^3 mol^{-1} cm^{-1}), which means yellow colour is formed. Two new bands owe to the formation of closed-ring form (**III**) shown in Scheme 1. After irradiation with a light of wavelengths at 400 or 458 nm, the yellow colour disappeared. The quantum yields for open-to-closed (irradiation with 254-nm light) and closed-to-open (irradiation with 400-nm light) photochromic processes were determined to be 0.31 and 0.33, respectively.

An interesting property was found for the acidichromism of the PC film of compound II. The PC (polycarbonate) film (thickness ca. 1×10^{-5} m) was fabricated with the CH_2Cl_2 solution (2×10^{-5} M) of DIN-BTE in PC matrix on quartz substrate by the vertical dipping method. The film was purged with N_2 gas before spectral measurements. When it was exposed to HCl (g), the PC film turned yellow colour immediately, as shown by curve b in Figure 2. A new absorption peak was observed at around 400 nm ($\varepsilon = 2.7 \times 10^4$ dm^3 mol^{-1} cm^{-1}). Then, when the yellow PC film was subjected to NH_3 (g), it returned to colourless immediately and almost the same spectrum as that of the initial PC film was obtained (curve c in Figure 2). After repeated this operation of 20 cycles, i.e., the PC film was exposed to HCl and NH_3 gases separately for 5 s as shown in Figure 2, its absorbance has not altered obviously. It indicates that compound **II** can be transferred to a new delocalization enlargement form through some kinds of chemical treatment without irradiation. We conclude it is because of the formation of **IV** (Scheme 1), which change one of the exocyclic double bonds of the pentagon-basic cycle into cyclic olefin bond. So, it increases the conjugated π-electron system and makes the maximum absorption bathochromic shift. **IV** has two obvious new IR peaks of –NH_2 and C=N at

3400.6 and 1628.5 cm^{-1} respectively, compared with compound **II**. In addition, compound **IV** shows good thermal stability up to 80 °C for several hours.

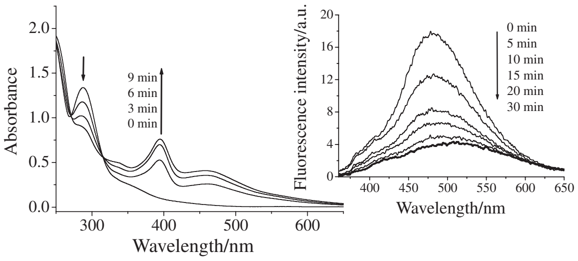


Figure 1. Absorption spectra of compound DIN-BTE in CH_2Cl_2 (3.0×10^{-5} M) and the spectral changes under different irradiation time by light of 254 nm. Insert figure: The emission spectral changes of **II** in CH_2Cl_2 (excited at 355 nm) with different irradiation times by 254 nm.

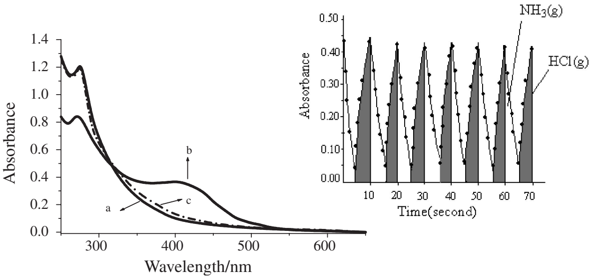


Figure 2. The acidichromism of DIN-BTE in the PC film. a) The spectra before exposed to HCl (g); b) Exposed to HCl (g); c) subjected to NH_3 (g) after exposed to HCl (g) to complete one cycle. Insert: Modulated optical density difference at 400 nm during alternating exposure to HCl and NH_3 gases every 5 s for compound DIN-BTE in PC film.

Both UV light and proton can result the change of the fluorescent intensity of **II**, as shown in the insert figure of Figure 1 and 3. In CH_2Cl_2, the open form of compound **II** displays significant fluorescence intensity at around 460 nm. Upon irradiation with 254-nm light, the closed-ring form (**III**) was produced and the fluorescence intensity was reduced to less than 15% for 30 min UV irradiation, and the maximum of fluorescence also shifted to longer wavelengths (red shift). When the solution of HCl was dropwised into THF solution of **II** in the dark (Scheme 1), the colourless solution became yellow slowly and the fluorescence was quenched accordingly. With the proton concentration of 21×10^{-5} M, the fluorescent intensity was quenched to less than 10% of the initial value. The back reaction of **IV** with a base regenerates **II** and restores the luminescence to its original value. There exists proportional dependence between the content of the **IV** form and the luminescence intensity in the present system. Therefore, the fluorescent intensity of compound **II** can be modulated by chemical stimuli or UV–vis light alternative irradiation, which would provide new potential applications.

