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Short communication

Synthesis and properties of new polymethine dyes based on bis-dimethylaminophenylethylene moiety

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Abstract

Polymethine dyes have attracted much attention due to their potential functions for high-tech uses as organic colorants. The work herein comprises an investigation of a new class of polymethine dyes **3** and **5** which have been synthesized by the reaction of 4,4′-vinylidene-bis(*N*,*N*-dimethylaniline) **1** with two aldehydes such as 4-diphenylaminobenzaldehyde **2** and *N*-ethylcarbazole-3-carboxaldehyde **4**. Both methine dyes based on bis-dimethylaminophenylethylene moiety showed broad absorption spectra with high molar extinction coefficient in the range of 600–700 nm and their maximum absorption spectra were exhibited at 650 and 647 nm, respectively. The absorption spectra of the reversible colored form which converted from leuco form appeared with addition of acid.

Keywords: Methine dye; Absorption spectra; Leuco form; Reversible color formation; Bis-dimethylaminophenylethylene

1. Introduction

Polymethine dye [1–4] is a well known and important class of synthetic coloring materials and has attracted much attention due to their potential functions for specialty and high-technology applications, namely functional dyes. Nowadays, the most exciting developments in dye chemistry and dye application are occurring in these areas. For example, unprecedented demands for the use of written text copying or photographic imaging are greatly increasing towards the subject matter of these concerns [5]. However, the use of methine dyes for traditional application is limited to the dyeings or colorations for wool, silk, leather and polyacrylonitrile fibers [1,2]. In this context, the research of synthesis and characterization for new methine compound has become increasingly important for many color formation systems, including chromic property application in response to the increased consumer and producer demands.

Leuco dyes could play a great role in the color-occurring reaction in so many new high-technology applications [6]. The color forming precursors, leuco dyes, have received less attention in the literature. The largest portion of the annual production of this class of leuco dyes is consumed in the manufacturing of various copying papers. In this context, to provide a reversible color-occurring system, two types of polymethine dye, which, based on bis-dimethylaminophenylethylene moiety [7] were synthesized using 4-diphenylaminobenzaldehyde and *N*-ethylcarbazole-3-carboxylaldehyde. The leuco form of these methine dyes was also prepared by the treatment using methanol with NaOH. The corresponding spectroscopic properties for the original form and the leuco form were determined.

Thus, the work herein comprises an investigation of synthesis and properties of the new polymethine dyes based on bis-dimethylaminophenylethylene moiety and their corresponding reversible color formation reactions. The absorption spectral changes caused by leuco dye properties were also examined.

