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Short communication

Electrochromism and X-ray crystal structure of a new azomethine dye derived from diaminomaleonitrile

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Abstract

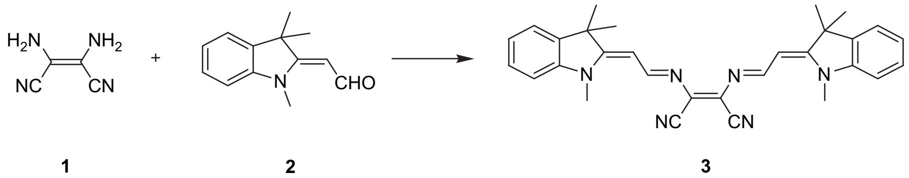
The electrochromic properties of a new azomethine dye were studied by using propylenecarbonate/chloroform/methanol solution with tetra-*n*-butylammonium perchlorate as supporting electrolyte. The dye was also found to form J-aggregate-like structure in single crystals by X-ray analysis.

Keywords: Azomethine dye; Electrochromism; Crystal structure; J-aggregates

1. Introduction

Electrochromic materials have been extensively studied for potential use in information display and solar control windows [1,2]. Electrochromism is a reversible colour change in a material caused by an applied electric field or current. Although inorganic systems are now in practical use, organic systems have advantages over inorganic systems in several ways, viz. operation at low voltage, colouration over a wide range, colour distinction, multi-colouration, etc. A large number of organic compounds develop absorption bands in the visible region of the spectrum upon redox reaction and most compounds in this class exhibit electrochromic phenomena by reversible electrode deposition, e.g. viologens [3–6], pyridines [7], *o*-toluidines [8], and anthraquinones [9].

We have also reported that response improved electrochromic colour display using new fluorophores having triphenylamine [10]. In this study, we report the electrochromic properties and crystal structure of a new azomethine dye **3** derived from diaminomaleonitrile **1**.



1 2 3

2. Electrochromism

It has been shown that the reaction of diaminomaleonitrile **1** with Fisher aldehyde **2** gives 2,3-bis-[2-(1,3,3-trimethyl-1,3-dihydro-indol-2-ylidene)-ethylideneamino]-but-2-enedinitrile **3** which has been evaluated as red-light-emitting materials in

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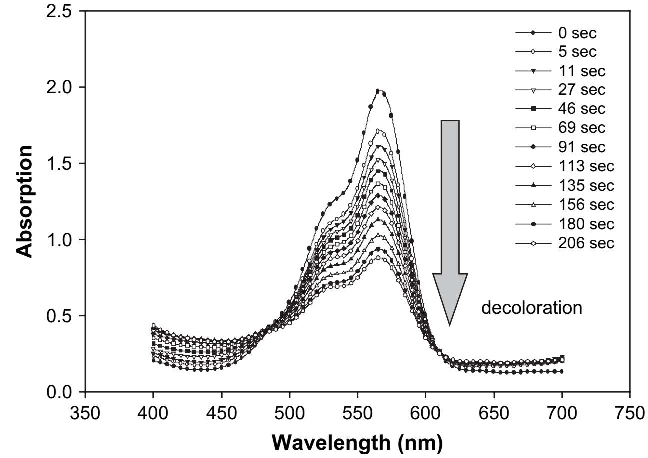

Fig. 1. Spontaneous bleaching of the absorption spectrum for dye **3** in open-circuit.

organic EL devices [11]. It is well known that the amino groups of diaminomaleonitrile **1** react with carbonyl groups to afford azomethine linkages. The condensation of **1** with arylaldehydes proceeded in the presence of piperidine in benzene, removing the generated water with a Dean–Stark trap. Dye **3** absorbs at 566 nm and emits at 709 nm in chloroform. During the course of our investigation on the synthesis and optical properties of the light-emitting materials containing indoline moiety, we have found that dye **3** exhibits electrochromic properties in solution. The electrochromic cell comprised two glass sheets separated by a 0.1 mm thick spacer of PET film. The glass sheets were coated on one side with transparent conductive electrodes of indium-doped tin oxide (ITO), and these sides were placed so as to face each other on the inside of the cell, and the edges of the cell were sealed with insulating epoxide resin. Prior to the final sealing, the space between the electrodes was filled with a propylenecarbonate/chloroform/methanol solution of 0.05 mmol azomethine dye **3** and 1.5 mmol of tetra-*n*-butylammonium perchlorate as electrolyte. Viologen, bis-quarternary salts of bipyridine, undergoes a one-electron reduction to give a coloured radical cation. However, the absorption spectra of the coloured electrochromic cell were produced on the anode after electrocolouration (Fig. 1). The threshold voltage for the colouration is about 2 V. At an applied voltage of 2 V in the device, the absorption maximum was observed at around 540 nm and the colour was red, but in open-circuit condition the colour rapidly changed to original pale red colour within 200 s.