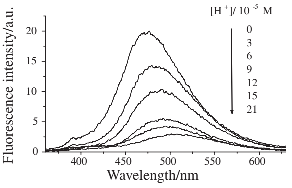


Figure 3. The emission spectra of compound DIN-BTE in THF (3.0×10^{-5} M; excited at 355 nm) and the changes when it was transformed to **IV** with different acidity.

In summary, a new yellow photochromic compound DIN-BTE, 1, 2-bis(2,4,5-trimethyl-3-thienyl)diiminopyrroline that turns yellow when it was irradiated with UV light or exposed to acid (gas or solution), has been reported. This character makes it the potential use in full-colour photo-electronic device, rewritable materials, and pH sensor.

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References

1 B. L. Feringa, in "Molecular Switches," Wiley-VCH, Weinheim (2001).
2 T. Fukaminato, T. Kawai, S. Kobatake, and M. Irie, *J. Phys. Chem. B*, **107**, 8372 (2003).
3 M. Matumoto, D. Miyazaki, and M. Tanaka, *J. Am. Chem. Soc.*, **120**, 1479 (1998).
4 A. Peters, C. Vitols, R. McDonald, and N. R. Branda, *Org. Lett.*, **5**, 1183 (2003).
5 a) M. Irie, *Chem. Rev.*, **100**, 1685 (2000). b) S. Yamamoto, K. Matsuda, and M. Irie, *Angew. Chem., Int. Ed.*, **42**, 3537 (2003).
6 a) B. Z. Chen, M. Z. Wang, Y. Q. Wu, and H. Tian, *Chem. Commun.*, **2002**, 1060. b) H. Tian, B. Z. Chen, H. Y. Tu, and K. Müllen, *Adv. Mater.*, **14**, 918 (2002). c) Q. F. Luo, B. Z. Chen, M. Z. Wang, and H. Tian, *Adv. Funct. Mater.*, **13**, 233 (2003).
7 Y. Yokoyama, H. Shiraishi, Y. Tani, Y. Yokoyama, and Y. Yamaguchi, *J. Am. Chem. Soc.*, **125**, 7194 (2003).
8 T. B. Norsten and N. R. Branda, *Adv. Mater.*, **13**, 347 (2001).
9 S. M. Shrestha, H. Nagashima, Y. Yokoyama, and Y. Yokoyama, *Bull. Chem. Soc. Jpn.*, **76**, 363 (2003).
10 M. Morimoto, S. Kobatake, and M. Irie, *J. Am. Chem. Soc.*, **125**, 11080 (2003).
11 M. Takeshita, M. Nagai, and T. Yamato, *Chem. Commun.*, **2003**, 1496.
12 K. Uchida, E. Tsuchida, Y. Aoi, S. Nakamura, and M. Irie, *Chem. Lett.*, **1999**, 63.
13 K. Uchida and M. Irie, *Chem. Lett.*, **1995**, 969.
14 a) R. Matsushima, H. Morikane, and Y. Kohno, *Chem. Lett.*, **32**, 302 (2003). b) Y. Yokoyama, M. Miyasaka, S. Uchida, and Y. Yokoyama, *Chem. Lett.*, **1995**, 479.
15 X. D. Sun, M. G. Fan, Y. Liang, Y. Zhao, Y. Ming, and E. T. Knobbe, *J. Photochem. Photobiol., A*, **102**, 213 (1997).
16 H. Gong, C. Wang, M. Liu, and M. Fan, *J. Mater. Chem.*, **11**, 3049 (2001).
17 M. Irie and M. Mohri, *J. Org. Chem.*, **53**, 803 (1988).
18 L. N. Lucas, J. J. D. Jong, J. H. van Esch, R. M. Kellogg, and B. L. Feringa, *Eur. J. Org. Chem.*, **2003**, 155 (2003).

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