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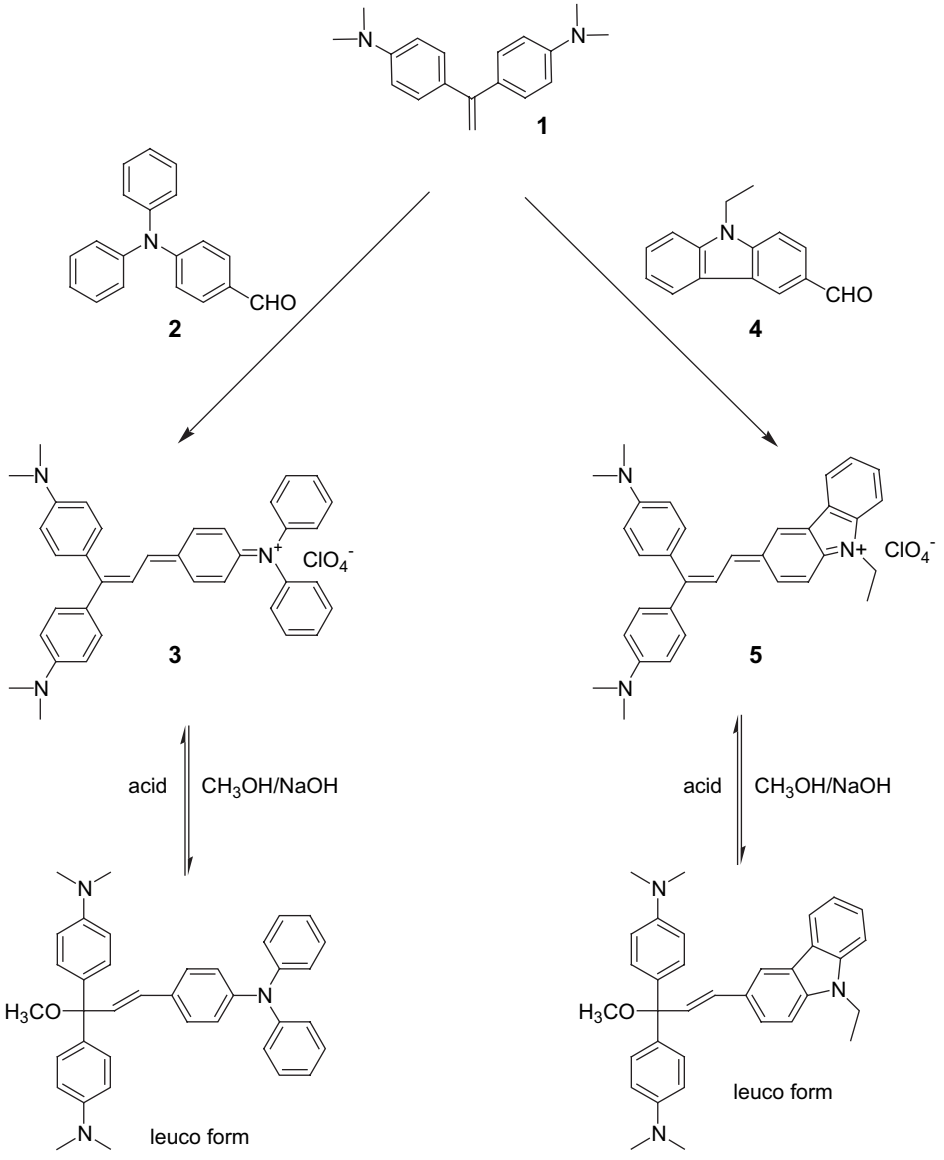
2. Synthesis

It is well known that the active methylene groups react with carbonyl groups, especially an aldehyde. The general procedures to prepare the polymethine dyes **3**, **5** are shown in Scheme 1. 4,4′-Vinylidenebis(*N*,*N*-dimethylaniline) **1** (1.88 mmol, 0.50 g) and 4-diphenylaminobenzaldehyde **2** (0.51 g) were added into a solution of 5 ml acetic anhydride. A mixture of perchloric acid (0.94 mmol, 0.13 g) and acetic anhydride (5 ml) was added into the prepared solution. The solution was refluxed for 2 h. The mixture was then cooled at room temperature and poured into excessive ethyl ether. And then the precipitate was filtered and the solid product **3** was obtained. Another synthetic approach using 4,4′-vinylidenebis(*N*,*N*-dimethylaniline) **1** (1.88 mmol, 0.5 g) and *N*-ethylcarbazole-3-carboxylaldehyde **4** (1.88 mmol, 0.42 g) was carried out as shown in Scheme 1 and the solid product **5** was obtained [8]. To investigate the reversible color forming system, the leuco form of two methine dyes was prepared by the treatment using methanol with NaOH (Scheme 1). The corresponding colorless conversion properties caused by leuco moiety were determined by absorption spectra.

3. Absorption spectra

Polymethine dyes are well known and important dye classes for synthetic color materials. In this work, based on 4,4′-vinylidenebis(*N*,*N*-dimethylaniline) **1**, two methine dyes were synthesized using two aldehyde compounds, namely 4-diphenylaminobenzaldehyde **2** and *N*-ethylcarbazole-3-carboxyaldehyde **4**. Figs. 1 and 2 show absorption spectra of these prepared methine dyes in ethyl acetate. Both methine dye compounds based on bis-dimethylaminophenylethylene moiety showed broad absorption spectra with high extinction



Scheme 1.