3. X-ray crystal structure [12]

Dye **3** was also found to form unique molecular arrangement in single crystals. X-ray analysis revealed the single crystals, grown by diffusion method using chloroform and diethylether, include one disordered diethylether molecule per dye (Fig. 2(a)). The disordered molecule was refined on the assumption that the molecule is disordered in two positions with 50% occupancy. The dye molecule was found to have a planar π-conjugated system with s-*trans* conformations of the chromophoric system. J-aggregate-like molecular arrangement of **3** is the most important structural feature in the present analysis. As shown in Fig. 2(b), dye molecules are stacked along the *c*-axis being parallel with its long molecular axis to form a two-dimensional staircase structure [13]. The slip angles between molecules with respect to the long molecular axis calculated were about 13° and 26°. These angles are smaller than the magic angle, 54.7° [14]. Similar molecular arrangement was found in the related azomethine dyes forming J-aggregates in vapor deposited films [15–18]. This result is considered to indicate its potential to form J-aggregates in the solid state. This chromophoric system based on diaminomaleonitrile can therefore be regarded as a potential chromophore for J-aggregate formation.

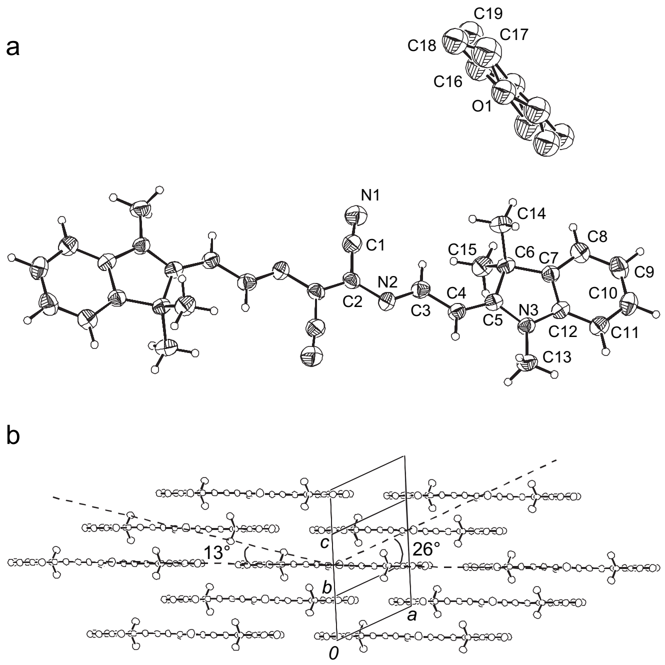

Fig. 2. (a) Molecular and (b) packing diagrams for dye **3**. Diethylether molecules are omitted for clarity in the packing diagram.

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References

[1] Randin JP. Electronics 1981;29:89.
[2] Svensson JSEM, Granqvist CG. Applied Physics Letters 1994;45:828.
[3] Bookbinder DC, Wrighton MS. Journal of Electrochemical Society 1983;130:1080.
[4] Kim SH, Bae JS, Hwang SH. Dyes and Pigments 1996;31:89.

[5] Kim SH, Bae JS, Hwang SH, Gwon TS, Doh MK. Dyes and Pigments 1997;33:167.

[6] Kim SH, Hwang SH. Dyes and Pigments 1998;36:139.

[7] Yamana M, Nashiwazaki N, Yamamoto M, Nakao T. Display 1988;9:190.

[8] Chang IF, Gilbert BL, Sun TI. Journal of Electrochemical Society 1975;122:955.

[9] Van Vitert LG, Zydzik GJ, Singh S, Camlidel I. Applied Physical Letters 1980;36:109.

[10] Kim SH, Ryu JH, Choi HJ, Kim HS. Dyes and Pigments 2005;64:279.

[11] Kim SH, Yoon SH, Kim SH, Han EM. Dyes and Pigments 2005;64:45.

[12] Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number (CCDC283723).

[13] Smith DL. Photographic Science and Engineering 1974;18:309.

[14] Kasha M. In: Bartolo BD, editor. Spectroscopy of the excited state. Plenum Press; 1976. p. 337.

[15] Matsumoto S, Kobayashi T, Aoyama T, Wada T. Chemical Communications 2003;1910.

[16] Matsumoto S, Shirai K, Kobayashi K, Wada T, Shiro M. Zeitschrift fuer Kristallographie 2004;219:239.

[17] Matsumoto S, Kobayashi T, Aoyama T, Wada T. Transactions of Materials Research Society of Japan 2004;29:3171.

[18] Matsumoto S, Satoh M, Tsuchida D, Kobayashi T, Aoyama T, Wada T. Transactions of Materials Research Society of Japan 2005;30:345.