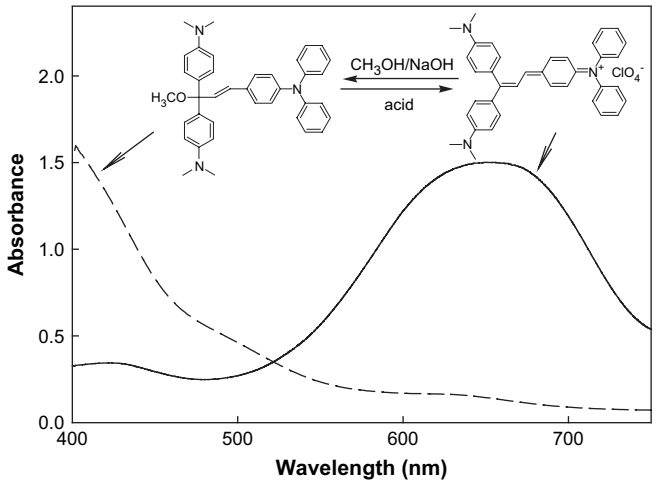


Fig. 1. Absorption spectra of methine dye **3** and its leuco form in ethyl acetate.

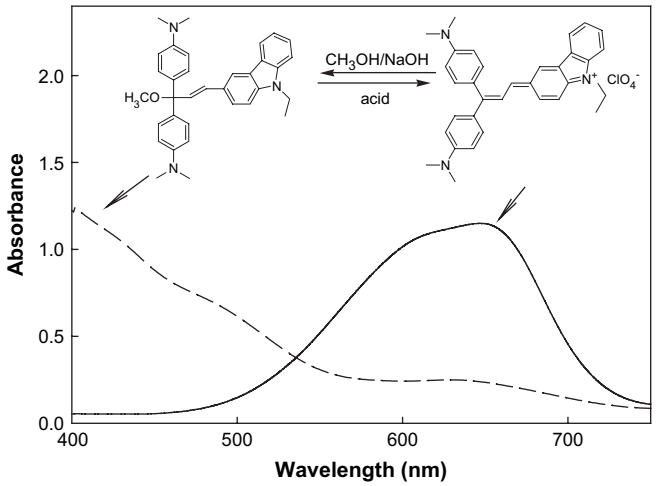


Fig. 2. Absorption spectra of methine dye **5** and its leuco form in ethyl acetate.

coefficient in the range of 600–700 nm and their maximum absorption peaks were exhibited at 650 and 647 nm. In addition, the leuco form of these dyes was prepared by the treatment using methanol with NaOH. The absorption spectra for the converted leuco form of the methine dyes are also shown in Figs. 1 and 2. In general area of imaging and copying, leuco dyes have a major part to play and this brings to the subject matter of this investigation. Originally, the term of leuco, representing white, was applied to the reduced form of vat dyes in alkaline medium, which were often colorless. Commonly, the alkali soluble leuco vat dyes have been, of course, extremely important in textile dyeings. However, nowadays, the applications of leuco dyes are far more diverse than the conventional concept, and the term is now applied to describe the reversibly reduced form of any class of dye. Furthermore, the leuco dyes are also considered to the colorless form of a dye which may be produced by a nonreductive process such as pH change, heat or light in the case of intramolecular reactions or cyclizations. Thus, the leuco forms in Figs. 1 and 2 show the colorless properties of the methine dyes compared to the original spectra and their corresponding characteristics could be considered as leuco moieties. This reversible color formation of an intense absorption band in visible region (600–700 nm) is of importance from the viewpoint of functional color-occurring systems. It is also an interesting concept that the prepared colorless or nearly colorless compounds react with acid to provide extension of the conjugated double bond system, enabling color formation. In this context, the color-occurring reaction caused by the addition of acid can be considered as a reversible color formation system of novel methine dyes.

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[8] Analytical data agree with the proposed structure for **3** and **5**, (**3**) yield: 38.6% (0.45 g); calculated for $C_{37}H_{36}ClN_3O_4$: C, 71.43; H, 5.83; N 6.75, found: C, 71.26; H, 6.50; N, 6.97; *m/z* (M^+): 622; λ_{max} (ethyl acetate) 650 nm, ε: 1.93×10^4, (**5**) yield: 35.2% (0.38 g); calculated for $C_{33}H_{34}ClN_3O_4$: C, 69.28; H, 5.99; N, 7.34, found: C, 68.94; H, 6.17; N, 6.89; *m/z* (M^+): 572; λ_{max} (ethyl acetate) 647 nm, ε: 2.98×10^4.